Computational Materials Science 82 (2014) 202–218

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Anisotropic elasticity, sound velocity and thermal conductivity of TiO_2 polymorphs from first principles calculations

Yingchun Ding [a], Bing Xiao [b,*]

[a] College of Optoelectronics Technology, Chengdu University of Information Technology, Chengdu 610225, People's Republic of China
[b] Department of Physics, College of Science and Technology, Temple University, Philadelphia, PA 19122, USA

ARTICLE INFO

Article history:
Received 7 April 2013
Received in revised form 12 June 2013
Accepted 29 September 2013
Available online 22 October 2013

Keywords:
Elasticity
Sound velocity
Thermal conductivity
Anisotropy

ABSTRACT

We have investigated the anisotropies in mechanical properties, sound velocity and thermal conductivity of seven TiO_2 polymorphs using the computed elastic constants by PBEsol functional. The computed equilibrium lattice constants in this work are in agreement with those experimental values. We plot the planar contours of Young's moduli and sound velocities of TiO_2 structures at several crystallographic planes to reveal their anisotropic properties. The minimum thermal conductivities of them are calculated using either Cahill–Pohl model or Cahill model. Our results imply that TiO_2 polymorphs have strong anisotropic elasticity, but they exhibit weak anisotropies in sound velocities. Otherwise, Cahill–Pohl model gives reasonable estimations for the minimum thermal conductivities for amorphous TiO_2 structures. The anisotropy in sound velocity revealed by Christoffel equation can be considered as a good starting point for investigating the anisotropy of lattice thermal conductivity in a crystalline material.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Titanium dioxide (TiO_2) is one of the best known metal oxides and which is of great interest due to its wide range of applications in the semiconductor technology and electrochemical industries [1]. In the last few years, titanium dioxide has been the subject of investigations in both the experimental and theoretical sides due to its unique properties like excellent photoactivity, long-term stability, low cost and non-toxicity. TiO_2 found potential applications in many products and processes such as pigments, dye-sensitized solar cells, air purification, anti-fogging and self cleaning films and hydrogen production by water splitting [2–4]. Titanium dioxide (TiO_2) also possesses a rich phase diagram with many polymorphs. Among them, rutile ($P4_2/mnm$), anatase ($I4_1/amd$), and brookite ($Pbca$) are naturally occurring phases. Otherwise, TiO_2 has different polymorphs that form naturally or under high pressure and temperature [5–10]. At elevated pressures, TiO_2 experiences a series of structural phase transitions. Its high-pressure polymorphs, i.e., columbite (TiO_2 II phase, space group Pbcn) [11], baddeleyite (MI, $P2_1/c$) [12], orthorhombic I (OI, $Pbca$) [13], and cotunnite (OII, $Pnma$) [5], were discovered experimentally. Recently, the theoretical calculations of the structural parameters, electronic, optical and elastic properties of the cubic polymorphs (fluorite-type Fm-3m and pyrite type Pa-3) of TiO_2 phases are reported [14–16]. And the other new TiO_2 polymorphs are found and reported by both density-functional ab initio calculations and high-pressure experiments [17–21]. Among all these TiO_2 polymorphs, the cotunnite-structured TiO_2 was reported to be the hardest oxide ever known [8,22]. But, these TiO_2 polymorphs were not superhard materials [16].

TiO_2 is one of important functional material. The optical and elastic properties have been intensively discussed in the previous works. However, the anisotropies in elasticity, sound velocity and thermal conductivity of TiO_2 polymorphs are lack of throughout investigations. In this paper, our main interests are aimed to study the anisotropies in mechanical properties (especially Young's modulus and sound velocities) and minimum thermal conductivities of seven TiO_2 polymorphs. The dependence of minimum thermal conductivity on temperature will be calculated using Cahill–Pohl model. The calculated properties are compared to experimental results.

2. Methods and computational details

The first principles calculations were performed using plane waves and pseudopotentials approximations as implemented in CASTEP code [23]. For the plane wave expansions in reciprocal space, the kinetic energy cutoff was set to 500 eV. The ultrasoft pseudopotentials of Ti and O were applied in this work, i.e., Ti ($3d^24s^2$) and O ($2s^22p^4$). The exchange-correlation energy was approximated by modified PBE functional for solids (PBEsol) which gives more accurate equilibrium lattice constants than LDA and PBE functionals [24]. The energy integrations were calculated in the first irreducible Brillouin zone using discrete k grids generated by Monkhorst–Pack method [25]. The k meshes were carefully

* Corresponding author. Tel.: +1 (215)900 4820.
E-mail address: tuf23889@temple.edu (B. Xiao).

0927-0256/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.commatsci.2013.09.061

adjusted for each TiO_2 structure to ensure that the obtained results were converged with respect to the total number of k points. The crystal structures of TiO_2 polymorphs were optimized using BFGS algorithm [26]. Within current settings, the total energy was converged to 1 meV/atom and the mean Feynman-Hellmann force acting on the atoms was reduced to 0.001 eV/Å. The independent elastic constants of each TiO_2 structure were calculated by stress–strain method in CASTEP code. The details about the evaluation of elastic constants from first principles calculations can be found in Refs. [27–29].

