

Ultrastiff Cubic TiO₂ Identified via First-Principles Calculations

Varghese Swamy* and Barry C. Muddle

Department of Materials Engineering, Monash University, Victoria 3800, Australia

(Received 14 June 2006; published 19 January 2007)

The crystal structures and compressibilities of fluorite- and pyrite-structured TiO₂ under varying hydrostatic pressures are calculated using gradient-corrected density functional as well as hybrid density functional-Hartree-Fock formulations. The results suggest that fluorite TiO₂ is a highly incompressible solid with a large bulk modulus value ($K_0 \sim 395$ GPa), approaching that of ultrahard cotunnite TiO₂ ($K_0 = 431$ GPa). The bulk modulus obtained for pyrite TiO₂ is considerably smaller ($K_0 \sim 220$ – 260 GPa), nonetheless larger than the value determined experimentally for cubic TiO₂. Calculated shear modulus values indicate that fluorite TiO₂ has the potential to be an ultrahard material, if it could be stabilized under ambient conditions.

DOI: [10.1103/PhysRevLett.98.035502](https://doi.org/10.1103/PhysRevLett.98.035502)

PACS numbers: 61.50.Ah, 61.50.Ks, 64.30.+t, 81.30.Hd

Searching for solids with large bulk and shear moduli is a strategy used for identifying potential ultrahard or superhard materials [1–3]. Implicit in such efforts is an assumption that the intrinsic hardness of a material is correlated with its bulk modulus (K) and shear modulus (G). Of these two elastic moduli, K is easier to determine experimentally and compute theoretically, especially using first-principles methods. It is now well recognized, however, that large K and G do not guarantee high hardness of a material. Several other factors, such as high electron density, short bond lengths, a high degree of covalent bonding, and a high symmetry facilitating near-isotropic deformation have been suggested to contribute to enhanced hardness.

These latter properties are highly characteristic of phases forming within the B-C-N-O system, exemplified by the archetypal superhard materials diamond (zero-pressure bulk modulus, $K_0 = 444$ GPa [4]) and cubic BN ($K_0 = 369$ GPa [4]). Outside of the B-C-N-O system, phases with high metal-anion coordination and large K_0 have been proposed as potential ultrahard materials. Within this category, the metal oxides TiO₂, ZrO₂, and HfO₂ have received significant attention from experimental and theoretical researchers searching for high density solids with large K_0 (e.g., [3,5–8]). High-pressure phase transitions at low temperatures in these oxides lead to the following series of structures as a function of increasing pressure (P), with each succeeding high-pressure phase possessing larger K_0 : baddeleyite (monoclinic ZrO₂, $P2_1/c$, referred to as MI) \rightarrow orthorhombic-I ($Pbca$, OI) \rightarrow cotunnite (PbCl₂, $Pnma$, orthorhombic-II, OII) (e.g., 5–7, 9). In fact, cotunnite TiO₂ synthesized at 61 GPa has large bulk modulus and hardness [6].

In addition to MI, OI, and OII, cubic polymorphs of these oxides are also stable to high pressures. Although cubic ZrO₂ and HfO₂ are well documented, it is only recently that the long-awaited experimental synthesis of cubic TiO₂ (c -TiO₂) finally materialized [9]. The c -TiO₂ was synthesized at 48 GPa by heating anatase to 1900–2100 K in diamond-anvil cells. A definitive identification

of the exact symmetry (fluorite-type $Fm\bar{3}m$ versus pyrite-type $Pa\bar{3}$) of this phase was not possible from the experimental data; however, the authors have interpreted their results in terms of the fluorite structure.

