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Density functional theory study of tin and titanium dioxides: Structural and mechanical properties in the tetragonal rutile phase

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ABSTRACT

Structural and mechanical properties in rutile (tetragonal) phases of SnO_2 and TiO_2 are investigated by performing first-principle density functional theory (DFT) calculations. Generalized Gradient Approximation (GGA) potentials of electronic exchange and correlation part parameterized by Perdew–Burke–Ernzerhof (PBE) are used. Second order elastic stiffness constants, bulk modulus, first-derivative of bulk modulus, and pressure behavior of these mechanical properties are studied up to pressure of 10 GPa. Structural properties and elastic constants of SnO_2 and TiO_2 calculated in this study are compatible with experimental and other available theoretical studies. Electronic band gap energies of these semiconductors are also calculated. As expected, the calculated values by standard DFT calculations are underestimated in comparison to experimental values.

1. Introduction

SnO_2 and TiO_2 are two wide band gap semiconductor materials having numerous applications in recent technologies. Both of them have photo catalytic properties. SnO_2 is used to enhance performance of dye-sensitized solar cells, Li-ion batteries and selective gas sensors [1–3].

TiO_2 is used for cleaning and health purposes in addition to its photovoltaic and optoelectronic applications [4–8]. Haines and Leger, Shieh et al. and Huang et al. measured structural parameters of SnO_2 experimentally by x-ray diffraction [9–11]. Elastic constants of SnO_2 were determined using ultrasonic pulse superposition method by Chang and Graham [12] and Brillouin and Raman spectroscopy by Hellwig et al. [13]. Frochlich et al. [14] and Schweitzer et al. [15] measured the electronic band gap energy of SnO_2 by employing two-photon spectroscopy. Theoretical studies are also performed to investigate its mechanical, electronic and optical properties [16–23]. Neutron powder diffraction and x-ray diffraction methods were used to determine the structural parameters of TiO_2 experimentally [24–26]. While Grimsditch and Ramdas [27]used Brillouin scattering to obtain elastic constants of TiO_2 at room temperature, Isaak et al. [28] applied the rectangular parallel piped (RPR) technique to measure them at the temperature range of 300–1800 K –. Tang et al. [29] measured the band gap energy of TiO_2 by performing polarized optical transmission measurements, Amtout and Leonelli [30] hired both time-integrated photo-luminescence and resonant-Raman scattering spectra „. Structural parameters, mechanical properties and electronic band gap of TiO_2 were studied theoretically as well [31–38].

SnO_2 has seven and TiO_2 has nine known polymorphs among which the rutile structure is the most abundant and stable one at ambient conditions [16,31]. So the aim of this study is to investigate structural, mechanical properties and band gap of rutile phases of SnO_2 and TiO_2. The parts of paper are organized as follows: Computational method is explained in Section 2. Results are compared to those of other available

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experimental and theoretical studies in Section 3. Conclusion is given in the last Section 4.

2. Computational method

Calculations within density functional theory (DFT) have been performed by a projector augmented-wave method (PAW) with Blochl corrections as implemented in Vienna ab-initio Simulation Package (VASP) [39–41]. Generalized Gradient Approximation (GGA) potentials which include electronic exchange and correlation part parameterized by Perdew–Burke–Ernzerhof (PBE) were employed [42]. The kinetic cut-off energy was 500 eV for both structures, rutile SnO_2 and TiO_2 in this study. For Brillouin zone integrations the k-point meshes converged at $8\times8\times10$ according to Monkhorst–Pack method [43]. Primitive cell of rutile structure contains 2 formula units. Convergence criteria difference between two-steps of total-energy calculations was taken as 10^{-6} eV per formula unit. Third-order Birch–Murnaghan equations of state (EoS) are used to predict the structural parameters of the semiconductors in this work [44]. Unit cell of each material is constructed by means of an experimental result as a starting point of simulations. Band gap calculations are performed in two steps. Charge distributions were obtained by self-consistent calculation. Then, band diagrams are evaluated by non self-consistent calculation along the paths between high symmetry points Γ, X, M, Γ, Z, R, A and Z in the Brillouin zone in reciprocal space.

