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First-principles calculations for elastic properties of rutile TiO_2 under pressure*

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This paper studies the equilibrium structure parameters and the dependences of the elastic properties on pressure for rutile TiO_2 by using the Cambridge Serial Total Energy Package (CASTEP) program in the frame of density functional theory. The obtained equilibrium structure parameters, bulk modulus B_0 and its pressure derivative B_0' are in good agreement with experiments and the theoretical results. The six independent elastic constants of rutile TiO_2 under pressure are theoretically investigated for the first time. It is found that, as pressure increases, the elastic constants C_{11},C_{33}, C_{66}, C_{12} and C_{13} increase, the variation of elastic constant C_{44} is not obvious and the anisotropy will weaken.

Keywords: density functional theory, elastic properties, TiO_2
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1. Introduction

Titanium dioxide (TiO_2) is one of the wide-band-gap semiconductors and the most utilized particulate semiconductor materials in the world. Although discovered more than 200 years and commercially processed for 90 years, TiO_2 is still extensively studied for its interesting electric, magnetic, catalytic, photocatalytic, electrochemical and other properties.[1−8] TiO_2 admits three polymorphic forms in nature, i.e. rutile, anatase, and brookite. They are commonly encountered in inorganic syntheses while only rutile and anatase are commercially important. Both rutile and anatase have a tetragonal unit cell and the structures can also be considered consisting of (TiO_6) octahedra, but belonging to different space groups. Rutile has the space group $P4_2/mnm$ (136) with two TiO_2 formula units in one unit cell and the anatase has the space group $I4_1/amd$ (141) with four TiO_2 formula units in one unit cell.

At elevated pressures, TiO_2 has a rich phase diagram with a series of structural phase transformation. Rutile TiO_2 is the most common in the three polymorphic forms in nature. In bulk form and with a large crystallite size, rutile form is the thermodynamically stable form at normal pressure and at temperatures up to its melting point 1830 K. On the other hand, Mammone *et al* [9] and Arashi *et al* [10] have revealed that rutile TiO_2 can transform to a columbite structure above 10 GPa by applying Raman spectroscopy method.

Since rutile TiO_2 has a high refractive index and a measure of the ability to band light, it is widely used as a pigment for providing brightness, whiteness, and opacity to such products as paints and coatings, plastics and rubber, paper products, and so on. There have been many scientific investigations in rutile TiO_2,[11−17] however, few works have reported its elastic properties under pressure. Therefore, in this work, we focus on the elastic properties of rutile TiO_2 under pressure (up to 10 GPa) by the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) program.[18,19] The six independent elastic constants of rutile TiO_2 under pressure are theoretically studied for the first time. In Section 2, we have made a brief review of the theoretical method. The results and some discussions are presented in Section 3.

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2. Theoretical method

2.1. Total energy electronic structure calculations

In our calculations, we employ the norm-conserving pseudopotentials introduced by Hammer *et al* [20] for the interactions of the electrons with the ion cores, together with the local density approximation (LDA) proposed by Vosko, Wilk and Nussair[21] for exchange-correlation potential. The electronic wave functions are expanded in a plane wave basis set with energy cut-off of 550 eV. Pseudo-atom calculations are performed for O $2s^2 2p^4$ and Ti $3d^2 4s^2$. For the Brillouin-zone sampling, we use the 5×5×6 Monkhorst-Pack mesh,[22] where the self-consistent convergence of the total energy is 10^{-6}eV/Atom. All the electronic structure calculations are implemented through the CASTEP code.[18,19]

2.2. Elastic constants and Debye temperature

Elastic constants are defined by means of a Taylor expansion of the total energy, $E(V, \delta)$, for the system with respect to a small strain δ of the lattice primitive cell volume V. The energy of a strained system is expressed as follows[23]

$$E(V,\delta) = E(V_0,0) + V_0\left[\sum_i \tau_i\xi_i\delta_i + \frac{1}{2}\sum_{ij} C_{ij}\delta_i\xi_i\delta_j\right], \quad (1)$$

where $E(V_0, 0)$ is the energy of the unstrained system with equilibrium volume V_0, τ_i is an element in the stress tensor, and ξ_i is a factor to take care of Voigt index. It is known, there are six independent components of elastic constants for rutile TiO_2, i.e. C_{11}, C_{33}, C_{44}, C_{66}, C_{12} and C_{13}.

The Debye temperature may be estimated from the average sound velocity V_m[24]

$$\Theta = \frac{\hbar}{k}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} V_m, \quad (2)$$

where $\hbar$ is Planck's constants, k is Boltzmann's constant, N_A is Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, $\rho(= M/V)$ is the density, and V_m is obtained from

$$V_m = \left[\frac{1}{3}\left(\frac{2}{V_S^3} + \frac{1}{V_L^3}\right)\right]^{-1/3}, \quad (3)$$

where V_S and V_L are the shear and longitudinal sound velocities, respectively.

