

You may also like

Elasticity of $SrTiO_3$ perovskite under high pressure in cubic, tetragonal and orthorhombic phases

To cite this article: A Hachemi et al 2010 Phys. Scr. 82 025602

View the article online for updates and enhancements.

New high-pressure tetragonal polymorphs of SrTiO₃—molecular orbital and Raman <u>band change under pressure</u> Takamitsu Yamanaka, Muhtar Ahart, Hokwang Mao et al.

- Fluorite-structure antiferroelectrics Min Hyuk Park and Cheol Seong Hwang
- $\begin{array}{l} \label{eq:phase transformation behavior of ultrathin} \\ \frac{H_{0.5}Zr_{0.5}Q_2}{M_{0.5}} films investigated through} \\ \frac{wide range annealing experiments}{M_{0.5}} \\ Shinji Migita, Hiroyuki Ota, Keisuke \\ Shibuya et al. \end{array}$

Elasticity of SrTiO₃ perovskite under high pressure in cubic, tetragonal and orthorhombic phases

A Hachemi, H Hachemi, A Ferhat-Hamida and L Louail

Laboratory of Quantum Physics and Systems Dynamics, Department of Physics, Faculty of Sciences, University of Setif, Algeria

E-mail: akhachemi@yahoo.fr

Received 25 March 2010 Accepted for publication 17 June 2010 Published 9 July 2010 Online at stacks.iop.org/PhysScr/82/025602

Abstract

We investigated the athermal high-pressure behavior of the elastic properties of SrTiO₃ (STO) up to 26 GPa in cubic, tetragonal and orthorhombic phases using the *ab initio* pseudo-potential method. Our results for the cubic phase are in good agreement with experiment and previous pseudo-potential calculations. There are no studies for the tetragonal and orthorhombic phases under high pressure available for comparison. To date, there are no global data on elastic parameters under high pressure for STO. We establish data when we report the results of our structural and elastic study under high pressure in the three phases. Our calculations show that the cubic–tetragonal phase transition occurs at 6 GPa and the tetragonal–orthorhombic phase transition at 14 GPa. A third and unknown phase transition from orthorhombic *Cmcm* to monoclinic $P2_1/m$ was observed at 24 GPa, but no study has explored it. The orthorhombic phase is unstable and this instability may be due to ferroelectricity at high pressure. The elastic properties of STO are also strongly pressure dependent with instabilities near the phase transition pressure. STO is more resistant to plastic deformation and to fracture in the cubic phase than in the tetragonal and orthorhombic phases.

PACS numbers: 62.20.Dc, 62.20.de, 71.15.Mb, 68.18.Jk, 63.70.+h, 61.50.Ks

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

The understanding of the ceramic perovskite behavior under high pressure, which is often determined by the electronic and atomic structure in any phase, is very important in many fields, such as geology, environmental chemistry, catalysis, thermal coatings, microelectronics and bioengineering.

Strontium titanate is a typical ceramic perovskite with a wide range of technological applications because of its special properties related to ferroelectricity [1–3], semiconductivity [4–6], superconductivity [7] and analytic activity [8]. It has been studied over the past several years as a structural analogue of MgSiO₃, which is a major mineral in the earth's lower mantle [9, 10]. Since the 1960s, SrTiO₃ (STO) has been extensively studied for understanding its properties with temperature variation in both the cubic and tetragonal phases but has not been examined under high

pressure. The orthorhombic phase remains totally unknown, and until now there are no definitive data on STO under high pressure.

In this paper, we report first-principles determinations of the elastic parameters of STO as a function of hydrostatic pressure up to 26 GPa in the cubic, tetragonal and orthorhombic phases.

Under high pressure, strontium titanate exhibits two phase transitions. The first one is in the 5–7 GPa range. This phase transition is well known and is from cubic $Pm\overline{3}m$ (O_h^1) to tetragonal phase I4/mcm (D_{4h}^{18}) . This structural phase transition involves the rotation of the TiO₆ octahedra about the [0 0 1] axis. This leads to a tetragonal lattice with a unit cell $\sqrt{2}a \times \sqrt{2}a \times 2a$, where *a* is the lattice parameter of the original cubic unit cell; therefore the volume of the tetragonal unit cell is about four times that of the cubic unit cell.

