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The structural, elastic, and electronic properties of the pyrite-type phase for SnO_2

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Abstract

We have studied some structural, thermodynamic, elastic, and electronic properties of pyrite-type SnO_2 polymorph by performing ab initio calculations within the LDA approximation. The basic physical properties, in particular lattice constant, bulk modulus, second-order elastic constants (C_{ij}), and the electronic structure, are calculated, and compared with the available experimental data. In order to gain some further information on the mechanical properties, we have also calculated the Young's modulus, Poison's ratio (ν), anisotropy factor (A), sound velocities, and Debye temperature for the same compound.

Keywords: C. ab initio calculations; D. Elastic properties; D. Electronic structure; D. Thermodynamic properties

1. Introduction

After improvements in high-pressure experimental devices such as the diamond anvil cell, research on high-pressure polymorphs has become an attractive area of analysis, especially in solid-state physics, crystal chemistry, geophysics, and materials science. Meanwhile, there has been considerable interest in the high-pressure behaviour of metal dioxides, including SnO_2, since it is considered a low-pressure analogue of SiO_2 [1]. It is well known that tin and its oxides are technologically important materials due to their applications in solar cells, gas-sensing element sensors, electronic components, and lithium ion batteries [2–4].

Experimental observations [1,5–12] made under different conditions and theoretical predictions [13–16] show that the SnO_2 crystallizes in the rutile structure ($a=b=4.7374$ Å, $c=3.186$ Å) with two cations at positons $2a$: (0 0 0) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and the six O atoms at positions $4f\pm(u, u, 0, \frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}$ with u=*0.3056*, [2]) at ambient conditions, and it transforms to $CaCl_2$-type, then α-PbO_2–type, and finally a pyrite (modified fluorite)-type structures under high-pressure.

In an early theoretical study on the rutile phase of SnO_2 nanocrystalline grains, Mazzone [13] investigated the binding and fragmentation energies of SnO_2 based on the extended Debye–Hükel approximation. Terra and Guenzburger [14] studied the electronic structures of clusters representing crystalline compounds of Sn (II) and Sn (IV) in rutile phase, employing the first-principles discrete-variation method and local density theory. Sevik and Bulutay [15] recently investigated the elastic, electronic, and lattice dynamical properties of some metal dioxides (SiO_2, GeO_2, and SnO_2) in "i-phase", by using the ab initio density functional theory within the local density approximation (LDA). Errico [16] made some calculations on the structural and electronic properties of the rutile phase of SnO and SnO_2 using the full-potential linearized-augmented plane waves method within the local density and the generalized gradient approximations. Postnikov et al. [17] calculated the bulk and surface properties of rutile SnO_2 using the same method in their work. Parlinski and Kawazoe [18] studied the lattice dynamical properties of SnO_2 using the first-principles calculations for the same structure.

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Ono et al. [10] have recently synthesized and analysed the pyrite-type structured phase of SnO_2 with Pa-3 space group (No. 205) symmetry at high pressure using a laser-heated diamond anvil cell and the synchrotron X-ray diffraction method. The difference between the fluorite- and pyrite-type structures mainly occurs in the different positions of the oxygen atoms in each structure. In the case of the fluorite-type structure, the oxygen atoms are located at $u = 0.25$ in the 8c Wyckoff position with space group Fm–3 m. However, in the case of the pyrite-type structure, the oxygen atoms are situated at $u = 0.34$ in the 8c Wyckoff position with space group Pa-3 ([19], and Refs. therein).

Although a few theoretical studies exist on the rutile structure (D_{4h}) of SnO_2, to the best of our knowledge, there is no other theoretical study on the pyrite-type phase of the same compound. This study aims to gain some basic theoretical information on the structural, elastic, electronic, and thermodynamical behaviour of this compound at ambient conditions and higher pressures. The layout of this paper is given as follows: The method of calculation is given in Section 2. The results and overall conclusion are presented and discussed in Section 3.