A puzzling feature of this c -TiO₂ is the low K_0 of 202 ± 5 GPa determined experimentally. This K_0 value is comparable to or, in some cases, lower than those of the less-dense forms of TiO₂ in which Ti is octahedrally coordinated to O: e.g., anatase (179 ± 2 GPa [10]), rutile (211 ± 1 GPa [11]), brookite (255 ± 10 GPa [12]), and columbite TiO₂ (258 ± 8 GPa [10]). Published theoretical predictions using the local density approximation (LDA) and Hartree-Fock (HF) functionals [13,14] indicate much larger K_0 for c -TiO₂. In this Letter, we present first-principles calculations of pyrite and fluorite TiO₂ that suggest that a c -TiO₂ with either symmetry will have a significantly larger K_0 than the experimental datum [9], and that fluorite TiO₂, in fact, is a highly incompressible solid.

The calculations were performed using the all-electron linear combination of atom-centered orbitals (LCAO) CRYSTAL [15] code. The generalized-gradient approximation (GGA) to the density functional theory (DFT) as implemented by Perdew *et al.* [16] and the hybrid DFT-HF treatment according to Becke's exchange functional [17] combined with the Lee-Yang-Parr [18] correlation (B3LYP) functional were used. The K_0 , its pressure derivative K' , and zero-pressure volume V_0 were obtained with the third-order Birch-Murnaghan equation of state [19].

The equilibrium 0 GPa lattice constants calculated for the two structures using the two functionals (Fig. 1) suggest a smaller fluorite TiO₂ unit cell ($a \sim 4.8$ Å) compared to that of pyrite TiO₂ ($a \sim 4.9$ Å). The calculated P - V relations of the two phases are strikingly different (Fig. 1 and Table I). The calculated Birch equation parameters for fluorite TiO₂ are K_0 of ~ 395 GPa and $K' \sim 2$; these values are suggestive of a highly incompressible solid with K_0 approaching that of cotunnite TiO₂ and diamond. The

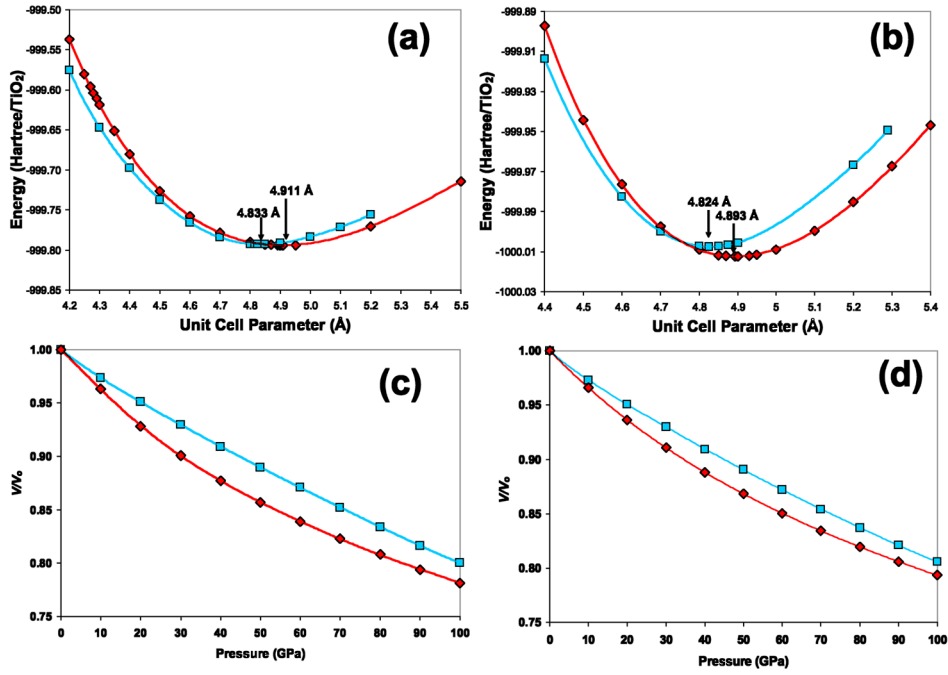


FIG. 1 (color online). Calculated equilibrium crystal structure and P - V relations for fluorite (squares) and pyrite (diamonds) forms of TiO_2 . The zero-pressure lattice constant a calculated using the GGA (a) and the hybrid B3LYP functionals (b) and the P - V data obtained using the GGA (c) and B3LYP functionals (d) suggest a smaller and significantly stiffer fluorite TiO_2 lattice.