Phase	Space group	Lattice parameters	Atom positions	References
Cubic	$\frac{Pm\overline{3}m-O_h^1}{(\text{No. 221})}$	$a_{\rm c} = 3.905 \text{\AA}$	Sr(0.0, 0.0, 0.0) Ti(0.5, 0.5, 0.5) O(0.5, 0.5, 0.0)	[21]
Tetragonal	$I4/mcm - D_{4h}^{18}$ (No. 140)	$a_{\rm T} = b_{\rm T} = a_{\rm c}\sqrt{2}$ $c_{\rm T} = 2c_{\rm c} = 2a_{\rm c}$	Ti(0.0, 0.0, 0.0) Sr(0.0, 0.5, 0.25) O(0.0, 0.0, 0.25) O(x, 0.5 + x, 0.0) x = 0.244	[18] [21] [22]
Orthorhombic	$Cmcm - D_{2h}^{17}$ (No. 63)	$a_{\rm Or} = 2a_{\rm c}$ $b_{\rm Or} = 2b_{\rm c} = 2a_{\rm c}$ $c_{\rm Or} = 2c_{\rm c} = 2a_{\rm c}$	Ti(0.0, 0.0, 0.0) Sr(0.0, 0.2498, 0.25) O(0.0, 0.4331, 0.25) O(0.0, 0.1296, 0.0553)	[20] [23]

The cubic-tetragonal phase transition has been observed by several authors, e.g. Lyttle *et al* using x-ray diffraction [11], Okay *et al* using ultrasound [12], Bonello *et al* using Brillouin scattering [13], Ishidate *et al* using Brillouin spectroscopy [14] and Raman scattering [15], Grzechnik *et al* [16], Fleury *et al* using Raman scattering [17] and Shirane *et al* using inelastic scattering [18].

Previous results show a phase transition at about 6 GPa and at room temperature and it is identified as that which occurs at atmospheric pressure and 105 K [19].

The second phase transition in STO is the tetragonal–orthorhombic phase transition. It has been shown in many previous works to occur with temperature variation but has not been identified [11, 14, 18]. Under high pressure it was observed at 15.5 GPa by Grzechnik *et al* [16] and at 14 GPa by Cabaret *et al* [20] who identified it.

Structural phase transitions in STO perovskite provide typical examples of displacive systems. Under pressure the lattice symmetry changes from cubic to tetragonal and then from tetragonal to orthorhombic. It is a sequence of thermodynamically continuous transitions possible from the cubic to tetragonal to orthorhombic:

$$Pm\overline{3}m \rightarrow I4/mcm \rightarrow Cmcm$$
.

This last phase was considered with the CaIrO₃ orthorhombic perovskite structure with space group Cmcm (D_{2h}^{17}) [20]. The unit cell of the orthorhombic phase is about $2a \times 2a \times 2a$, where *a* is the lattice parameter of the original cubic unit cell; therefore the volume of the orthorhombic unit cell is about eight times that of the cubic unit cell. All the parameters and atom positions in the three phases are summarized in table 1 [21–23].

2. Calculation method

In order to investigate the elastic and structural properties of $SrTiO_3$ under hydrostatic pressure, we performed *ab initio* calculations within the framework of the density-functional theory (DFT) as implemented in the CASTEP package [24, 25].

For both cubic and tetragonal phases, we have treated exchange and correlation effects by the generalized gradient approximation (GGA) potential of Perdew *et al* (PW91) [26]. Norm-conserving pseudo-potentials [27] and plane wave

expansion of the Kohn–Sham orbital up to a kinetic cutoff of 660 eV are used. Brillouin zone (BZ) integration has been performed over Monkhorst–Pack meshes [28] of $6 \times 6 \times$ 6 and $5 \times 5 \times 3$ K-points for cubic and tetragonal phases, respectively.

Determination of the elastic stiffness coefficients requires a knowledge of the equilibrium structure at zero pressure. We first fully optimize the unit cell of STO at different pressures up to 26 GPa. The structural optimization technique uses energy optimization with variable cell shape. The elastic stiffness coefficients are then determined from direct computation of the stresses. The differences in energies and stresses are well converged so that the computational uncertainties in the elastic parameters are less than 1%.

For the orthorhombic phase, the calculations have been done using ultra-soft pseudo-potentials and GGA approximation. A plane wave basis is used to expand the wavefunctions. These chosen pseudo-potentials and the plane-wave cutoff of 340 eV and $3 \times 3 \times 3$ K-points are adequate to correctly represent the properties of STO with a good convergence in a range of 16–26 GPa. No other result could be obtained with good precision. These pseudo-potentials include O 2s and 2p, Ti 3s, 3p, 3d and 4s and Sr 4s, 4p and 5s, as the valence electrons.

3. Results and discussion

The elastic parameters determine the response of the crystal to external forces, as characterized by elastic stiffness coefficients C_{ij} , bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*) and Poisson's ratio (ν), and obviously play an important part in determining the strength of the materials. The values of elastic parameters provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability [29, 30].

The elastic stiffness coefficients are a measure of the resistance of a crystal to an externally applied stress and are determined by Hooke's law. The shear modulus *G* represents the resistance to plastic deformation, whereas the bulk modulus *B* represents the resistance to fracture. ν is defined as the ratio of lateral strain and axial strain, and measures the stability of a crystal against shear. *E* is the ratio of stress to strain on the loading plane along the loading direction.

