Mechanical properties and structural identifications of cubic TiO_2

Yongcheng Liang,[1] Bin Zhang,[2] and Jianzhi Zhao[3]
[1]*College of Engineering Science and Technology, Shanghai Fisheries University, Shanghai 200090, People's Republic of China*
[2]*College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People's Republic of China*
[3]*Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Science, Beijing 100080, People's Republic of China*

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First-principles calculations on the mechanical properties and structural identifications of the fluorite- and pyrite-TiO_2 under high pressure have systematically been performed by the plane-wave basis pseudopotential method. Our calculated bulk modulus (272–324 GPa), shear modulus (97–128 GPa), elastic constant C_{44} (40–73 GPa), and theoretical hardness (13 GPa) of the fluorite-TiO_2 show that it *cannot* be regarded as a potential candidate of superhard materials. Our results indicate that the differences of mechanical properties between the fluorite- and pyrite-TiO_2 are very small, which are at odds with the previous conclusions. In addition, we find that c-TiO_2 in the previous experiment is closer to the fluorite phase by analyzing the high-pressure behaviors of both cubic phases.

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I. INTRODUCTION

Titanium dioxide (TiO_2) has attracted much attention, not only because it possesses a rich phase diagram with many polymorphs, such as the rutile, anatase, brookite, columbite, baddeleyite, and cotunnite phases, but also because of their unique physical and chemical properties.[1–13] These characters include high refractive index, excellent optical transmittance in the visible and near-infrared region, high dielectric constant,[8] and photocatalysis for water cleavage,[9] and make TiO_2 widely used in a variety of industrial applications. Recently, the cubic TiO_2 (c-TiO_2) was synthesized at a pressure of 48 GPa and temperatures of 1900–2100 K by heating anatase in a diamond-anvil cell.[10] Because its absorption in the visible range of the solar spectra is 3 or 4 orders of magnitude larger than the conventional state of the art solar cell with anatase TiO_2, c-TiO_2 will serve as an important promising material for future generation solar cells.[11,12] Furthermore, Swamy and Muddle[13] reported that the cubic fluorite TiO_2 was a highly incompressible (bulk modulus ~395 GPa), potentially ultrahard material (shear modulus ~230 GPa).

However, the exact structure (fluorite-type $Fm3m$ versus pyrite-type Pa-3) of c-TiO_2 was not definitively determined in high-pressure experiments since the technical difficulties were involved in identifying the small number of Bragg reflections due to the cubic phase that are hidden among the reflections of other possible coexisting phases. It has been controversial that c-TiO_2 is assigned as either the fluorite or the pyrite structure. For instance, in the above synthesis of experiment,[10] the authors have interpreted their results in terms of the fluorite structure. Nevertheless, Swamy and Muddle[13] have calculated the bulk and shear modulus of the fluorite and pyrite phases using the linear combination of atomic orbital (LCAO) method and claimed that the experimental observation was closer to the pyrite phase. Other theoretical studies[2,3] were also conducted in order to identify the cubic phase by examining both the fluorite and the pyrite model system. It was demonstrated that the pyrite form is more stable than the fluorite structure when they are in equilibrium states. Indeed, the fluorite or the pyrite structure is closely related. The Ti atoms lie on Wyckoff 4a (0, 0, 0) sites and form a face-centered-cubic sublattice, while O atoms are positioned at 8c (u, u, u) sites. However, the internal parameter $u \sim 0.34$ is adopted in the pyrite structure instead of $u = 0.25$ in the fluorite structure. This displacement of the O atoms transforms the coordination polyhedron from regular rhombohedral to cubic, yielding the Ti coordination number of 8 instead of 6+2. Nevertheless, elastic properties for fluorite- and pyrite-type TiO_2 are largely different according to the calculations of Swamy and Muddle.[13] Such a small structural distortion results in enormous changes in macroscopical mechanical properties. However, this result is a bit surprising.

To address those issues, systematic accurate first-principles calculations are highly demanded, and this is the main purpose of the present paper. In the present work, the mechanical properties, stabilities, and pressure behaviors of the fluorite- and pyrite-TiO_2 under high pressure are systematically investigated from first-principles calculations. On the basis of these calculated results, the exact structure of experimental synthesis c-TiO_2 is also discussed.

