First principles study of the structural, elastic and thermodynamic properties of the cubic perovskite-type SrTiO₃

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ABSTRACT

Structural, elastic modulus for the SrTiO₃ crystal in the cubic (Pm3m) phase were calculated by the first-principles calculations using the plane wave pseudo potential calculations (PP-PW) im-plemented in the ABINIT package within density functional theory and the generalized gradient approximation based on the Perdew–Burke–Ernzerhof (PBE-GGA) functional. The thermody-namic properties have been investigated by using the GIBBS program, which is based on the qua-si-harmonic model of Debye.
The structural parameters (lattice constant, bulk modulus), mechanical (elastic constant, Young's Modulus, shear modulus and Poisson's ratio), thermodynamic properties (the variation of the volume, bulk modulus and thermal expansion coefficient, heat capacity at constant volume CV, heat capacity at constant pressure CP and entropy) as function of temperature of the SrTiO₃ cubic phase, are studied. The results of our simulations are discussed and compared to experi-mental and theoretical results when available.

1. INTRODUCTION

The ABO3 perovskite-type oxides, where A is a monovalent or divalent cation, B is penta- or tetravalent transition metal atom and O is oxygen, display a wide range of interesting electrical and optical properties and therefore have wide applications in the manufacture of electronic and optoelectronic devices such as various sensors, electro-optic modulators, infrared detectors, catalytic activity, optical waveguides in various applications [1-2]. Strontium titanate (SrTiO₃) is a typical perovskite dielectric with a wide range of technological applications. Because of its special properties related to ferroelectricity, semi conductivity, superconductivity and catalytic activity, it has been extensively studied over the past several years.

From the literature data, SrTiO₃ undergoes the following sequence of phase transitions [1]: $I4/mcm \xrightarrow{105K} Pm-3m$

In the present study SrTiO₃ perovskite is assumed to have ideal cubic structure (e.g. Pm3m) where atomic positions in the elementary cell are Ti: 1a (0, 0, 0); O: 3d (1/2,1/2, 0); and Sr: 1b (1/2, 1/2, 1/2). Here, the noble gas cores are distinguished from the sub-shells of valence electrons. Plane waves method has been employed as a basis set for the electronic wave functions. Hartwigsen-Goedecker-Hutter pseudopotentials have been used in our calculations.

2. COMPUTATIONAL DETAILS

The present calculations were performed in the density functional theory (DFT) framework implemented in the ABINIT package [3]. The exchange-correlation energy is evaluated in the generalized gradient approximation GGA [4] using the Teter "extended norm-conserving" [5] pseudopotentials. The electronic wave functions were expanded in terms of a plane-wave basis set and the kinetic energy cut off needed to obtain a convergence better than 1 mHa (Ha =Hartree) for total energy is found to be equal to 220 Ha (cubic phase). With the application of norm-conserving pseudopotentials, the taken valence configurations are 4s24p6 5s2 for Sr, 3s2 3p6 3d2 4s2 for Ti and 1s2 2s2 2p4 for O. The sampling over the Brillouin zone was treated by a 4x4x4 Monkhorst-Pack mesh grid [6]. The calculation was perfrmed at the equilibrium lattice constants that are determined from the plot of total energy against the unit cell volume fitted to the Birch-Murnaghan equation of state [7]. The elastic constants (C_{ij}) are obtained with a total energy method [8-9] using density functional perturbation theory (DFPT),

$$C_{ij} = \frac{1}{V_0} \frac{\partial^2 E}{\partial^2 \xi_i \xi_j} \tag{1}$$

where V_0 is the cell equilibrium volume. The second derivatives of the total energy with respect to all the perturbation have been determined by computing the energy of the system with respect to the strain perturbation.