We calculated all the parameters in the pressure range from 0 to 26 GPa in the three phases. We present our results in each phase and we infer the elasticity of $SrTiO_3$ under high pressure.

We also calculated mono-crystalline bulk modulus and shear modulus in the Reuss approximation (B_R, G_R) [31] and in the Voigt approximation (B_V, G_V) [32]. Then, we utilized the Voigt–Reuss–Hill approximation (B, G). In this approach, according to Hill [29], the Voigt and Reuss averages are limits and the actual effective moduli for polycrystals could be approximated from the arithmetic mean of these two limits. The general expressions for the Voigt and Reuss approximations for bulk and shear moduli are

$$B_{\rm R} = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})},\tag{1}$$

$$B_{\rm V} = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23}), \qquad (2$$

$$G_{\rm R} = \frac{1}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})},\tag{3}$$

$$G_{\rm V} = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{1}{5}(C_{44} + C_{55} + C_{66}).$$
(4)

The S_{ij} are the elastic compliance constants.

The Voigt-Reuss-Hill approximation gives

$$B = \frac{B_{\rm V} + B_{\rm R}}{2},\tag{5}$$

and

$$G = \frac{G_{\rm V} + G_{\rm R}}{2}.\tag{6}$$

For isotropic material, Young's modulus (E) and Poisson's ratio (v) are given by the relation [29]

$$E = \frac{9BG}{3B+G},\tag{7}$$

and

$$\nu = \frac{3B - 2G}{2(3B + G)}.$$
 (8)

3.1. Cubic phase

We calculated the variation of the fractional volume V/V_0 as a function of the pressure, where V_0 is the conventional volume at 0 GPa ($V_0 = 60.33 \text{ Å}^3$). As shown in figure 1, the volume decreases with increasing pressure.

The elasticity of a cubic crystal is characterized by three independent moduli: C_{11} , C_{12} and C_{44} . Figure 2 shows the variation of the different coefficients: C_{11} , C_{12} and C_{44} as a function of the pressure up to 6 GPa for the studied phase.

The calculated values at zero pressure are reported in table 2 and compared with available experimental and calculated data. Our results at zero pressure are in good agreement with experimental results and previous pseudo-potential calculations [33-37]. When the pressure increases, the experimental studies of Beattie *et al* [38] and Ishidat *et al* [14] are in disagreement. Our calculations also disagree with these results. Much of the differences



Figure 1. Fractional volume as a function of the hydrostatic pressure in cubic, tetragonal and orthorhombic phases of STO.



Figure 2. The elastic stiffness coefficients as a function of the pressure in cubic, tetragonal and orthorhombic phases of STO.

between our results and experiment can be attributed to the temperature; our calculations were done at T = 0 K but the experiment was done at 300 K. The disagreement between theoretical results may be due to the approximation used.

We remark that the material is mechanically stable in this cubic phase because the stability conditions are satisfied: $C_{11} > 0$, $C_{11} > C_{12}$ and $C_{44} > 0$ up to 6 GPa.

Elastic stiffness coefficients increase monotonically with increasing pressure. However, at several pressures, they may decrease with increasing pressure, implying an elastic instability like at 4–6, 12–14 and 22–24 GPa, which indicates that a displacive transition phase occurs at these pressures. The analysis of elastic instabilities plays an important role in the theoretical understanding of phase transitions.

The coefficient C_{11} sharply increases with pressure, while C_{12} and C_{44} do not vary much with pressure. The C_{11} and C_{12} curves show a leap at about 6 GPa due mainly to the phase transition. For pressures under 6 GPa, the three axes a, b and c are the least compressible because $C_{11} > C_{44} > C_{12}$ ($C_{11} = C_{22} = C_{33}$) and C_{44} is very close to C_{12} , indicating that the shear along the (100) plane is easy.

For the cubic system we have $C_{12} = C_{23} = C_{13}$, $C_{44} = C_{55} = C_{66}$ and $S_{11} = S_{22} = S_{33}$, $S_{12} = S_{23} = S_{13}$, $S_{44} = S_{55} = S_{66}$.

We obtain $B_{\rm R} = B_{\rm V} = B$.

Table 2. Lattice parameters, elastic tensor (C_{ij}) , bulk (B) and shear (G) moduli (in GPa) of cubic STO perovskite at zero pressure compared with previous studies.