TABLE I. Zero-pressure bulk moduli and related properties of dense TiO_2 phases.^a

Phase	Method	V_0 (\AA^3)	K_0 (GPa)	K'	Reference
Fluorite	GGA	112.75 ± 0.06	395 ± 4	1.75 ± 0.05	This study
	B3LYP	112.13 ± 0.06	390 ± 4	2.06 ± 0.06	This study
	LCAO-HF	110.18	331 ± 10		[14]
	LCAO-LDA	107.04	308 ± 10		[14]
	PW-LDA ^b	114.80	282		[13]
	Experiment	115.50 ± 2	202 ± 5	1.3 ± 1	[9]
Pyrite	GGA	118.62 ± 0.12	220 ± 4	4.86 ± 0.11	This study
	B3LYP	117.26 ± 0.04	258 ± 2	4.35 ± 0.04	This study
	LCAO-HF	114.79	318 ± 10		[14]
	LCAO-LDA	110.66	273 ± 10		[14]
Rutile	GGA	63.78 ± 0.01	215 ± 1	5.35 ± 0.16	This study
	B3LYP	63.42 ± 0.04	224 ± 8	5.64 ± 0.90	This study
	Experiment	62.44	211 ± 1	6.76	[11]
Columbite	GGA	125.21 ± 0.58	250 ± 23	2.64 ± 0.7	This study
	B3LYP	125.00 ± 0.27	257 ± 12	2.57 ± 0.4	This study
	LCAO-HF	122.79	264 ± 10		[14]
	Experiment	122.37	258 ± 8	4.1 ± 3	[10]
Baddeleyite	LCAO-HF		300 ± 10		[14]
	Experiment	110.48 ± 5	303 ± 6	3.9 ± 2	[20]
Orthorhombic-I	B3LYP	226.47 ± 0.44	272 ± 9	3.38 ± 0.19	This study
	Experiment	218.10^d	318 ± 3	4.0	[21]
Cotunnite	LCAO-HF		380 ± 20		[6]
	FP-LMTO ^c		386 ± 10		[6]
	Experiment	105.09^d	431 ± 10	1.35 ± 0.1	[6]

^aSee also Table S1 [15].

^bPlane-wave LDA.

^cFull-potential linear muffin-tin orbital method.

^dCalculated from molar volume.

Birch equation parameters obtained for pyrite TiO_2 are significantly different (K_0 of 220 GPa with $K' = 4.86$ and K_0 of 260 GPa with $K' = 4.35$). Consistent K_0 values were also obtained from elastic stiffness constants (C_{ij} s) [15]. The computed K_0 values for the two structures are significantly larger than the experimental result [9]. It is possible that the extreme difficulties involved in identifying the small number of Bragg reflections due to the cubic phase that are subsumed by the reflections of other possible coexisting phases (OI, OII, Au, Re, or Ir) in the high-pressure experiment may have caused problems in extracting accurate P - V data on the cubic phase.

It is to be recalled that the symmetry of the cubic phase was not unambiguously determined in the experimental study. The 210 reflection, absent in the fluorite x-ray diffraction (XRD) pattern but characteristic of the pyrite XRD pattern [22], is not detected in the experimental XRD data presented in [9]. The relative volume change with P observed in the experiment, however, is closer to that obtained for pyrite TiO_2 in our study.