II. CALCULATION METHODS

Our calculations on two cubic TiO_2 phases are performed by the BSTATE code[14] using the first-principles plane-wave basis pseudopotential method. The 2s, 2p states of O and 3p, 3d states of Ti are treated by the Vanderbilt ultrasoft pseudopotential,[15] while the norm-conserving scheme[16] is used for other states. The generalized gradient approximation (GGA-PBE96)[17] is used for the exchange-correlation energy. The special k-point meshes are generated using the Monkhorst-Pack scheme.[18] For the validity of our results, we carefully checked the convergence of total energy with respect to the number of k points and the cutoff energy. The mesh of $14 \times 14 \times 14$ k points and the cutoff energy of 30.25 Ry for the plane-wave expansion are used for all sys-

TABLE I. Calculated equilibrium volume V_0 (Å^3), bulk modulus B_0 (GPa), and its pressure derivative (B_0') at zero pressure, compared with other available data for the fluorite- and pyrite-TiO_2.

Phase	Method	V_0	B_0	B'	Reference
Fluorite	BSTATE-GGA	112.11	272	4.66	This study
	BSTATE-LDA	105.73	324	4.68	This study
	VASP-LDA	107.08	309	4.46	This study
	CASTEP-LDA	106.46	289	4.19	This study
	LCAO-GGA	112.75	395	1.75	13
	LCAO-B3LYP	112.13	390	2.06	13
	LCAO-HF	110.18	331		3
	LCAO-LDA	107.04	308		3
	PW-LDA	114.80	282		2
	Experiment	115.50	202	1.3	10
Pyrite	BSTATE-GGA	116.65	272	4.58	This study
	BSTATE-LDA	110.36	320	4.61	This study
	VASP-LDA	112.10	298	4.15	This study
	CASTEP-LDA	110.95	304	4.32	This study
	LCAO-GGA	118.62	220	4.86	13
	LCAO-B3LYP	117.26	258	4.35	13
	LCAO-HF	114.79	318		3
	LCAO-LDA	110.66	273		3

tems. The equilibrium volume (V_0), bulk modulus at ambient pressure (B_0), and its first pressure derivative (B_0') were obtained with the third-order Birch-Murnaghan equation of state (EOS).[19] The elastic constants are obtained by similar methods of Ref. 20. The shear modulus, Young's modulus, and Poisson's ratio are calculated according to the Voight-Reuss-Hill bounds.[21]

Considering the fact that the different exchange-correlation formulations and program codes perhaps affect the calculation results, we adopt the following: On the one hand, the VASP (Ref. 22) and CASTEP codes[23] are independently used to check the above results; on the other hand, the local density approximation (LDA-PW91)[24] is also used for the exchange-correlation energy for the comparison with GGA results.

III. RESULTS AND DISCUSSION

Table I presents our calculated results of equilibrium volume, bulk modulus, and its pressure derivative for the fluorite- and pyrite-TiO_2, in comparison with other available data. Let us see the fluorite phase first. From the BSTATE calculations, we can find that the GGA and LDA lead to the discrepancy of the bulk modulus by 16%. This can be attributed to two factors: One is the different exchange-correlation formulations; the other is the difference of the equilibrium volume at about 5.7% because the equilibrium volume, bulk modulus, and its first pressure derivative are known to be correlated. If the equilibrium volume is constrained to the average (108.92 Å^3) of the LDA and GGA results, we have consistent bulk moduli 299 GPa (LDA) and 293 GPa (GGA). Considering these factors and the errors of numerical procedures of different codes, our four calculations yield reasonable bulk moduli (272, 324, 309, and 289 GPa), which also agree well with the previous calculated data (331, 308, and 282 GPa).[2,3] However, theoretical bulk moduli (395 and 390 GPa) presented by Swamy and Muddle[13] deviate from the above data, although their equilibrium volumes accord with ours within the errors. For the same GGA calculations, their B_0 values are 45% larger than ours. The most surprising results of Swamy and Muddle[13] were the extremely low values of B_0' (1.75, 2.06) in fluorite TiO_2. Indeed, theory suggests that this value should be close to 4.00 in stiff materials.[25] Furthermore, the Birch-Murnaghan formulation itself is valid only where B_0' is sufficiently close to 4.00.[26] As expected, our values of B_0' (4.66, 4.68, 4.46, and 4.19) are all close to 4.00. For the pyrite phase, our consistent calculated values (272, 320, 298, and 304 GPa) of bulk modulus match the previous ones (318 and 273 GPa) (Ref. 3) if considering the errors of LDA and GGA. However, the calculations (220 and 258 GPa) of Swamy and Muddle[13] underestimate the bulk modulus by about 19% with comparison to the average of our results.

