



HAL
open science

First-principles structural stability in the Strontium-Titanium-Oxygen system

Olivier Le Bacq, Elias Salinas, Alexander Pisch, Claude Bernard, Alain
Pasturel

► **To cite this version:**

Olivier Le Bacq, Elias Salinas, Alexander Pisch, Claude Bernard, Alain Pasturel. First-principles structural stability in the Strontium-Titanium-Oxygen system. *Philosophical Magazine*, 2006, 86 (15), pp.2289-2298. 10.1080/14786430500509047 . hal-00513648

HAL Id: hal-00513648

<https://hal.science/hal-00513648>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



First-principles structural stability in the Strontium-Titanium-Oxygen system

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-05-Oct-0445
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	17-Oct-2005
Complete List of Authors:	Pasturel, Alain; Universite de Grenoble, Laboratoire de Physique et Modelisation des Milieux Condenses Le Bacq, Olivier; CNRS, Laboratoire de Thermodynamique et de Physico-Chimie Metallurgiques Salinas, Elias; CNRS, Laboratoire de Thermodynamique et de Physico-Chimie Metallurgiques PISCH, Alexander; CNRS, Laboratoire de Thermodynamique et de Physico-Chimie Metallurgiques Bernard, Claude; CNRS, Laboratoire de Thermodynamique et de Physico-Chimie Metallurgiques
Keywords:	first-principles calculations, titanium
Keywords (user supplied):	



1
2
3
4
5
6
7
8
9

**First-principles structural stability in the
Strontium-Titanium-Oxygen system**

10 O. Le Bacq, E. Salinas, A. Pisch, C. Bernard

11 Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques, UMR 5614 (CNRS,
12 INPG, UJF), Domaine Universitaire, B.P. 75, 38402 St Martin d'Hères Cedex, France
13
14

15
16
17
18
19 A. Pasturel

20 Laboratoire de Physique et Modélisation des Milieux Condensés (LPMMC), Maison des
21 magistères – CNRS, BP166, 38042 Grenoble Cedex09, France
22
23
24

25
26
27
28
29 **Abstract:**

30
31 First principles calculations have been made to theoretically interpret the structural stability of
32 SrTiO₃ as a function of pressure or strain. We show that the orthorhombic Pbnm structure is
33 more stable than the ideal perovskite one due to rotations of TiO₆ octahedra at high pressures
34 or deformations of TiO₆ octahedra at low pressures. Such a study is extended to the structural
35 stability of the Ruddlesden-Popper Sr_{n+1}Ti_nO_{3n+1} phases for n=1, 2 and 3, in which the lattice
36 constraints are induced by the intercalation of SrO layers in the perovskite structure.
37
38
39
40
41
42
43
44
45
46
47

48 Corresponding author: pasturel@grenoble.cnrs.fr
49
50
51
52
53
54
55
56
57
58
59
60

I. INTRODUCTION:

Strontium titanate (SrTiO_3) is a typical perovskite dielectric with a wide range of technological applications [1, 2]. Because of its special properties related to ferroelectricity [3, 4], semiconductivity [5-9], superconductivity [10-12], and catalytic activity [2], strontium titanate has been extensively studied over the years. Very recently, the high dielectric constant and electron spin polarization of SrTiO_3 make it attractive for further development of tunnelling semiconductor valves and magnetic tunnel junctions for spintronics applications [13-18].

However, there are many problems to be solved on the way to maintaining such devices. More particularly, understanding the effects of temperature, pressure, strain and substrate constraint as well as the effects of nonstoichiometric chemical compositions on the phase transitions of SrTiO_3 or parent compounds is a crucial issue in order to achieve desirable performance and reliability. At room pressure, SrTiO_3 transforms at 110 K from tetragonal to cubic. Up to its melting temperature, SrTiO_3 is known to remain cubic (space group $\text{Pm}\bar{3}\text{m}$) but in contrast, the isovalent SrZrO_3 compound is orthorhombic at room temperature and undergoes a series of phase transitions as a function of temperature. Interestingly, epitaxial SrTiO_3 films undergo phase transitions leading to either tetragonal or orthorhombic structures [19]. It is also known that excess strontium in SrTiO_3 results in a structural planar accommodation as Ruddlesden-Popper (RP) phases of general formula $(\text{SrO})(\text{SrTiO}_3)_n$ [20]. The presence of these layers, as ordered forms of a homologous series of $(\text{SrO})(\text{SrTiO}_3)_n$, or disordered forms of intergrown RP phase lamellae, were corroborated as stable phases by x-ray diffraction and transmission electron microscopy [21-24].