P (GPa)	a (Å)	<i>C</i> ₁₁	C_{12}	C_{44}	В	G_V	G_R	G
This study	3.92	366.1	91.39	102.20	182.96	116.26	113.86	115.06
Expt [33]	_	317.2	102.5	122.35	174	_	_	_
[34]	_	316	103	123	_	_	_	_
Calc.								
LDA [35]	_	_	_	121	203	_	_	_
LDA [36]	3.86	421	122.1	133.2	222	_	_	_
PWGGA [36]	3.95	312.9	98	113.4	170	_	_	_
PBE [36]	3.94	319.3	97.5	113	171	_	_	_
BLYP [36]	3.98	290.7	93.9	110.9	159	_	_	_
P3PW [36]	3.90	316	92.7	120.1	167	_	_	_
B3LYP [36]	3.94	328.3	105.7	124.6	180	_	_	_
HF [36]	3.92	416.8	71.1	105	186	_	_	_
FP-LaPW [37]	3.94	311.08	99.04	107.66	169.72	_	_	_
PW-PP [37]	3.94	313.86	97.46	112.16	169.59	_	_	-



Figure 3. The bulk and shear moduli as a function of the pressure in the cubic, tetragonal and orthorhombic phases of STO.

B is also given by a combination of both the C_{11} and C_{12} elastic stiffness coefficients [29]:

$$B = (C_{11} + 2C_{12})/3, (9)$$

and

$$G_{\rm V} = \frac{2C' + 3C_{44}}{5},\tag{10}$$

$$G_{\rm R} = \frac{5C'.C_{44}}{2C_{44} + 3C'},\tag{11}$$

and

$$C' = C_{11} - C_{12}. \tag{12}$$

Figure 3 shows the bulk modulus dependence on the hydrostatic pressure. B increases with pressure and a leap at about 6 GPa also appears in the bulk modulus curve.

Under hydrostatic pressure and in the cubic phase, the STO mechanical properties are the same in all orientations. However, we have

$$E_x = E_y = E_z$$
 and $v_{xy} = v_{yx} = v_{zx} = v_{xz} = v_{yz} = v_{zy}$.

All calculated values are reported in table 3. We remark that E increases with increasing pressure and presents instabilities near the phase transition pressure. The values

of Poisson's ratio are associated with volume change during uniaxial deformation.

If v = 0.5, no volume change occurs during elastic deformation. The low v value for STO means that a large volume change is associated with its deformation. In addition, Poisson's ratio provides more information about the characteristics of the bonding forces than any of the other elastic constants [39]. It has been proved that v = 0.25 is the lower limit for central-force solids and 0.5 is the upper limit, which corresponds to infinite elastic anisotropy [40]. The low v value (substantially smaller than 0.25) indicates that STO is relatively stable against shear and the inter-atomic forces are non-central.

3.2. Tetragonal phase

Most of the studies have been made to calculate the elastic stiffness coefficients of cubic STO from first principles, whereas only a very few have been made to calculate the elastic stiffness coefficients of low-symmetry systems such as tetragonal systems. The main problem in estimating elastic parameters from first principles is not only the requirement of accurate methods for calculating the total energy, but also the complicated heavy computations involved in the calculation of elastic stiffness coefficients. Further, if the symmetry of the system is reduced, the number of independent elastic constants increases and hence a larger number of distortions is required to calculate the full set of elastic parameters.

The variation of the fractional volume V/V_0 as a function of the pressure is shown in figure 1. We note a leap at about 6 GPa, which indicates that the phase transition under pressure is of first order.

The elasticity of a tetragonal crystal is characterized by six independent moduli: C_{11} , C_{12} , C_{13} , C_{33} , C_{44} and C_{66} [29], with $C_{11} = C_{22}$, $C_{13} = C_{23}$, $C_{44} = C_{55}$, $C_{14} = C_{15} = C_{24} = C_{25} = C_{34} = C_{35} = C_{36} = C_{45} = C_{46} = C_{56} = 0$.

And for class $I4/mcm C_{16} = -C_{26} = 0$.

Then we found

$$B_{\rm V} = \frac{1}{9} [(2C_{11} + C_{12}) + C_{33} + 4C_{13}] \tag{13}$$

and

$$B_{\rm R} = \frac{C^2}{M} \tag{14}$$

24 26

Table 3. Elastic tensor C_{ij} (in GPa) of cubic, tetragonal and orthorhombic STO perovskite under a pressure from 0 to 26 GPa.