The large difference in K_0 values computed for fluorite- and pyrite- TiO_2 is intriguing, considering that the two structures are closely related [Figs. 2(a) and 2(b)]. In the fluorite structure, Ti atoms occupy the (0,0,0) position defining a face-centered cubic (fcc) sublattice, while O

atoms occupy the $\pm(0.25, 0.25, 0.25)$ positions. Each Ti has eightfold cubic coordination to O, with a Ti-O distance ($d_{\text{Ti-O}}$) of 2.09 Å at 0 GPa. The pyrite structure is a slight distortion of the fluorite structure, with Ti atoms still defining an fcc sublattice, while O atoms positioned at $\pm(0.34, 0.34, 0.34)$. In pyrite, six O atoms form an inner shell at a $d_{\text{Ti-O}}$ of ~ 2.0 Å and two O atoms displaced to a $d_{\text{Ti-O}}$ of ~ 2.9 Å (zero-pressure values), yielding an average $\langle d_{\text{Ti-O}} \rangle$ of 2.2 Å and a unique rhombohedral Ti-O coordination of (6 + 2) [Figs. 2(a) and 2(b)].

The computed variation of Ti-O polyhedral volumes with pressure mirrors the P - V relations obtained for the bulk structures [Figs. 2(c) and 2(d)]. The higher compressibility of pyrite TiO_2 is perhaps accommodated by larger changes in Ti-O distances. In contrast to the proposed preference of metal oxides for a pyrite structure at high pressures [22], the present results on TiO_2 suggest that although at moderate pressures pyrite is a candidate structure, at extreme pressures the fluorite structure may be preferred for some families of oxides because it permits a more densely packed atomic arrangement.

A correlation between metal-oxygen coordination number (CN), taken on a first-coordination sphere basis, and K_0 is apparent in the available data for dense TiO_2 phases (see also Table I): rutile—CN = 6, $K_0 = 211 \pm 1$ GPa; co-