In contrast with results of Swamy and Muddle,[13] the differences of our B_0 values for the fluorite and pyrite phases is very small, which is very reasonable because of two closely related structures. To compare the compressibility of the pyrite and fluorite phases of TiO_2 under pressure, the pressure-volume (P-V) relations are displayed in Fig. 1. The available data for diamond, c-BN, and ReB_2 (Ref. 20) are also used for comparison. We can explicitly see that the two phases of TiO_2 are more compressible than diamond, c-BN, and ReB_2. Furthermore, the P-V curves of two TiO_2 phases are very close, so we do not reproduce the conclusions of Swamy and

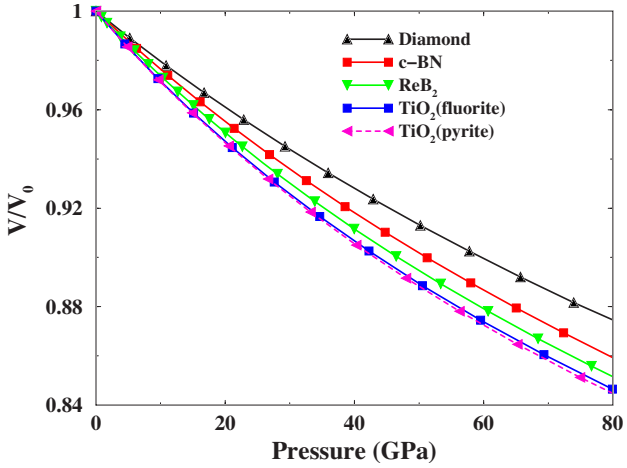

FIG. 1. (Color online) The calculated volume-pressure curves of the fluorite- and pyrite-TiO_2, compared with available data for diamond, *c*-BN, and ReB_2.

Muddle[13] that the *P-V* relations are strikingly different. At the present stage, it is still very hard to judge what causes the discrepancy between their calculations and ours. Nevertheless, it is worth noting that the artifact may arise due to insufficient convergence with respect to computational parameters. We have calculated the dependence of bulk modulus on the number of *k* points and the cutoff energy for the fluorite TiO_2 (Fig. 2). As can be seen, the calculated bulk modulus is very sensitive to the cutoff energy [Fig. 2(a)], although the number of *k* point hardly influences the results [Fig. 2(b)]. In addition, Swamy and Muddle[13] suggested that cation-oxygen coordination and polyhedral compressibility are among the most important factors in determining the bulk modulus systematics in these oxide systems. However, we want to point out that the bulk modulus has been shown theoretically to be a monotonic function of valence electron concentration,[27,28] whereas the metal-oxygen coordination number dependence of bulk modulus is not unequivocal and monotonic because the formula volume for different phases is different.

In order to gain a deeper insight into the macroscopic mechanical properties of two cubic TiO_2 phases, we have detailedly calculated their elastic constants, shear moduli, Young's moduli, and Poisson's ratios by the first-principles method. All calculated results are listed in Table II. First of all, we find that four calculated results of every phase are consistent with each other within the errors. And then, the mechanical stability of any crystal requires the strain energy to be positive, which implies that the whole set of elastic constant C_{ij} satisfies the Born-Huang criterion.[29] We have checked their elastic constants C_{ij} and found that both the fluorite- and pyrite-TiO_2 are mechanically stable. From Table II, C_{11} of the fluorite phase is about 26% larger than that of the pyrite phase, while C_{12} of the fluorite phase is about 38% smaller than that of the pyrite phase. The differences of their Young's moduli and Poisson's ratios are very small.

As we know, the shear modulus and the elastic constant C_{44} are the most important parameters indirectly governing the intrinsic hardness. We calculate TiO_2 in the fluorite structure to have the shear modulus of 97–128 GPa, which are