	D	$C_{11} = 0$	$C_{11} = C_{22} = C_{33}$		$C_{12} = C_{23} = C_{13}$		$C_{44} = C_{55} = C_{66}$		
-	Cubic phas	е							
()	36	366.1		1.39	10	02.20		
	2	38	6.66	9	6.28	10)3.50		
4	1	40	6.56	10	0.94	10)4.76		
(6	44	4.07	10	8.03	10	07.09		
P		$C_{11} = C_{22}$	C ₃₃	<i>C</i> ₁₂	$C_{13} =$	C_{23} C_4	$_{4} = C_{55}$	<i>C</i> ₆₆	
Tetragor	al phase								
6		315.46	416.03	104.22	132.3	30 1	08.11	143.82	
8		341.62	436.23	128.61	131.3	34 1	09.78	149.60	
10		358.10	453.75	141.74	134.6	50 1	10.97	155.27	
12		341.33	474.03	123.37	145.5	57 1	06.69	152.99	
14		377.24	489.91	153.72	146.	/5 1	09.43	165.11	
	C_{11}	<i>C</i> ₂₂	C ₃₃	<i>C</i> ₁₂	<i>C</i> ₁₃	<i>C</i> ₂₃	C_{44}	C ₅₅	C ₆₆
thorhombic phase									
	252.33	427.87	292.27	87.90	88.05	153.75	96.45	29.91	-149.87
	281.58	438.41	295.24	102.86	91.95	171.52	103.43	40.07	-137.78
	278.03	465.24	298.81	107.80	88.37	174.71	102.16	38.27	-138.16
	284.38	474.85	310.30	113.52	95.73	173.14	102.87	42.80	-153.34
	302.03	494.81	312.53	118.60	105.07	184.97	98.86	52.05	-158.81
	312.81	512.49	339.96	120 75	114 96	193.00	102.88	50 44	-11725

with

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}, \tag{15}$$

$$C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2$$
(16)

and

$$G_{\rm V} = \frac{1}{30} (M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}).$$
(17)

All these elastic constants are positive and satisfy the well-known Born's criteria for tetragonal crystals: $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$ and $\{2(C_{11} + C_{12}) + C_{33} + 4C_{13}\} > 0$ [41].

All calculated values are summarized in table 3.

As shown in figure 2, from 6 to 14 GPa we find $C_{33} > C_{11} > C_{66} > C_{13} > C_{12} > C_{44}$.

The unit cell is elongated along the *c*-axis. As a result, C_{33} is much larger than C_{11} . This indicates that the *c*-axis is the least compressible and the atomic bonds along the (001) planes between nearest neighbors are stronger than those along the (100) and (010) planes. The *a* and *b* axes become more compressible in this phase than in the cubic one.

The C_{44} coefficient is lower than C_{66} , indicating that the shear along the (100) planes is easier relative to the shear along the (001) planes.

The C_{11} elastic coefficient increases as a function of pressure in the cubic phase more sharply than in the tetragonal one and there is a jump of 29%. This indicates that the compression in the tetragonal phase is easier than in the cubic one. The C_{44} coefficient is relatively invariant in both the cubic and tetragonal phases, indicating that the shear along the (100) planes is the easiest and does not depend on the phase.

Our bulk modulus calculations, shown in figure 3 and in table 4, show that the material is harder in the cubic phase than in the tetragonal phase.

Young's modulus will change depending on the direction from which the force is applied. Anisotropy can be seen in Poisson's ratio. All calculated values are reported in table 5. In this phase we have

$$E_x = E_y \neq E_z$$
 and $v_{xy} = v_{yx}$,
 $v_{xz} = v_{yz}$ and $v_{zx} = v_{zy}$.

The Poisson's ratio value (for $v_{xy} = v_{yx}$ and $v_{zx} = v_{zy}$) indicates that the inter-atomic forces are central and non-central for $v_{xz} = v_{yz}$.

3.3. Orthorhombic phase

The task of calculating the elastic parameters of orthorhombic crystals becomes even more difficult when realizing that the strains needed to calculate some of them give rise to geometry with very low symmetry. Possibly this is the reason why so far no theoretical work on elastic parameters of orthorhombic systems based on first-principles methods have been published.

In the specific case of orthorhombic lattices, the elasticity is characterized by nine independent moduli: $C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}$ and C_{66} [29], with

$$C_{14} = C_{15} = C_{16} = C_{24} = C_{25} = C_{26} = C_{34}$$
$$= C_{35} = C_{36} = C_{45} = C_{46} = C_{56} = 0.$$

In our calculations, we cannot use the norm-conserving pseudo-potential [27] as for the cubic and tetragonal phases. After many calculations we have chosen ultra-soft pseudo-potential to correctly represent the elastic parameters of $SrTiO_3$ with good convergence, but only in a range of 16-26 GPa.

Table 4. Lattice parameters (a, b, c in Å), bulk (B_V, B_R) and shear (G_V, G_R) moduli (in GPa) of cubic, tetragonal and orthorhombic STO perovskite under pressure up 26 GPa.