In order to obtain the thermodynamic properties of SrTiO₃, the quasi-harmonic Debye model [10] is introduced, in which the non-equilibrium Gibbs function $G*(V, P, T)$ takes the form of

$$G^* (V, P,T) = E(V) + P(V) + A_{vib}(\Theta(V),T). \tag{2}$$

In Eq. (2), $E(V)$ is the total energy per unit cell of SrTiO₃, $P(V)$ corresponds to the constant hydrostatic pressure condition, $\theta(V)$ is the Debye temperature as a function of V, and A_{vib} is the vibrational Helmholtz free energy which can be expressed as [11]:

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

where $D(\theta/T)$ is the Debye integral, and is defined as:

$$D(\theta/T) = \frac{3}{(\theta/T)^3} \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx \quad (4)$$

where n represents the number of atoms per formula unit, θ the Debye temperature is expressed as [11-12]:

$$\theta = \frac{\hbar}{k} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\sigma) \sqrt{\frac{B_s}{M}} \quad (5)$$

M is the mass of per formula unit, σ is the Poisson ratio and B_s is the adiabatic bulk modulus approximated by the following formulae:

$$B_s \cong B(V) = V \left(\frac{d^2 E(V)}{dV^2} \right) \quad (6)$$

and the f (a) is given by

$$f(\sigma) = \left\{ 3 \left[2 \left(\frac{2(1+\sigma)}{3(1-\sigma)} \right)^{3/2} + \left(\frac{1+\sigma}{3(1-\sigma)} \right)^{3/2} \right]^{-1} \right\}^{1-3} \quad (7)$$

Therefore, for a given pressure P and temperature T with respect to the volume V, the non-equilibrium Gibbs function merely depends on V (P, T) and can be solved as

$$\left(\frac{\partial G^*(V,P,T)}{\partial V} \right)_{P,T} = 0 \quad (8)$$

As a result, the isothermal bulk modulus B_T, the heat capacity C_V (at constant volume), the heat capacity C_p (at constant pressure), and the thermal expansion α are given by:

$$B_T(P,T) = V \left(\frac{\partial^2 G^*(V,P,T)}{\partial^2 V} \right)_{P,T} \quad (9)$$

$$C_V = 3nk_B \left[4D(\theta/T) - \frac{3\theta/T}{e^{\theta/T} - 1} \right] \quad (10)$$

$$C_p - C_V (1 + \alpha\gamma T) \quad (11)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (12)$$

The entropy is described by

$$S = nk_B \left[4D(\theta/T) - 3\ln(1 - e^{\theta/T}) \right] \quad (13)$$

where the Grüneisen parameter is defined as:

$$\gamma = -\frac{d \ln \theta(V)}{d \ln V} \quad (14)$$

3. RESULTS AND DISCUSSION

3.1 Structural properties

In Fig 1, we present the total energy as a function of the volume of the unit cell for $SrTiO_3$ fitted to the Murnaghan's equation of state [7, 13] to determine the ground state properties, such as equilibrium lattice parameter (a_0), total energies (E_0), bulk modulus (B_0) and its pressure derivatives (B_0'). The calculated ground state parameters obtained by using GGA approximation are summarized in Table I together with previous results.
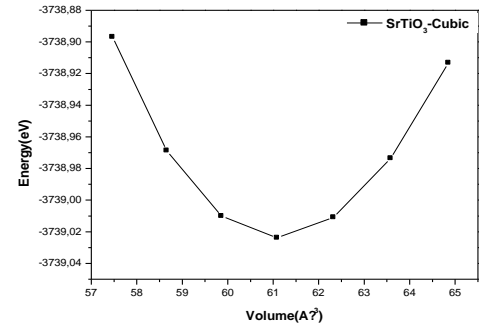

Figure 1. The total energy as a function of volume for $SrTiO_3$ with GGA calculation in the cubic perovskite structure

Table 1. Calculated lattice constant a_0 (Å), bulk modulus B_0 (GPa), its first pressure derivative B_0' for $SrTiO_3$ compared to the experimental data and previous theoretical calculations

Material Parameters	Present Work	Other calculations	Exp
a_0	3.94[a]	3.94[b] 3.95[c]	3.905[d,e]
$SrTiO_3$ B_0	169.2[a]	169.72[b] 175[c]	175[f]
B_0'	4.33[a]	4.44[b]	4.31[g]

[a]This work; [b]Theor. Ref. [22]; [c]Theor. Ref. [23] [d]Exp. Ref. [24]; [e] Exp. Ref. [25]; [f] Exp. Ref. [26]; [g] Exp. Ref. [27];

The agreement between our calculated results for lattice constant for $SrTiO_3$ using GGA with the experimental data is reasonably good [24,25]. When analysing the results of B_0 and B_0, we find that there is a good agreement between our results and previous theoretical calculations [22] and experiment data [26,27]. A conclusion can be drawn for the bulk modulus where the deviation between our calculation and experiment is less than 3%.