According to the Voigt approximation,[25] there is a simple relation between the isotropic bulk moduli B_V and shear moduli G_V of a polycrystalline aggregate and the single-crystal elastic constants C_{ij}

$$B_V = \frac{1}{9}[2(C_{11}+C_{12}) + C_{33} + 4C_{13}], \quad (4)$$

$$G_V = \frac{1}{15}(2C_{11} - C_{12} + C_{33} - 2C_{13} + 6C_{44} + 3C_{66}). \quad (5)$$

Reuss[26] derived a linear relation between the isotropic bulk B_R and shear moduli G_R of a polycrystalline aggregate, and the corresponding single-crystal elastic constants S_{ij}

$$B_R = \frac{1}{2S_{11} + S_{33} + 2S_{12} + 4S_{13}}, \quad (6)$$

$$G_R = \frac{15}{8S_{11} + 4S_{33} - 4S_{12} - 8S_{13} + 6S_{44} + 3S_{66}}. \quad (7)$$

For rutile TiO_2, we can obtain the relations between C_{ij} and S_{ij} as follows

$$S_{11} = \frac{C_{33}C_{11} - 2C_{33}^2}{(C_{11}-C_{12})[C_{33}(C_{11}+C_{12}) - 2C_{13}^2]}, \quad (8)$$

$$S_{12} = \frac{C_{13}^2 - C_{33}C_{12}}{(C_{11}-C_{12})[C_{33}(C_{11}+C_{12}) - 2C_{13}^2]}, \quad (9)$$

$$S_{13} = -\frac{C_{13}}{C_{33}(C_{11}+C_{12}) - 2C_{13}^2}, \quad (10)$$

$$S_{33} = \frac{C_{11}+C_{12}}{C_{33}(C_{11}+C_{12}) - 2C_{13}^2}, \quad (11)$$

$$S_{44} = \frac{1}{C_{44}}, \quad (12)$$

$$S_{66} = \frac{1}{C_{66}}. \quad (13)$$

Hill[27] proved that the Voigt and Reuss equations represent upper and lower limits of the true polycrystalline constants. He showed that the polycrystalline moduli are the arithmetic mean values of the Voigt and Reuss moduli and thus given by

$$G_H = \frac{1}{2}(G_R + G_V), \quad B_H = \frac{1}{2}(B_R + B_V). \quad (14)$$

The probable values of the average shear and longitudinal sound velocities can be calculated from Hill's equations as follows

$$V_S = \sqrt{\frac{G_H}{\rho}}, \quad V_L = \sqrt{\frac{\left(B_H + \frac{4}{3}G_H\right)}{\rho}}. \quad (15)$$

3. Results and discussion

Rutile TiO_2 belongs to space group $P4_2/mnm$ (D_{4h}^{14}), two Ti atoms are arbitrarily set at (0, 0, 0; 1/2, 1/2, 1/2) and four O atoms are set at $\pm(u, u, 0; u + 1/2, 1/2 - u, 1/2)$ in one unit cell, where u is the cell-internal dimensionless parameter, which denotes the position of the O atom along the c-axis. It is found from our calculations that the most stable structure of rutile TiO_2 occurs at the axial ratio c/a=0.648, corresponding to the equilibrium lattice parameters: a=0.4.5997 nm, c=0.29806 nm. By fitting the calculated energy-volume ($E - V$) data to the Birch–Murnaghan equation of state (EOS)[28]

$$\Delta E(V) = E - E_0 = B_0 V_0 \left[\frac{V_n}{B_0'} + \frac{1}{1 - B_0'} + \frac{V_n^{1-B_0'}}{B_0'(B_0' - 1)} \right], \quad (16)$$

where E_0 is the equilibrium energy, we can obtain the bulk modulus B_0 and its pressure derivative B_0'. All these results are listed in Table 1, together with other theoretical results[12,29−35] and the experimental data.[1636−40] Our results are in good agreement with them.

Table 1. The lattice parameters (0.1nm), bulk modulus B_0 (GPa) and its pressure derivative B_0', together with the experimental data and other theoretical results.