	Р	<i>a</i> :	= b = c	$B_{\rm R} =$	$= B_{\rm V}$	G_{R}	$G_{ m V}$	-	
	Cubic pha	ise						-	
	0		3.92	182	.96	13.86	116.26	5	
	2		3.91	193	.07	16.93	118.58	3	
	4		3.89	202	.81	19.83	121.90)	
	6		3.88	220	.04 1	25.26	128.36)	
	P	a = b	С	B _R		B _V	G _R	Gv	7
	Tetragonal phase								
	6	5.44	7.82	193.2	20 19	8.29	115.10	117.	21
	8	5.42	7.81	208.7	76 21	1.34	119.84	122.	38
	10	5.40	7.79	219.3	31 22	1.31	122.92	126.0	04
	12	5.41	7.74	214.2	21 22	0.63	119.33	122.	75
	14	5.37	7.75	234.9	96 23	7.65	125.47	129.9	94
P		а	b	с	B _R	В	ev C	G _R	$G_{\rm V}$
Orth	orhombic phase								
16		3.09	12.84	6.01	181.32	168	3.49 38	.15	87.60
18		3.08	12.84	5.98	194.21	181	.58 44	.40	106.16
20		3.06	12.82	5.95	198.20	181	.62 45	.20	104.48
22		3.04	12.80	5.92	203.81	188	3.23 44		110.72
24		3.03	12.78	5.89	214.07	198	8.26 45	.14	120.60
26		3.01	12.77	5.87	224.74	209	0.75 56	.32	130.05

The calculated elastic stiffness coefficients are shown in table 3. All constants, except for C_{66} , obey the mechanical stability criteria given by $(C_{22} + C_{33} - 2C_{23}) > 0$, $(C_{11} + C_{13}) = 0$, $(C_{11$ $C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23})>0, \ C_{11}>0, \ C_{22}>0, \ C_{33}>$ 0, $C_{44} > 0$, $C_{55} > 0$ and $C_{66} > 0$ [42].

At 14 GPa it was not possible to calculate the parameters; then we extrapolated the curve volume versus pressure for determining the volumes $V_0 = 270 \text{ Å}^3$ at 0 GPa and V =241.6 $Å^3$ at 14 GPa. In figure 1, we show that the phase transition tetragonal-orthorhombic is of first order and the leap is 7.39%.

No data for the elastic stiffness coefficients of the orthorhombic SrTiO₃ perovskite are currently available for any pressure. Our elastic stiffness coefficients at high pressures from 16 to 26 GPa are shown in figure 2 and table 3. We find $C_{22} > C_{33} > C_{11} > C_{23} > C_{12} > C_{44} > C_{13} > C_{55}$. This indicates that, in this phase, the *b*-axis is the least compressible and the *a*-axis is more compressible than the c-axis. Elastic stiffness coefficients associated with shear strains also change with pressure in different manners. At high pressure, C_{55} becomes much smaller than C_{44} , indicating that the shear along the (010) plane becomes easy relative to the shear along the (100) planes.

The negative values of C_{66} indicate that the shear along the (001) plane is unstable.

The possibility of STO crystallizing in orthorhombic phase is not eliminated because this phase was observed experimentally [20], but this instability may be due to other causes like ferroelectricity.

It has been commonly accepted for more than 30 years that hydrostatic pressure in insulating perovskites tends to suppress ferroelectricity. It is shown that such a trend is no longer valid at high pressure, both experimentally and theoretically. The ferroelectricity appears above a critical value of pressure. This unexpected high-pressure ferroelectricity is different in nature from conventional ferroelectricity, because it is driven by an original electronic effect rather than by long-range ionic interactions [43–45]. For STO, the critical pressure inducing this instability is the phase transition tetragonal-orthorhombic pressure (14 GPa).

The Reuss bulk and shear moduli and the Voigt bulk and shear moduli are calculated from equations (1)–(4) [29]. All calculated values are summarized in table 4. In figure 3, we remark that B and G are lower than in tetragonal and cubic phases, indicating that STO is more resistant to plastic deformation and to fracture in cubic phase than in tetragonal and orthorhombic phases.

All calculated values of Young's modulus and Poisson's ratio are reported in table 5. In this orthorhombic phase, we have: $E_x \neq E_y \neq E_z$ and

$$v_{xy} \neq v_{yx} \neq v_{xz} \neq v_{yz} \neq v_{zx} \neq v_{zy}.$$

We clearly show the anisotropy in Young's modulus and Poisson's ratio as a function of the pressure along different directions.

4. Octahedral tilting in cubic perovskites

The octahedral tilting in cubic perovskites has been identified by a number of authors [46–50]. Howard and Stokes [50], using more formal group theoretical methods, listed 15 possible space groups for perovskites with octahedral tilting and gave a schematic representation of space groups derivable

Table 5.	Young's modulus (in	n GPa) and Poissor	's ratio of cubic	, tetragonal and	l orthorhombic STC) perovskite under	pressure from 0 to
26 GPa.							