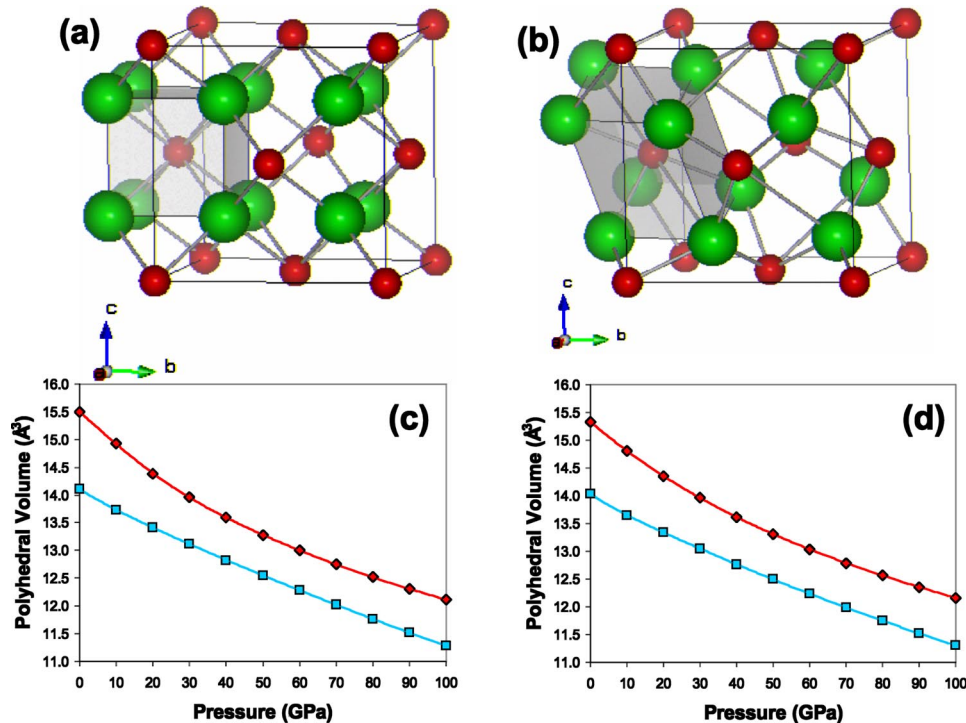


FIG. 2 (color online). The fluorite (a) and pyrite (b) structures showing Ti-O coordination polyhedra. Small and large spheres represent Ti and O atoms, respectively. The Ti atom centered on the (010) plane is surrounded by eight oxygen atoms in a cubic (eightfold) coordination in the fluorite structure, whereas Ti is surrounded by (6 + 2) oxygens forming a rhombohedral coordination polyhedron in the pyrite structure. The calculated zero-pressure volume of the Ti-O coordination polyhedron in fluorite is 14.1 \AA^3 with GGA and 14.03 \AA^3 with the hybrid functional, while that of the pyrite structure is 15.5 \AA^3 with GGA and 15.3 \AA^3 with the hybrid functional. The calculated pressure dependencies of the Ti-O polyhedral volume using the GGA (c) and hybrid (d) functionals suggests a higher compressibility of the pyrite rhombohedra (diamonds) compared to the cubic polyhedron of fluorite (squares).

lumbite—CN = 6, $K_0 = 258 \pm 8$ GPa; pyrite—CN = (6 + 2), $K_0 = 220\text{--}258$ GPa; MI—CN = 7, $K_0 = 303 \pm 6$ GPa; OI—CN = 7, $K_0 = 318 \pm 3$ GPa; fluorite—CN = 8, $K_0 = 395 \pm 4$ GPa; and OII—CN = 9, $K_0 = 431 \pm 10$ GPa. The K_0 values obtained for *c*-TiO₂ using first-principles calculations, and included above, may depend on factors such as the functional (LDA, GGA, or hybrid DFT-HF), the basis functions, and the numerical procedures of optimization employed; however, the overall trend in K_0 versus CN is unmistakable. The two functionals yield consistent results and there is every reason for confidence in the performance of the basis sets as well as the numerical procedures [15]. The K_0 -CN correlation and the systematic changes in the *P* dependence of polyhedral volumes affirm that cation-oxygen coordination and polyhedral compressibility are among the most important factors in determining the bulk modulus systematics in these oxide systems.

Considering the case of cubic RuO₂, for which first-principles theory and experiment confirmed large K_0 (299–399 GPa) associated with moderate values of experimentally determined hardness (19–20 GPa) [23], it would be premature to speculate on the basis of computed K_0 values that fluorite TiO₂ may be ultrahard. However, polycrystalline shear modulus (G_0) values calculable from the elastic constants may be used as an approximate guide to hardness [24,25] of *c*-TiO₂. Accordingly, the Voigt-Reuss-Hill average G_0 s obtained [15] for fluorite are 239 GPa (GGA) and 227 GPa (B3LYP). For pyrite, they are 131 GPa (GGA) and 154 GPa (B3LYP). The Hashin-Shtrikman averages [15] are 244 GPa (GGA) and 234 GPa (B3LYP) for fluorite and 132 GPa (GGA) and 154 GPa (B3LYP) for pyrite. These values are larger than the only available experimental data on TiO₂, namely, a $G_0 = 113.1 \pm 3.6$ GPa for rutile [11]. In view of these data and the fact that cotunnite TiO₂ is the hardest known oxide, it is highly plausible that fluorite TiO₂ is ultrahard with a hardness greater than that of a number of known hard materials (e.g., SiC, Si₃N₄, TiN, corundum, and stishovite).

In summary, our first-principles calculations of the *P*-*V* relations for fluorite- and pyrite-TiO₂ suggest significantly different compression behaviors for the two closely related structures, with the former being a highly incompressible solid. Our calculated shear modulus data point to the potential for fluorite TiO₂ to be an ultrahard material with useful applications (e.g., in hard coatings), if it can be stabilized under ambient conditions.