The crystal structures of TiO_2 polymorphs studied in our paper are shown in Fig. 1. Most TiO_2 crystals are consisted of TiO_6 octahedral chains in three-dimensional space. The coordinate numbers of Ti and O atoms are usually 6 and 3, respectively. In columbite and cotunnite, the coordination number of O atom is 4. The distortions of TiO_6 octahedral are also significant in some high density polymorphs due to their low symmetries.

3. Results

3.1. Lattice constants and stability

In the present paper, we have considered the most studied seven TiO_2 polymorphs in literatures. The computed equilibrium lattice constants, formation enthalpies and cohesive energies of them are given in Table 1 and Fig. 2. The optimized lattice parameters of

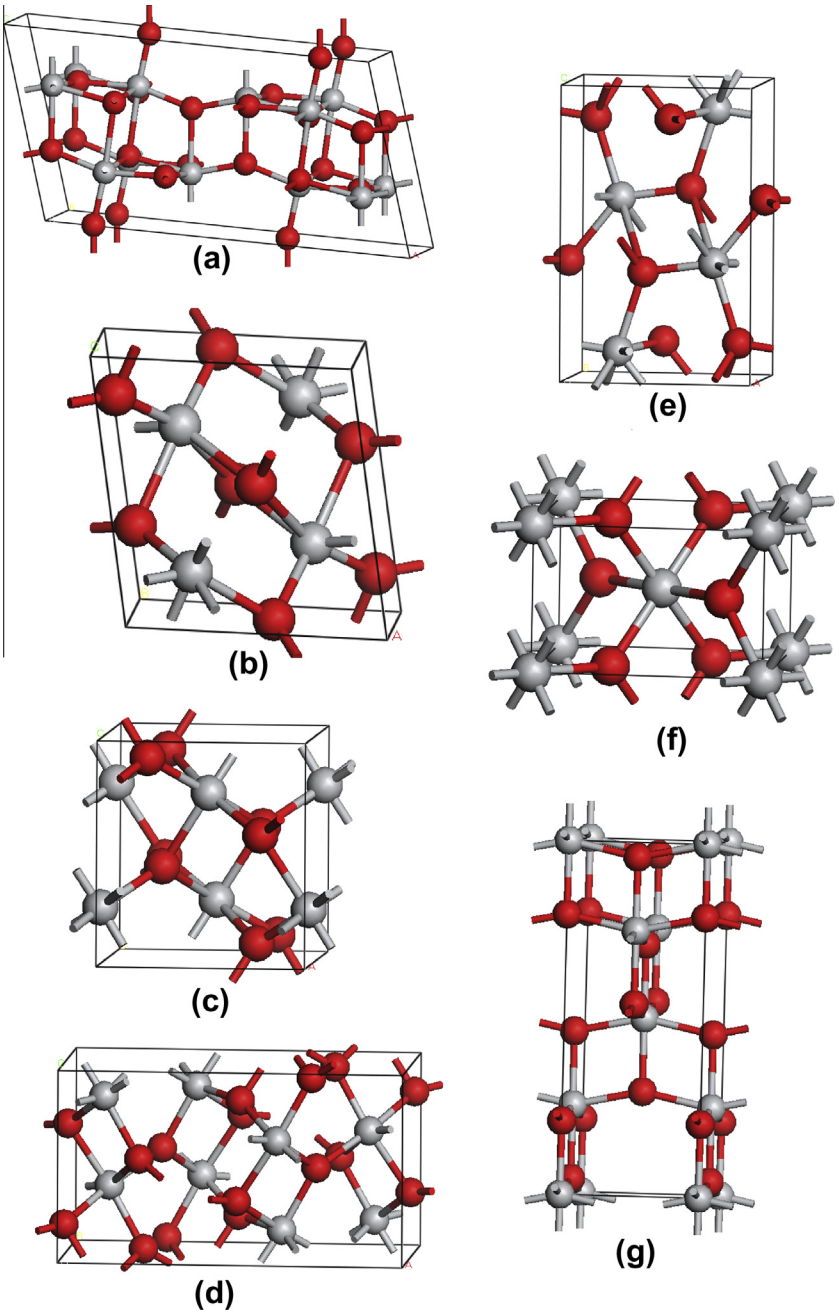

Fig. 1. The crystal structures of seven TiO_2 polymorphs. Gray atoms are titanium and red atoms are oxygen: (a) TiO_2 (B) (monoclinic system, $C2/m$, No. 12, $Z = 8$), (b) hp-TiO_2 (monoclinic system, $P2_1/c$, No. 14, $Z = 4$), (c) columbite (PbO_2 type structure) (orthorhombic system, *Pbcn*, No. 60, $Z = 4$), (d) brookite (orthorhombic system, *Pbca*, No. 61, $Z = 8$), (e) cotunnite (Orthorhombic system, *Pnma*, No. 62, $Z = 4$), (f) rutile (tetragonal system, $P4_2/mnm$, No. 136, $Z = 2$), and (g) anatase (tetragonal system, $I4_1/amd$, No. 141, $Z = 4$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

https://daneshyari.com/en/article/7961040

Download Persian Version:

https://daneshyari.com/article/7961040

Daneshyari.com