	Present work	Other theoretical calculations	Experiments
a	4.5997	4.653[a] 4.536[b], 4.536[c] 4.529[d], 4.548[e], 4.567[f], 4.690[g], 4.555[h]	4.594[j], 4.593[k], 4.587[l]
c	2.9806	2.965[a], 2.914[b], 2.915[c], 2.942[d], 2.993[e], 2.932[f], 2.990[g], 2.998[h]	2.958[j], 2.959[k], 2.954[l]
c/a	0.648	0.637[a],	
u	0.3042	0.305[a], 0.304[b], 0.304[c], 0.304[d], 0.305[e], 0.305[f], 0.306[g], 0.306[h]	0.305[j], 0.305[k], 0.305[l]
B_0	258	240[a], 265[b], N/A[c]264[d], 281[i]	211±7[m], 230±20[n], 216[o]
B_0'	4.736	4.63[a]	6.76[o]

[a]The *ab initio* pseudopotential approach and local-density approximation.[12] [b]Obtained from the Vienna ab initio simulation package (VASP).[29] [c]Obtained from PW-LDA LC method.[30] [d]Obtained from LCAO-LDA AE method.[31] [e]Obtained from LCAO-HF AE method.[32] [f]Obtained from PW-LDA SC method.[33] [g]Obtained from PW-GGA LC method.[34] [h]Obtained from LCAO-HF LC method.[35] [i]Obtained from LCAO-HF method.[31] [j]From X ray experiment at 298 K.[36] [k]From Neutron experiment at 295 K.[37] [l]From Neutron experiment at 15 K.[37] [m]From X ray experiment.[38] [n]From X ray experiment.[39] [o]Taken from Ref.[16，40].

To obtain the bulk modulus B_0 as a function of temperature T and the bulk modulus B as a function of pressure P, we here apply the quasi-harmonic Debye model,[41] which is successfully applied to some materials.[42−47] In Fig.1 and Fig.2, we present the bulk modulus B_0 as a function of temperature T up to 2000 K at zero pressure and the bulk modulus B as a function of pressure P up to 10 GPa at T=0 K, 1000 K, and 2000 K, respectively. It is shown from Fig.1 that when T <150 K, the bulk modulus B_0 nearly keeps constant; when T >150 K, as temperature T increases, B_0 decreases dramatically. We also find that the lattice parameters a and c nearly keep constant when temperature T <150 K, which results in very little change in primitive cell volume$V$. However, once the temperature T >150 K, both lattice parameters a and c increase rapidly as temperature T increases. Therefore, the volume will be changed dramatically. The dramatic volume variation leads to the rapid decrease in the bulk modulus B_0. On the other hand, it is noted from Fig.2 that the relationships between bulk modulus B and pressure P are all nearly linear at 0 K, 1000 K and 2000 K. The bulk modulus increases with pressure at a given temperature, while decreases with temperature at a given pressure. These results are consistent with the fact that the effect of increasing pressure on the material is the same as decreasing temperature of the material.

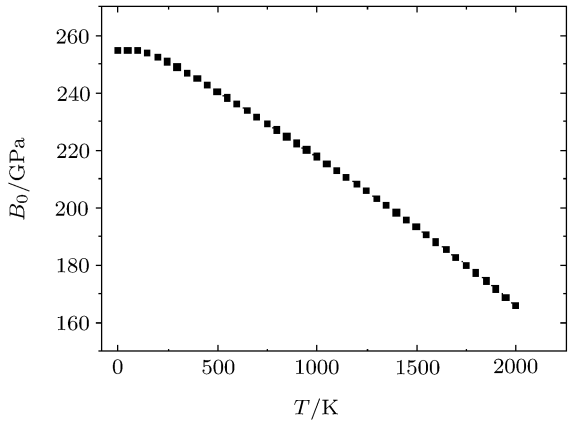


Fig.1. Bulk modulus B_0 as a function of temperature T at zero pressure.

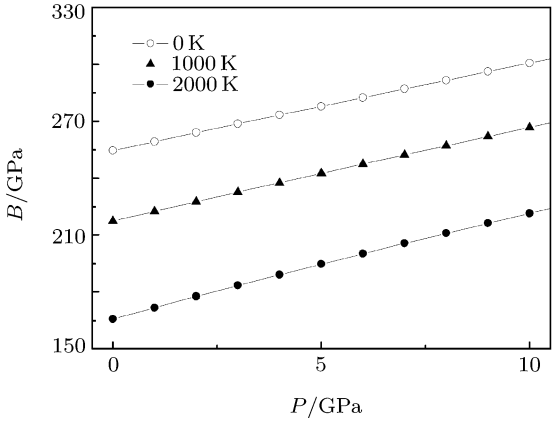


Fig.2. Bulk modulus B as a function of pressure P at T=0, 1000 and 2000 K.