This work was partially supported by the Australian Research Council (ARC). Computations were carried out at the Australian Partnership for Advanced Computing National Facility and the Victorian Partnership for Advanced Computing facilities. We thank Nick Wilson (CSIRO Minerals, Clayton) for help with the software. Crystallographic visualizations were created using the VENUS software.

*Corresponding author.

Email address: Varghese.Swamy@eng.monash.edu.au

- [1] J. Haines, J.M. Léger, and G. Bocquillon, *Annu. Rev. Mater. Res.* **31**, 1 (2001).
- [2] P.F. McMillan, *Nat. Mater.* **1**, 19 (2002).
- [3] J.E. Lowther, *MRS Bull.* **28**, 189 (2003).
- [4] C.M. Sung and M. Sung, *Mater. Chem. Phys.* **43**, 1 (1996).
- [5] S. Desgreniers and K. Lagarec, *Phys. Rev. B* **59**, 8467 (1999).
- [6] L.S. Dubrovinsky, N.A. Dubrovinskaia, V. Swamy, J. Muscat, N.M. Harrison, R. Ahuja, B. Holm, and B. Johansson, *Nature (London)* **410**, 653 (2001).
- [7] O. Ohtaka, H. Fukui, K. Funakoshi, W. Utsumi, T. Irifune, and T. Kikegawa, *High Press. Res.* **22**, 221 (2002).
- [8] J. Kang, E.-C. Lee, and K.J. Chang, *Phys. Rev. B* **68**, 054106 (2003).
- [9] M. Mattesini, J.S. de Almeida, L. Dubrovinsky, N. Dubrovinskaia, B. Johansson, and R. Ahuja, *Phys. Rev. B* **70**, 212101 (2004).
- [10] T. Arlt, M. Bermejo, M.A. Blanco, L. Gerward, J.Z. Jiang, J. Staun Olsen, and J.M. Recio, *Phys. Rev. B* **61**, 14414 (2000).
- [11] D.G. Isaak, J.D. Carnes, O.L. Anderson, H. Cynn, and E. Hake, *Phys. Chem. Miner.* **26**, 31 (1998).
- [12] W. Luo, S.F. Yang, Z.C. Wang, Y. Wang, R. Ahuja, B. Johansson, J. Liu, and G.T. Zou, *Solid State Commun.* **133**, 49 (2005).
- [13] J.K. Dewhurst and J.E. Lowther, *Phys. Rev. B* **54**, R3673 (1996).
- [14] J. Muscat, V. Swamy, and N.M. Harrison, *Phys. Rev. B* **65**, 224112 (2002).
- [15] See EPAPS Document No. E-PRLTAO-98-041702 for details of computational methods, and calculated supporting data on the bulk modulus and elastic constants of TiO₂ polymorphs. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- [16] J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [17] A.D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [18] C. Lee, W. Yang, and R.G.Parr, *Phys. Rev. B* **37**, 785 (1988).
- [19] O.L. Anderson, *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford University Press, Oxford, U.K., 1995), p. 405.
- [20] V. Swamy, N.A. Dubrovinskaia, and L.S. Dubrovinsky, *J. Alloys Compd.* **340**, 46 (2002).
- [21] N.A. Dubrovinskaia, L.S. Dubrovinsky, R. Ahuja, V.B. Prokopenko, V. Dmitriev, H.-P. Weber, J.M. Osorio-Guillen, and B. Johansson, *Phys. Rev. Lett.* **87**, 275501 (2001).
- [22] J. Haines, J.M. Léger, and O. Schulte, *Science* **271**, 629 (1996).
- [23] J.M. Léger, P. Djemia, F. Ganot, J. Haines, A.S. Pereira, and J.A.H. da Jornada, *Appl. Phys. Lett.* **79**, 2169 (2001).
- [24] D.M. Teter, *MRS Bull.* **23**, 22 (1998).
- [25] V.V. Brazhkin, A.G. Lyapin, and R.J. Hemley, *Philos. Mag. A* **82**, 231 (2002).