



First-principles study of structural, elastic, electronic, and thermal properties of SrTiO₃ perovskite cubic

A. Boudali^{a,*}, M. Driss Khodja^a, B. Amrani^b, D. Bourbie^c, K. Amara^a, A. Abada^a

^a Laboratoire d'Etudes Physico Chimiques, Centre Universitaire de Saida "Dr. Moulay Tahar", Saida 20000, Algeria

^b Département de Physique, Institut des sciences & Technologie, Centre Universitaire de Mascara, Mascara 29000, Algeria

^c Laboratoire de Sciences de la Matière Condensée, Université d'Oran Es Sénia, Oran 31000, Algeria

ARTICLE INFO

Article history:

Received 12 October 2008

Received in revised form 3 December 2008

Accepted 10 December 2008

Available online 16 December 2008

Communicated by A.R. Bishop

PACS:

71.15.Ap

71.15.Mb

65.40.-b

Keywords:

FP-LAPW

Thermodynamic properties

Quasi-harmonic Debye model

ABSTRACT

In this Letter, we study the structural, elastic and electronic properties of perovskite semiconductor SrTiO₃ using two different methods: the full-potential linearized augmented plane wave (FP-LAPW) method and the pseudo-potential plane wave (PP-PW) scheme in the frame of generalized gradient approximation (GGA). We have evaluated the ground state quantities such as lattice parameter, bulk modulus and its pressure derivative as well as the elastic constants. Also, we have presented the results of the band structure, densities of states and charge densities. These results were in favourable agreement with previous theoretical works and the existing experimental data. To complete the fundamental characteristics of this compound we have analyzed the thermodynamic properties such as thermal expansion coefficient, and specific heats in the whole pressure range from 0 to 20 GPa and temperature range from 0 to 1200 K.

© 2008 Published by Elsevier B.V.

1. Introduction

Strontium titanate, SrTiO₃, belongs to ABO₃ perovskite oxides group where A and B are elements with various valences and ionic radii. The structure and the properties of ABO₃ perovskite oxides are intimately related to anions and cations sizes [1]. The majority of these oxides show a cubic to tetragonal phase transition with, of course, marked changes at the critical temperature [2]. Similarly to BaTiO₃, SrTiO₃ suffers a structural transition phase around 110 K. Nevertheless, tetragonal SrTiO₃ is not ferroelectric. This had led to a series of papers regarding more particularly SrTiO₃ structural properties [3–7]. In Refs. [2] and [8] there is a phase transition at 110 K and 105 K, respectively, with $c/a = 1.0005$ obtained experimentally [9] and $c/a = 1.0006$ by calculation [8]. However for others [10], the phase transition is obtained theoretically at 300 K and experimentally at 298 K [11]. Other work by they fixed the cubic phase is maintained up to 1273 K [12]. These results justified the weak variations of volume and energy. In other words, the tetragonal phase is considered as pseudo-cubic.

SrTiO₃ gave rise to great deal of attention due mainly to its catalytic, dielectric, and ferroelectric properties [3–7]. Recently, SrTiO₃

attracts a considerable interest in microelectronics industry owing to the need of materials with small flight current. SrTiO₃ is used, in particular, at large scale, as substrate at the time of growth of thin films perovskite compounds, like high temperature superconductors. In this connection, it is noteworthy that the substrate surface structure and its control are determinant factors [13]. To our knowledge, there is less or none theoretical studies in the literature devoted to SrTiO₃ thermal properties.

The aim of this work is to provide information regarding SrTiO₃ thermal properties. Section 2 concerns the procedure calculation. The results are reported and discussed in Section 3. Finally, in Section 4, we present our conclusions.

2. Theoretical method

The zero-temperature energy calculations are performed using both the all-electron full-potential linear augmented-plane-wave method (FP-LAPW) [14] and the plane-wave pseudopotential (PPs-PW) [15] method. In both cases exchange-correlation effects were described using the Perdew et al. (GGA96) form [16].

The FP-LAPW calculations have been carried out using the WIEN2k code [14]. The sphere radii used in the calculations are 2.03, 1.88 and 1.66 a.u. for Sr, Ti and O, respectively. Within these spheres, the charge density and potential are expanded in terms of crystal harmonics up to angular moment $L = 10$, and a plane

* Corresponding author.

E-mail address: boudaliabdel@yahoo.fr (A. Boudali).

wave expansion has been used in the interstitial region. The Brillouin zone integrations for the total energy have been carried out using 35 special k -points in the irreducible Brillouin zone. Well converged solutions were found for $R_{\text{cut}}K_{\text{max}} = 8$, where K_{max} is the plane wave cut-off and R_{cut} is the atomic sphere radii. Both the muffin-tin radius and the number of k -points are varied to ensure convergence. Core states are treated fully relativistic but for valence states relativistic effects have been included in a scalar relativistic treatment.

The PP-PW calculations were performed using the CASTEP computer code [15]. The basic idea of the code is to solve the Kohn-Sham equations by minimizing the total-energy functional rather than by diagonalizing the Hamiltonian matrix. We use a plane wave basis with a cut-off of 450 eV to expand the (pseudo) valence wave function; the band-by-band minimization is achieved by the preconditioned conjugate gradient search in the space of the expansion coefficients. The ion–electron interaction is represented by non local norm-conserving pseudopotential in Kleinman–Bylander form [17]. The major advantages of this approach are: the ease of computing forces and stresses; good convergence control with respect to all computational parameters employed; favourable scaling with number of atoms in the system and the ability to make cheaper calculations by neglecting core electrons. Two parameters that affect the accuracy of calculations are the kinetic energy cut-off which determines the number of plane waves in the expansion and the number of special k -points used for the Brillouin zone (BZ) integration. We performed convergence with respect to BZ sampling and the size of the basis set. Converged results were achieved with $9 \times 9 \times 2$ special k -points mesh [18]. Careful convergence tests show that with these parameters relative energy converged to better than 10^{-6} eV/atom.