3.2 Elastic properties

Elastic properties of a solid are important because they are related to various fundamental solid-state properties such as interatomic potentials, equation of state and phonon spectra. A cubic crystal has only three independent elastic constants, namely C_{11}, C_{12} and C_{44}. C_{11} give the resistance to the unidirectional compression, C_{12} is the modulus for dilation on compression, and C_{44} reflects the resistance to the shear deformation. Once we have calculated the three elastic

constants namely C_{11}, C_{12} and C_{44} the bulk modulus can be obtained by the as:

$$B = \frac{(C_{11} + 2C_{12})}{3} \qquad (15)$$

The Zener anisotropy factor (A) is an indicator of the degree of anisotropy in the solid structures. For a completely isotropic material, the A factor takes the value of 1, when the value of A is smaller or greater than unity it is a measure of the degree of elastic anisotropy. Poisson's ratio v, Young's modulus (E) and shear modulus (G) can be calculated using the following relations [14]:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \qquad (16)$$

$$E = \frac{9BG}{3B + G} \qquad (17)$$

$$v = \frac{3B - E}{6B} \qquad (18)$$

and

$$G = \frac{1}{2} + (G_R + G_V) \qquad (19)$$

G_V is Voigt's shear modulus corresponding to the upper bound of G values, and G_R is Reuss'es shear modulus corresponding to the lower bound of G values, and can be written as [15]:

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \qquad (20)$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \qquad (12)$$

And shear modulus is given by [16]:

$$C' = \frac{(C_{11} - C_{12})}{2} \qquad (22)$$

The values of elastic constants (C_{11}, C_{12} and C_{44}) in the cubic phase for SrTiO$_3$ are presented in Tables 2 and compared with available theoretical and experimental results.

Table 2. Calculated elastic constants (in GPa) for C$_{11}$, C$_{12}$, C$_{44}$ for SrTiO$_3$ in the cubic structure

Material Parameters	Present Work	Other calculations	Exp
C$_{11}$	312.56[a]	311.08[b] 334[c]	317.2[d]
SrTiO$_3$ C$_{12}$	98.25[a]	99.04[b] 96[c]	102.5[d] 123.5[d]
C$_{44}$	109.26[a]	107.66[b] 108[c]	

[a]This work; [b]Theor. Ref. [22]; [c]Theor. Ref. [23]; [d]Exp. Ref. [28];

The calculated elastic constants (C$_{11}$, C$_{12}$, C$_{44}$) are in very good agreement with the predictions of other computational methods [22]. In terms of experimental results, our values especially for C_{11} and C_{12} are in good agreement with those reported in Ref. [28]. The deviation from experiment is less than 4%. However, a somewhat larger discrepancy between our calculated C$_{44}$ and that of Ref. [28] can be noticed. Note

that the values of C$_{44}$ are smaller than those of C_{11} and C_{12}. This reflects the weak resistance to shear deformation compared to the compressional deformations.

It is well known that for cubic crystal structure, the necessary conditions for mechanical stability are: [17]

$(C_{11} - C_{12}) > 0$, $C_{11} > 0$, $C_{44} > 0$, $(C_{11} + 2C_{12}) > 0$

Our results for elastic constants satisfy all these criteria indicating thus that the material of interest is mechanically stable in the perovskite cubic structure. The calculated Zener anisotropy factor (A), shear modulus G, Young's modulus E, Poisson's ratio v and shear modulus C' in the present work for perovskite structure SrTiO$_3$ are listed in Table 3.

Table 3. Calculated bulk modulus B (in GPa), Zener anisotropy factor A, shear modulus G (in GPa), Young's modulus E (in GPa), Poisson's ratio v and shear modulus C' (in GPa)

Material Parameters	Present Work	Other calculations	Exp
B	169.69[a]	175.33[b]	175[c]
A	1.02[a]	0.91[b]	_
SrTiO$_3$ G	108.41[a]	112.23[b]	_
E	268.13[a]	277.44[b]	_
B/G	1.57[a]	1.56[b]	_
v	0.24[a]	0.24[b]	_
C'	107.16[a]	118.79[b]	119[d]

[a]This work; [b]Theor. Ref. [23]; [c]Exp. Ref. [26]; [d]Exp. Ref. [29];