P (GPa)	Young's modulus, E (GPa) Poisson's ratio, ν									
	E_{z}	$E_y = E_y = E_y$	E_z		$v_{xy} = v_{yx} = v_{zx} = v_{xz} = v_{yz} = v_{zy}$					
Cubic phase										
0		329.59			0.1998					
2		348.27					0.1994			
4		366.41					0.1989			
6	401.79				0.1957					
P (GPa)	$E_r =$	= <i>E</i> _v	E_{z}		Vrv	$= \nu_{yx}$	$v_{xz} = v_{yz}$	$v_{zx} = v_z$		
Totraconal phase	~	,	~		~,	94	<i>AL JL</i>			
	250	26	222 61		0 /	272	0.2457	0 2152		
0	239	.20 .	332.01 262.86		0.2273		0.2457	0.5152		
8	275	.81 .	302.80		0.2949		0.2123	0.2793		
10	285	.59 .	381.26		0	3200	0.2017	0.2693		
12	275	.77 .	382.83		0.2	2652	0.2257	0.3133		
14	297	.14 4	408.79		0.3	3293	0.2009	0.2764		
P (GPa)	E_x	Ey	E_z	v_{xy}	v_{yx}	v_{xz}	v_{yz}	v_{zx}	v_{zy}	
Orthorhombic phase										
16	220.82	339.33	223.41	0.1198	0.1842	0.2382	0.4706	0.2410	0.3098	
18	245.73	329.10	217.75	0.1459	0.1955	0.2267	0.5201	0.2009	0.3441	
20	243.22	350.58	224.14	0.1546	0.2228	0.2054	0.5188	0.1892	0.3317	
22	245.30	364.06	235.68	0.1589	0.2358	0.2198	0.4852	0.2112	0.3141	
24	258.45	373.40	229.90	0.1464	0.2115	0.2495	0.5207	0.2220	0.3206	
26	266.30	391.68	250.29	0.1377	0.2025	0.2600	0.4992	0.2444	0.3190	

by octahedral rotations from the cubic parent structure $Pm\overline{3}m$. Structures are also identified by the pattern of octahedral rotation in the notation of Glazer [46]. According to this schematic representation, the anomaly observed in figures 2 and 3 at 22–24 GPa may be a third phase transition from *Cmcm* to monoclinic $P2_1/m$ at about 24 GPa. Further experimental works can verify this observation.

5. Conclusion

In summary, by means of first-principles PW91-GGA total energy calculations, we have predicted the elastic properties of SrTiO₃. We have established data for structural and elastic parameters under pressure up to 26 GPa for cubic, tetragonal and orthorhombic phases. Our analysis of these data showed that, for SrTiO₃, the cubic and tetragonal phases are stable. We noted at 4, 12 and 22 GPa nonlinear behavior of the elastic stiffness coefficients. Theses anomalies are due to the pre-transitional phases. The orthorhombic phase is unstable and this instability may be due to a transition from paraelectric to ferroelectric. The easiest deformation mechanism in both cubic and tetragonal phases is the shear along the (100) plane and is independent of the two phases. We predict a third phase transition orthorhombic-monoclinic at 24 GPa. All our computations reveal that more experiments need to be performed to ascertain the true nature of the instability of orthorhombic STO and the monoclinic phase.

The elastic properties of STO are also strongly pressure dependent. STO is more resistant to plastic deformation and to fracture in cubic phase than in tetragonal and orthorhombic phases.

Acknowledgments

We acknowledge helpful discussions with Professor Robert J Cava of Department of Chemistry, Princeton University, USA, and Professor Abdelmadjid Ayadi and Professor Maouche Djamel of Department of Physics, Faculty of Sciences, University of Setif, Algeria. We are grateful to them for their comments and encouragement.

References

- [1] Lines M E and Glass A M 1977 Principles and Applications of Ferroelectrics and Related Materials (Oxford: Clarendon)
- [2] Bednorz J G and Müller K A 1984 *Phys. Rev. Lett.* **52** 2289–92
- [3] Itoh M, Wang R, Inaguma Y, Yamaguchi T, Shan Y-J and Nakamura T 1999 Phys. Rev. Lett. 82 3540–3
- [4] Frederikse H P R, Thurber W R and Hosler W R 1964 Phys. Rev. A 134 442–5
- [5] Balachandran U and Eror N G 1981 J. Solid State Chem. 39 351–9
- [6] Kim K H, Yoon K H and Choi J S 1985 J. Phys. Chem. Solids 46 1173–8
- [7] Koonce C S, Cohen M L, Schooley J F, Hosler W R and Pfeiffer E R 1967 Phys. Rev. 163 380–90
- [8] Henrich V E 1985 Rep. Prog. Phys. 48 1481-541
- [9] Fischer G J, Wang Z and Karato S 1997 Phys. Chem. Mineral. 20 97–103
- [10] Carpenter M A 2007 Am. Mineral. 92 309-27
- [11] Lyttle F W 1964 J. Appl. Phys. 35 2212–5
- [12] Okai B and Yoshimoto J 1975 J. Phys. Soc. Japan 39 162-5
- [13] Bonello B, Fischer M and Polian A 1989 J. Acoust. Soc. Am. 86 2257–60
- [14] Ishidate T, Sasaki S and Inoue K 1988 High Pressure Res. 1 53–65
- [15] Ishidate T and Isonuma T 1992 Ferroelectrics 137 45-52