To investigate the thermodynamic properties of SrTiO₃, we apply the quasi-harmonic Debye model [14,19], in which the non-equilibrium Gibbs function $G^*(V, P, T)$ can be written in the form of

$$G^*(V, P, T) = E(V) + PV + A_{\text{vib}}(\theta, T), \quad (1)$$

where $E(V)$ is the total energy per unit, PV corresponds to the constant hydrostatic pressure condition, $\theta(V)$ is the Debye temperature, and A_{vib} is the vibrational term, which can be written using the Debye model of the phonon density of states as [20,21].

$$A_{\text{vib}}(\theta; T) = nkT \left[\frac{9\theta}{8T} + 3 \ln(1 - e^{-\theta/T}) - D\left(\frac{\theta}{T}\right) \right], \quad (2)$$

where n is the number of atoms per formula unit, $D(\theta/T)$ represents the Debye integral, and for an isotropic solid, θ is expressed as [20].

$$\theta = \frac{\hbar}{k} (6\pi^2 V^{1/2} n)^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}}, \quad (3)$$

where M is the molecular mass per unit cell; B_s is the adiabatic bulk modulus, which is approximated by the static compressibility [19]

$$B_s \cong V \frac{d^2 E(V)}{dV^2}. \quad (4)$$

$f(\sigma)$ is given by Refs. [22,23]; the Poisson σ is taken as 0.25 [24]. Therefore, the non-equilibrium Gibbs function $G^*(V, P, T)$ as a function of (V, P, T) can be minimized with respect to volume V

$$\left[\frac{\partial G^*(V; P, T)}{\partial V} \right]_{P, T} = 0. \quad (5)$$

By solving Eq. (5), one can obtain the thermal equation of $V(P, T)$. The heat capacity C_V and the thermal expansion coefficient α are given by [25].

$$C_V = 3nk \left[4D\left(\frac{\theta}{T}\right) - \frac{3\theta/T}{e^{\theta/T} - 1} \right], \quad (6)$$

$$S = nk \left[4D\left(\frac{\theta}{T}\right) - 3 \ln(1 - e^{-\theta/T}) \right], \quad (7)$$

$$\alpha = \frac{\gamma C_V}{B_T V}, \quad (8)$$

where γ is the Grüneisen parameter, which is defined as

$$\gamma = - \frac{d \ln \theta}{d \ln V}. \quad (9)$$

Through the quasi-harmonic Debye model, one could calculate the thermodynamic quantities of any temperatures and pressures of SrTiO₃ from the calculated $E-V$ data at $T = 0$ and $P = 0$. By using the method above, the thermodynamic properties of BaTiO₃, BaZrO₃, and BaNbO₃ are successfully obtained [26].

3. Results and discussion

3.1. Structure and elastic constants

We firstly calculate the structural and elastic properties using FP-LAPW and PPs-PW methods. The total energy is obtained as a function of volume and fitted to a Murnaghan equation of state [27] to obtain the equilibrium lattice constant, bulk modulus, and its pressure derivative. The results are summarized in Table 1, together with some theoretical results and the available experimental data. Obviously, the results that we calculated by FP-LAPW are in better agreement with the experiment compared to our results calculated by PP-PW.

The elastic constants are also presented in Table 1 are in agreement with the theoretical results and experimental work. Calculations exploring the elastic constants were performed to use for SrTiO₃, our data will be beneficial to future investigation.

3.2. Electronic properties

Density of states and electronic band structure often provide sufficient information for a through characterization of the electronic properties of a material. The energy band structure, total and partial density of states (DOS) of SrTiO₃ were calculated by FP-LAPW and PPs-PW methods. Because of similarity, only the results of FP-LAPW are presented in Fig. 1 (1.82 eV) and Fig. 2 (1.74 eV). There is an overall topological resemblance of the present band structure and those calculated recently by Samantaray et al. [28]. Our calculations show that the valence band maximum and the conduction band minimum are located at R .

From Fig. 2, we can find that the DOS can be mainly divided into four parts. The first part extending from -17.65 eV to -15.86 eV is of the combination of Sr p Ti p , O s and Ti d states,

Table 1

Cubic phase. Lattice constant a , bulk modulus B , pressure derivative of bulk modulus B' and elastic constants parameters of SrTiO₃ at zero pressure and zero temperature, compared with the experimental data and other theoretical works.

	Present work (FP-LAPW)	Present work (PW-PP)	Experiment	Other theoretical works
a (Å)	3.94	3.94	3.92 ^a	3.94 ^c , 3.95 ^d
B_0 (GPa)	169.72	169.59	169 ^a	171 ^c , 170.0 ^d
B'	4.44	4.43		
C11 (GPa)	311.08	313.86	317.2 ^b	319.3 ^c , 312.9 ^d
C12 (GPa)	99.04	97.46	102.5 ^b	97.5 ^c , 98.0 ^d
C44 (GPa)	107.66	112.16	123.5 ^b	113.0 ^c , 113.4 ^d

^a Ref. [35], at room temperature.

^b Ref. [36], at room temperature.

^c Ref. [37], using PPE.

^d Ref. [37], using PWGGA.

Download English Version:

<https://daneshyari.com/en/article/1862290>

Download Persian Version:

<https://daneshyari.com/article/1862290>

[Daneshyari.com](https://daneshyari.com)