2. Method of calculation

The SIESTA (The Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [20–22] was utilized in this study to calculate the energies and atomic forces. It solves the quantum mechanical equation for the electrons within the density functional approach in the local density approximation (LDA) parameterized by Ceperley and Alder [23]. The interactions between electrons and core ions are simulated with separable Troullier–Martins [24] norm-conserving pseudopotentials. The basis set is based on the finite range pseudoatomic orbitals (PAOs) of the Sankey–Niklewsky type [25], generalized to include multiple-zeta decays. We have generated atomic pseudopotentials separately for both atoms, Sn and O, by using the $5s^2 5p^3 5d^0 4f^0$ and $2s^2 2p^4 3d^0 4f^0$ atomic configurations, respectively. The cut-off radii for the present atomic pseudopotentials are taken as s: 2.60, p: 2.45, d: 2.60, and f: 2.50 au for Sn, and 1.15 au for s, p, d, and f channels for O. The relativistic effects are taken into account for Sn, due to its heavy mass in pseudopotential calculations.

SIESTA calculates the self-consistent potential on a grid in real space. The fineness of this grid is determined in terms of an energy cut-off E_c in analogy to the energy cut-off when the basis set involves plane waves. Here, by using a double-zeta plus polarization (DZP) orbitals basis and the cut-off energies between 100 and 300 Ry with various basis sets, we found an optimal value of around 250 Ry. Atoms were allowed to relax until atomic forces were less than 0.04 eV Å. For the final computations, 196 k-points were found to be adequate for obtaining the total energy with an accuracy of about 1 meV/atom.

3. Results and discussion

3.1. Structural and electronic properties

First, the equilibrium lattice parameter was computed by minimizing the crystal's total energy calculated for the different values of lattice constant by means of Murnaghan's equation of state (EOS) [26] as in Fig. 1. The bulk modulus and its pressure derivative have also been estimated based on the same Murnaghan's EOS, and the results are given in Table 1 along with the experimental values [1,6,10]. The calculated lattice constant (a_0) is in excellent agreement with the experimental values [1,6,10]. The present value of bulk modulus is about 5% higher than the experimental value of Heines and Leger [1], and is about 15% higher than the recent experimental value calculated by Ono et al. [10]. Since the calculation of EOS is an essential step to examine the accuracy of a theoretical calculation, the variation in volume as a function of pressure is compared with experimental values of Ono et al.

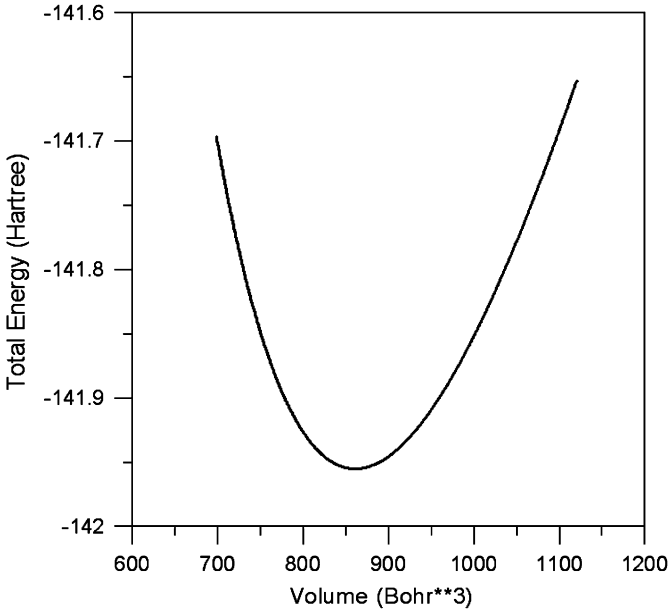

Fig. 1. Energy versus volume curve of pyrite-type SnO_2 polymorph.

Table 1
Calculated equilibrium lattice constant (a_0), bulk modulus (B), and the pressure derivative of bulk modulus (B'), together with the experimental values, for pyrite-type SnO_2 polymorph

Material	Reference	a_0 (Å)	B (Gpa)	B'
SnO_2	Present (LDA)	5.0447	345.017	3.96
	Experimental[a]	5.0409	307(10)	4.00
	Experimental[b]	5.0579	328(16)	4.00
	Experimental[c]	5.0735	252	3.5

[a]Ref. [10].
[b]Ref. [1].
[c]Ref. [6].