- [16] Grzechnik A, Wolf G H and McMillan P F 1997 J. Raman Spectrosc. 28 885–9
- [17] Fleury P A, Scott J F and Worlock J M 1968 Phys. Rev. Lett. 21 16–9
- [18] Shirane G and Yamada Y 1969 Phys. Rev. 177 858-63
- [19] Bonello B, Fischer M and Zarembowitch A 1989 Ultrasonics 27 343–8
- [20] Cabaret D, Couzinet B, Flank A-M, Itié J-P, Lagarde P and Polian A 2007 Ti K pre-edge in SrTiO₃ under pressure: experiments and full-potential first-principles calculations *Proc. XAFS13: 13th Conf. Int. (Stanford (EUA), 9–14 July 2006) (AIP Conf. Proc.* vol 882) ed B Hedman and P Pianetta pp 120–2
- [21] Madelung O, Rössler U and Schulz M (ed) 2006 Landolt–Börnstein—Group III Condensed Matter. Numerical Data and Functional Relationships in Science and Technology (Ternary Compounds, Organic Semiconductors vol 41E) (Berlin: Springer) pp 1–3
- [22] Tsuda K and Tanaka M 1995 Acta Crystallogr. A 51 7-19
- [23] Rodi F and Babel D 1965 Z. Anorg. Allg. Chem. 336 17–23
- [24] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M J, Refson K and Payne M C 2005 Z. Kristallogr. 220 567–70
- [25] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 J. Phys.: Condens. Matter 14 2717–44
- [26] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 Phys. Rev. B 46 6671–87
- [27] Troullier N and Martins J L 1991 Phys. Rev. B 43 1993-2006
- [28] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188–92
- [29] Schreiber E, Anderson O L and Soga N 1973 Elastic Constants and their Measurement (New York: McGraw-Hill)
- [30] Nye J F 1957 Physical Properties of Crystals (Oxford: Oxford Science Publications)
- [31] Reuss A 1929 Z. Angew. Math. Mech. 9 55
- [32] Voigt W 1928 Lehrbuch der Kristallphysik (Leipzig: Teubner) p 739

- [33] Bell R O and Rupprecht G 1963 Phys. Rev. 129 90-4
- [34] Lheureux D 2000 Nonlinear elastic properties under pressure and phase diagram of strontium titanate *Thèse* nouveau doctorat (No. 00 PA06 6295) Université de Paris 06, Paris
- [35] Liborio L M, Sanchez C G, Paxton A T and Finnis M W 2005 J. Phys.: Condens. Matter 17 L223–30
- [36] Piskunov S, Heifets E, Eglitis R I and Borstel G 2004 Comput. Mater. Sci. 29 165–78
- [37] Boudali A, Driss Khodjaa M, Amranib B, Bourbiec D, Amaraa K and Abadaa A 2009 Phys. Lett. A 373 879–84
- [38] Beattie A G and Samara G A 1971 J. Appl. Phys. 42 2376-81
- [39] Koster W and Franz H 1961 Metall. Rev. 6 1
- [40] Ledbetter M H 1983 Materials at Low Temperatures ed R P Reed and A F Clark (Metals Park, OH: American Society for Metals) p 1
- [41] Wallace D C 1972 Thermodynamics of Crystals (New York: Wiley) chapter 1
- [42] Beckstein O, Klepeis J E, Hart G L W and Pankratov O 2001 Phys. Rev. B 63 134112
- [43] Pantou R, Dubourdieu C, Weiss F, Kreisel J, Köbernik G and Haessler W 2002 Mater. Sci. Semicond. Process. 5 237–41
- [44] Kreisel J, Dkhil B, Bouvier P and Kiat J M 2002 Phys. Rev. B 65 172101
- [45] Dubourdieu C, Pantou R, Weiss F, Sénateur J P, Koebernik G, Haessler W, Dooryhée E, Hodeau J L and Nemoz M 2002 *Ferroelectrics* 268 137–42
- [46] Glazer A M 1972 Acta Crystallogr. B 28 3384–92
- [47] Megaw H D 1973 Crystal Structures: A Working Approach (Philadelphia, PA: Saunders)
- [48] Aleksandrov K S 1976 Ferroelectrics 14 801-5
- [49] Baèrnighausen H 1980 Commun. Math. Chem. 9 139
- [50] Howard C J and Stokes H T 1998 Acta Crystallogr. B 54 782–9
 - Howard C J and Stokes H T 2002 Acta Crystallogr. B 58 565 (erratum)