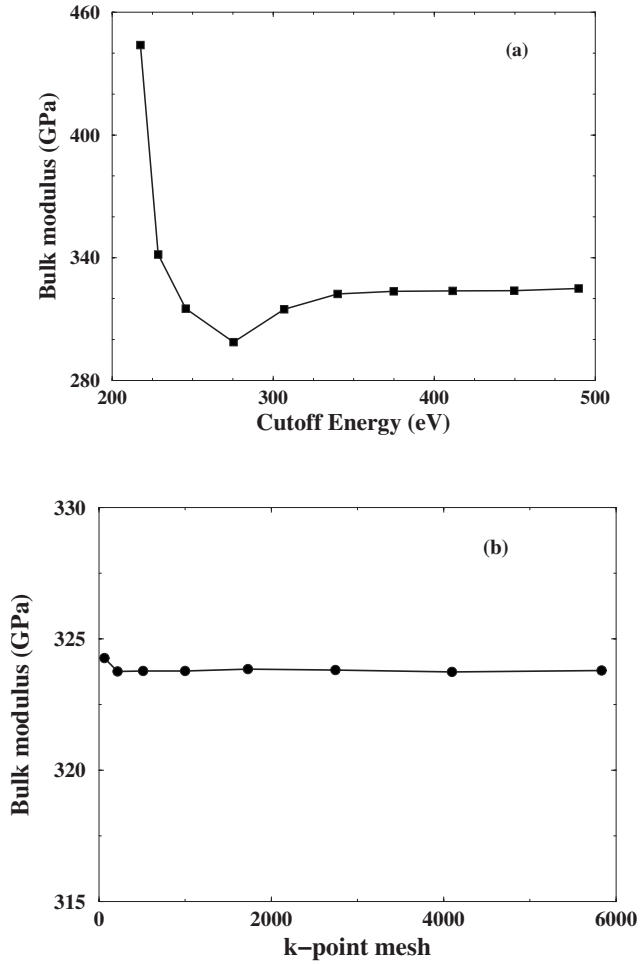

FIG. 2. The convergence of calculated bulk modulus as a function of (a) cutoff energy and (b) *k*-point mesh for the fluorite-TiO_2.

only half of the values (227–239 GPa) reported by Swamy and Muddle.[13] Also, the calculated elastic constants C_{44} are only in the range of 40–73 GPa. Both values of the fluorite-TiO_2 are much lower than the counterparts of superhard diamond (G=550 GPa, C_{44}=604 GPa), *c*-BN (G=403 GPa, C_{44}=479 GPa), and ReB_2 (G=310 GPa, C_{44}=290 GPa),[20] and only approach those of hard, not superhard OsB_2 (G=174 GPa, C_{44}=61 GPa).[30] Therefore, the present calculations indicate that the fluorite TiO_2 phase *cannot* be regarded as a potential candidate of superhard materials, which is at odds with the conclusion of Swamy and Muddle.[13] For the pyrite phase, our calculated shear moduli (110–130 GPa) are slightly smaller than the results (131–154 GPa) of Swamy and Muddle[13] and nearly equal to those of the fluorite phase. However, the elastic constant C_{44} for the pyrite-TiO_2 is twice as that for the fluorite-TiO_2. This is because the distortion of the O atoms from cubic to rhombohedral largely enhances the rigidity against the shape deformations at some directions.

On the other hand, the theoretical hardness of crystals can be estimated from first-principles calculations[31] and the semiempirical theory.[32–34] To demonstrate the applicability of the theory, we first calculate the hardest known oxide cotunnite-TiO_2 because its experimental hardness is avail-

TABLE II. Calculated elastic constants C_{ij} (GPa), shear modulus G (GPa), Young's modulus E (GPa), and Poisson's ratio υ for the fluorite- and pyrite-TiO_2.

Phase	Method	C_{11}	C_{12}	C_{44}	G	E	υ
Fluorite	BSTATE-GGA	604	107	52	104	276	0.331
	BSTATE-LDA	687	143	73	128	339	0.326
	VASP-LDA	671	128	40	97	263	0.358
	CASTEP-LDA	670	99	53	112	298	0.328
Pyrite	BSTATE-GGA	467	174	115	127	329	0.298
	BSTATE-LDA	545	201	133	130	344	0.318
	VASP-LDA	454	198	100	110	292	0.328
	CASTEP-LDA	491	199	113	125	328	0.315

able. Using the structural data presented in Ref. 5 and the semiempirical theory of Ref. 32, we obtain the hardness of the cotunnite-TiO_2 at 32 GPa, which is in good qualitative accordance with the measured hardness of 38 GPa.[5] This shows that the semiempirical theory can be applied for Ti-O crystals. For the fluorite-TiO_2, the bond length d_{12}(Ti-O) $=2.05$ Å and the parameters $e_1(\mathrm{Ti})=2.831$ and $e_2(\mathrm{O})=5.964$ are evaluated by the first-principles calculations.[31] Applying Eq. (3) in Ref. 32, we get the hardness $H(TiO_2)=13$ GPa indicating that the fluorite-TiO_2 is at most hard materials, but not superhard ones (>40 GPa). The hardness of the rutile-TiO_2 is 11.9 GPa from the semiempirical theory.[33] We find that the hardness of the fluorite-TiO_2 is between the values of rutile-TiO_2 and cotunnite-TiO_2, and thus our estimated values should be qualitatively reasonable.