Calculated A value for SrTiO$_3$ is 1.02 which is close to 1 considered as isotropic medium (Table III). The value of the Poisson ratio (v) for covalent materials is small ($v = 0.1$), whereas for ionic materials a typical value is 0.25 [18]. In our case the value of v is 0.24, i.e. a higher ionic contribution in intra-atomic bonding for this compound should be assumed. Higher values of Young's modulus in comparison to the bluk modulus for SrTiO$_3$ indicate that the material is hard to be broken. The hardness of a material can also be predicted in terms of isotropic shear modulus. The bulk modulus B represents the resistance to fracture [19], while the shear modulus G represents the resistance to plastic deformation [20]. A high Pugh B/G ratio is associated with ductility, whereas a low value corresponds to the brittle nature. The critical value which separates ductile and brittle material is 1.75; i.e., if $B/G > 1.75$, the material behaves in a ductile manner; otherwise the material behaves in a brittle manner [21]. Now we have found that the B/G ratio is 1.57 for this compound, classifying SrTiO$_3$ as brittle.
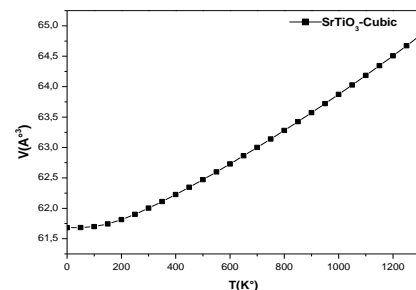
3.3 Thermodynamic properties

Figure 2. The variation of the primitive cell volume as a function of temperature of SrTiO$_3$

The thermodynamic properties are studied at different temperatures. The temperature effect on the volume of $SrTiO_3$ compound is shown in Figure 2. It can be seen that the volume increases with increasing temperature. The rate of increase is almost zero from T = 0 to 100 K and becomes very moderate for T > 100 K Generally speaking, the volume increases as the temperature increases.

The bulk modulus B at different temperature is shown in Figure 3. These results indicate that B decreases with increasing the temperature T. The decrease of the bulk modulus B with t increasing the temperature is explained by the increase of the volume for the studied material results from the temperature elevation. At 300 K°, the bulk modulus B is 160.36 GPa.
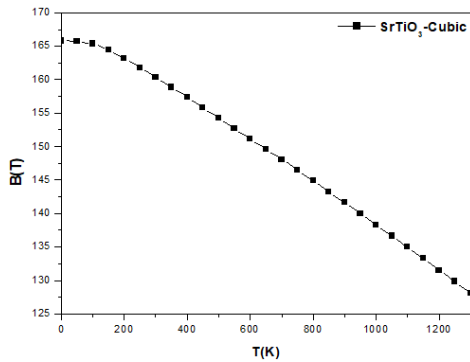

Figure 3. Calculated temperature dependence of bulk modulus B of $SrTiO_3$

In Fig 4, we present the effect of the temperature on the thermal expansion α. It is shown that the thermal expansion coefficient increases with increasing of temperature up to 400 K°. Above this temperature, α gradually approaches to a linear increase with enhanced temperature. At 300 K°, the thermal expansion α is 3.07 × 10^{-5} K^{-1}.
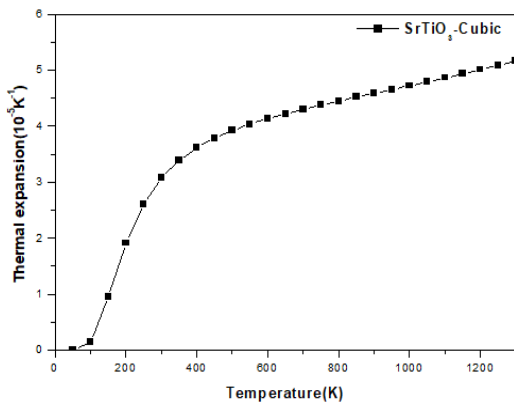