The obtained elastic constants of rutile TiO_2 under pressure up to 10 GPa are presented in Table 2. It is found that the elastic constants C_{11}, C_{33}, C_{66}, C_{12}, C_{13} increase with increasing pressure. The variation of elastic constant C_{44} is not obvious with increasing pressure. The six elastic constants calculated at T=0 K and P=0 GPa, together with other theoretical results[11,14] and the experimental data[13,16] are shown in Table 3. Our results are in agreement with the experimental data and the calculated results by Swamy and Gale,[14] and seem to be better than the calculated results by Ogata *et al.*[11] Unfortunately, there are no available theoretical or experimental data for comparison.

Table 2. Zero temperature elastic constants C_{ij} (GPa) of rutile TiO_2 under pressure P (GPa).

P	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	B_a	B_c	B	G	Θ_D
0	292	471	114	236	192	174	564	1231	233	113	884
2	306	485	110	242	205	182	599	1235	244	113	885
4	314	492	108	249	215	188	624	1239	252	113	884
6	324	497	111	256	228	197	656	1245	262	114	886
8	333	504	119	262	238	203	680	1260	270	117	898
10	344	511	127	269	249	214	712	1281	281	120	909

Table 3. Elastic constants C_{ij} (GPa) for the rutile TiO_2 at zero temperature and zero pressure.

	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
Present work	292	471	114	236	192	174
Ref.[11]	412	519	136	119	107	123
Ref.[14]	293.8	422.7	96.04	189.5	201.9	168.3
Exp.[13]	268	484	124	190	175	147
Exp.[16]	271	484	124	195	178	150

Using the above elastic constants, we calculate the bulk modulus B_a along a-axis with fixed c and the bulk modulus B_c along c-axis with fixed a under high pressure in order to investigate the mechanical anisotropy of rutile TiO_2. The B_a and B_c are defined as follows:

$$B_a = a\frac{\mathrm{d}P}{\mathrm{d}a} = \frac{\Lambda}{2+\alpha}, \tag{17}$$

$$B_c = c\frac{\mathrm{d}P}{\mathrm{d}c} = \frac{B_a}{\alpha}, \tag{18}$$

where

$$\Lambda = 2\,(C_{11}+C_{12}) + 4C_{13}\alpha + C_{33}\alpha^2, \tag{19}$$

$$\alpha = \frac{C_{11}+C_{12}-2C_{13}}{C_{33}-C_{11}}. \tag{20}$$

The calculated values of B_a and B_c under high pressure are also listed in Table 2, from which we

can find that the mechanical behaviour of rutile TiO_2 under zero pressure and zero temperature has strong anisotropy. In Fig.3, we illustrate the pressure dependence of the ratio B_a/B_c. It is shown that B_a/B_c has a trend of gradual decline with increasing pressure. It is suggested that, as pressure increases, the anisotropy in rutile TiO_2 will gradually weaken.

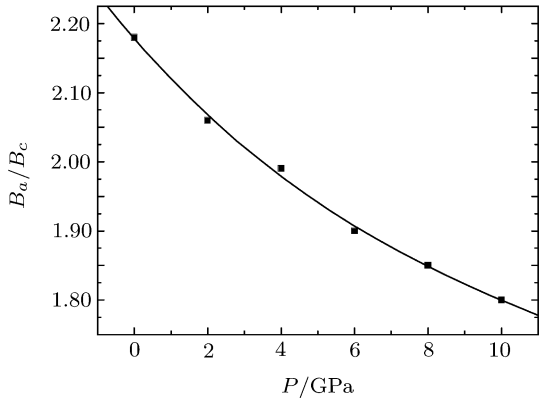


Fig.3. Pressure dependence of ratio B_a/B_c.

At 0 K, using the single crystal elastic constants of rutile TiO_2, we yield Debye temperature Θ_D= 884.65 K, which is well consistent with the value Θ_D= 900.25 K from the quasiharmonic Debye model. The obtained aggregate elastic moduli B and G, as well as Debye temperature Θ_D of rutile TiO_2 under pressure are also presented in Table 2. It is noted that as pressure increases up to 10 GPa, the aggregate elastic modulus B and G, as well as the Debye temperature Θ_D have a tendency of increase.

In summary, we have applied the CASTEP program in the frame of density functional theory to calculate the equilibrium structure parameters, bulk modulus and its pressure derivative of rutile TiO_2. The obtained equilibrium structure parameters, bulk modulus and its pressure derivative are well consistent with experiments and the theoretical results. We have obtained the dependences of elastic properties of rutile TiO_2 on pressure for the first time. It is found that, as pressure increases, the elastic constants C_{11}, C_{33}, C_{66}, C_{12} and C_{13} increase, the variation of elastic constant C_{44} is not obvious and the anisotropy will weaken.

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