We turn to the exact structure of the cubic phase not unambiguously determined in the experimental study. So far, the c-TiO_2 in the experiment cannot be identified via first-principles calculations because our results indicate that the calculated bulk modulus with either structure is significantly larger than the experimental datum and that our calculated P-V relations for both phases are very close. Thus, we will turn our eyes to other aspects. The dependences of the calculated total energy on the volume for the fluorite- and pyrite-TiO_2 are plotted in Fig. 3. We can see that the pyrite phase has the lower total energy and larger equilibrium volume at zero pressure, which is in accordance with the calculations of Muscat *et al.*[3] As the pressure increases, the fluorite phase of TiO_2 becomes stable. We focus on the region around the volume of ~155 bohr,[3] which corresponds to the experimental pressure of ~48 GPa. Near this point, the absolute total energy of the fluorite phase is ~0.4 eV lower than that of the pyrite phase, indicating that the fluorite phase is more stable under pressure. When the TiO_2 formula volume reduces from the equilibrium state to ~155 bohr,[3] the theoretical pressures for the fluorite and pyrite phases are ~60 and ~86 GPa, respectively. According to calculated total energies and pressure values, c-TiO_2 in the experiment is closer to the fluorite phase. Therefore, we think it to be correct that Mattesini *et al.*[10] assigned the experimental synthesis of c-TiO_2 as the fluorite structure, although they underestimated the B_0 (202 GPa) and B_0' (1.3) due to the extreme difficulties in extracting accurate P-V data on the cubic phase from other high-pressure coexisting phases. Furthermore, more recent studies[12] on the dynamical stability of the fluorite and pyrite phases using *ab initio* phonon calculations indicated that the fluorite TiO_2 stabilizes under pressure, whereas the pyrite TiO_2 shows instability throughout the whole pressure range of 0–114 GPa, which further supports that the exact structure of the experimental cubic phase is of the fluorite type.

IV. CONCLUSIONS

The EOSs, elastic constants, shear moduli, and other related mechanical properties for the fluorite- and pyrite-TiO_2 under high pressure have systematically been studied by performing the first-principles plane-wave basis pseudopotential calculations. Our calculated bulk modulus, shear modulus, and elastic constant C_{44} for the fluorite-TiO_2 are in the range of 272–324, 97–128, and 40–73 GPa, respectively. The theoretical hardness of the fluorite-TiO_2 (13 GPa) is estimated from first-principles calculations. These demonstrate that the fluorite TiO_2 do not have the potential to be superhard materials in contrast to the conclusion of Swamy and Muddle.[13] The mechanical properties of the pyrite-TiO_2 are close to those of the fluorite-TiO_2.

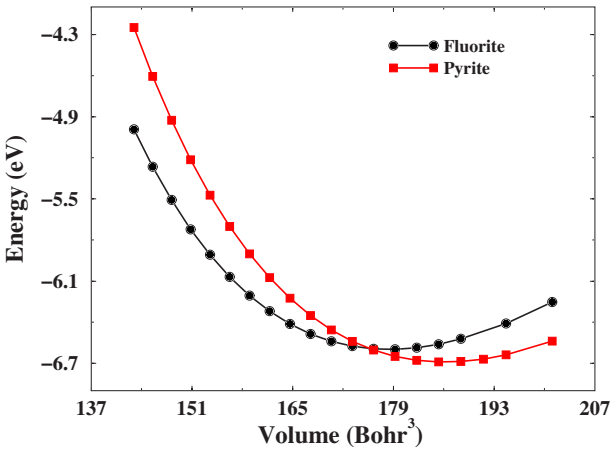

FIG. 3. (Color online) Calculated total energy versus volume for the fluorite- and pyrite-TiO_2.

The exact structure of experimental synthesis c-TiO_2 cannot be identified via first-principles calculations on mechanical properties. According to calculated total energies and pressure values in combination with *ab initio* phonon calculations from other literature,[12] we find that c-TiO_2 in the experiment is closer to the fluorite phase, which is at odds with the results of Swamy and Muddle.[13]

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