Figure 4. Thermal expansion as a function of temperature (T) of $SrTiO_3$

The heat capacity is an important parameter of the condensed matter physics. It does not only provide a fundamental insight into their vibrational properties but is also mandatory for many applications. At intermediate temperatures, temperature dependence of the heat capacity C_V is governed by the details of the vibrations of atoms and has been able to be determined only experimentally for a long time past [29]. Figures 5 and 6 show respectively the calculated specific heats at constant volume C_V and constant pressure C_P of $SrTiO_3$.
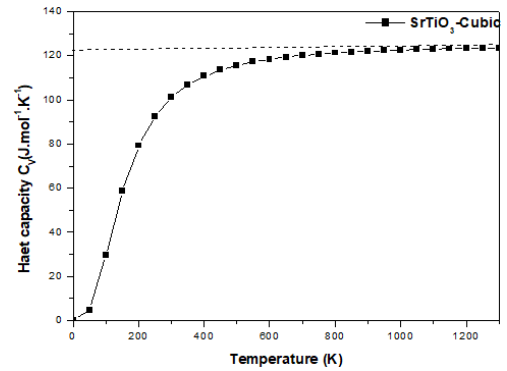

Figure 5. Calculated temperature dependence of heat capacity of $SrTiO_3$ at constant volume C_V
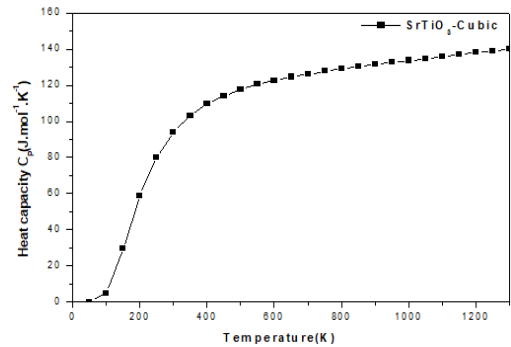

Figure 6. Calculated temperature dependence of heat capacity of $SrTiO_3$ at constant pressure C_P

At low temperatures, the shapes of curves of C_V and C_P are similar. The data of C_V and C_P are proportional to T^3. At higher temperatures, C_V becomes close to the Dulong–Petit limit ($C_V(T)\sim15R \cong124.08$ J.mol^{-1}. K^{-1}) [30] suggesting that the thermal energy at high temperature excites all phonon mode; when T > 400 K°, and C_P deviates from C_V and trends to be linear with the temperature. Our calculated value of C_V at 1300 K° is 123.51J.mol^{-1}K^{-1} for $SrTiO_3$. The entropy S under high temperature can be obtained according to Eq. (13). The variation of the entropy S as a function of temperature is displayed in Figure 7. The curve indicate that the entropy increases monotonously with increasing the temperature T. Then, the functional dependence of the entropy on temperature becomes more like a sublinear behaviour: the entropy is proportional to T^{α} with α <1.
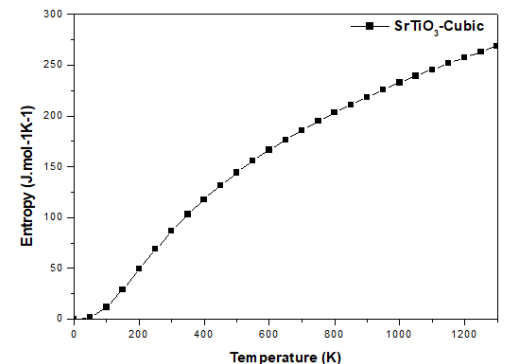

Figure 7. The variation of the entropy S as a function of temperature of $SrTiO_3$

The quasi-harmonic Debye model employed appeared to be effective for the description of the material properties, namely

an equilibrium volume, bulk modulus, thermal expansion coefficient, heat capacity at constant volume C_V, heat capacity at constant pressure C_P and entropy S at the temperature, in which the anharmonicity not significantly affects the thermodynamic parameters.

The thermodynamic properties of $SrTiO_3$ perovskite we have no literature data to which to compare our results. Hence, our results are predictions.

4. CONCLUSION

This manuscript presents a theoretical study, within the density functional theory framework (DFT) and the pseudopotential plane waves approach, of the structural, elastic, and thermodynamic properties for the perovskite compound $SrTiO_3$.The exchange-correlation of generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE-GGA) energy is employed, using the ABINIT package. In order to investigate the thermodynamic properties of $SrTiO_3$ perovskite under temperature effect, we have calculated the variation of the volume, bulk modulus and thermal expansion coefficient, heat capacity at constant volume C_V, heat capacity at constant pressure C_P, entropy S as function of temperature. Generally, the agreement between our results and the available experimental and previous theoretical data reported in the literature was found to be reasonably good.

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