3. Results

3.1. Structural and mechanical properties

The energy–volume data per unit formula calculated by DFT were fitted to one of equation of states for solids called as third-order Birch–Murnaghan EoS. Total energy of system is given as a function of volume as follows [44]:

$$E(V)=E_0+\frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]^3B_0'+\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]^2\left[6-4\left(\frac{V_0}{V}\right)^{2/3}\right]\right\}, \quad (1)$$

where E_0 is the total energy, V_0 is the equilibrium volume, B_0 is the bulk modulus at the pressure of 0 GPa and B_0' is the first derivative of B_0 with respect to pressure. Structural and mechanical properties of SnO_2 were investigated in our previous study [16]. Thus, the same calculations have also been performed for rutile TiO_2 beside electronic band gap calculations in this work. The phase of rutile structure (P_{42}/mnm space group number 136, $Z=2$) has tetragonal symmetry in which oxygen atoms are located at 2*a* Wyckoff sites $\pm(u, u, 0)$, $(½+u, ½-u, ½)$ and Sn (Ti) atoms at 4f Wyckoff sites (0, 0, 0), (½, ½,½) as shown in Fig. 1, where u is the unitless internal parameter which shows the fractional positions of oxygen and Sn (Ti) planes [45]. Our calculated structural parameters of SnO_2 (TiO_2) are given in Table 1 (Table 2) in comparison with experimental and other available theoretical results. It is a well-known fact that DFT calculations using GGA type

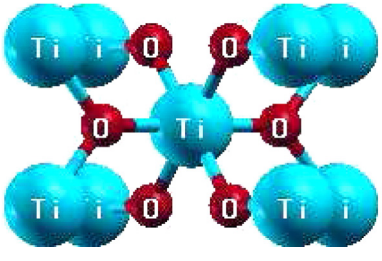

Fig. 1. Unit cell of rutile TiO_2 (P_{42}/mnm space group number 136 tetragonal).

Table 1
DFT calculation of equilibrium structural parameters of *a*(Å), *c*(Å), internal parameter *u*, bulk modulus at zero pressure B_0 (GPa) and its pressure derivative B'_0. The rutile structure of SnO_2 is compared with the data of experiments [9,10] and other available calculations [17,18].

	Present	Other	Calculations	Experiments	
a (Å)	4.830	4.776[a]	4.826[b]	4.737[c]	4.746[d]
c (Å)	3.236	3.212	3.237	3.186	3.189
u	0.306	0.306	0.307	0.307	
B_0 (GPa)	173	192	179	205	
B'_0	5.4	4.8	5.0	7.4	

[a] From Ref. [17]
[b] From Ref. [18]
[c] From Ref. [9]
[d] From Ref. [10]

Table 2
The calculated equilibrium parameters of rutile structured TiO_2, *a*(Å), *c* (Å), internal parameter *u*, bulk modulus at zero pressure B_0 (GPa) and its pressure derivative B'_0, are compared with the data of experiments [25,26] and other available calculations [31,33].

	Present	Other	Calculations	Experiments	
a (Å)	4.661	4.641[a]	4.681[b]	4.592[c]	4.594[d]
c (Å)	2.969	2.968	3.005	2.964	2.958
u	0.3046	0.305	0.304		0.3053
B_0 (GPa)	210.2			230	
B'_0	5.8			6.6	

[a] From Ref. [33]
[b] From Ref. [31]
[c] From Ref. [25]
[d] From Ref. [26]

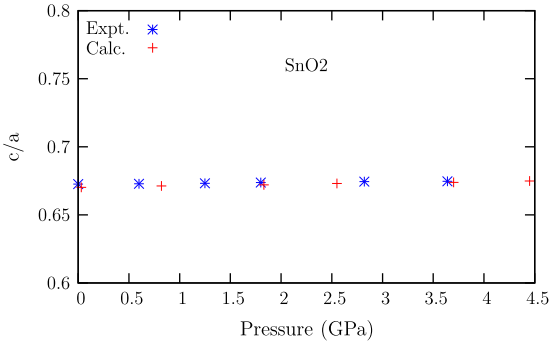

Fig. 2. Comparison of calculated *c*/*a* ratio of SnO_2 with an experimental study available up to 3.6 GPa.

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