Despite all the experimental efforts, little is known about the fundamental properties of SrTiO_3 and $(\text{SrO})(\text{SrTiO}_3)_n$ compounds and a comprehensive knowledge of the thermodynamic bulk properties of all these phases is still missing. More particularly, theoretical investigations of the relative structural stability of the different RP phases lead to contradictory results. Using first-principles-based calculations, Suzuki and Fujimoto [25] shows a lower exothermic formation energy for Sr_2TiO_4 than for $\text{Sr}_3\text{Ti}_2\text{O}_7$, which is opposite to the result obtained by Noguera using a semiempirical Hartree-Fock method [26]. Empirical simulations based on a parameterization description of the interatomic interactions give other

1
2
3 trends [21, 24]. The formation energy of RP phases are still exothermic but $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ is found
4 as stable as $\text{Sr}_3\text{Ti}_2\text{O}_7$ according to Udayakumar et al. [21] or less stable as obtained by McCoy
5 et al. [24]. Let us mention that Noguera [26] found an endothermic formation energy for
6 $\text{Sr}_4\text{Ti}_3\text{O}_{10}$.
7
8

9
10 In order to shed light on these open problems, we perform a series of ab initio
11 calculations in order to determine the structural competition occurring for SrTiO_3 as well as in
12 the range SrO-SrTiO₃. Our findings will be used to (i) study the phase stability of SrTiO_3
13 compound at room temperature and as a function of pressure, (ii) establish the ground state
14 line at T = 0K in the range SrO-SrTiO₃, and (iii) discuss our results in comparison with the
15 different experimental data presented in the literature.
16
17

18
19 The remainder of the paper is the following: in section 2 we present the method used
20 to performed ab initio calculations and the obtained results for SrTiO_3 . In section 3 we present
21 formation energies of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compounds for n=1, 2 and 3 and the stability of these
22 compounds is compared to experimental observations. Finally section 4 summarizes our
23 conclusions and presents our perspectives.
24
25
26
27
28
29
30

31 II. METHOD :

32
33
34 The density functional (DFT) calculations were performed by the Vienna ab initio
35 simulation package (VASP) [27], making use of the projector augmented waves (PAW)
36 technique [28]. For the exchange correlation functional, we use the generalized gradient
37 approximation (GGA) of Perdew and Wang [29]. In the present PAW potentials, the 3d and 4s
38 orbitals as well as the semicore 3p orbitals are treated as valence orbitals for Ti while 5s and
39 the semicore 4s and 4p orbitals are used as valence orbitals for Sr. 2s and 2p orbitals are used
40 for O. The cutoff energy for the plane wave basis set is equal to 400 eV. In all cases,
41 structures were fully relaxed with respect to volume as well as cell-internal and cell-external
42 coordinates. Care was taken that for each structure a sufficient number of k points for the
43 Brillouin-zone integration was chosen.
44
45
46
47
48
49
50
51
52

53 In a first step, we propose to study the structural stability of SrTiO_3 compound by
54 performing total energy calculations for the ideal perovskite-type crystal but also for two
55 other structures of the isovalent SrZrO_3 which are known to compete at room temperature
56 [30,31]. The first one is orthorhombic with the Pbnm space group while the other structure is
57 pseudocubic on the basis of a doubled cubic perovskite cell with the P2₁3 space group. In
58
59
60

1
2
3 Table I, we report the calculated structural parameters for all structures as well as the
4 experimental data of the cubic perovskite structure.
5

6
7 As mentioned in [31], the distortions which occur in the pseudocubic structure are
8 mainly due to rotation of the octahedral around the fourfold axes, which makes the parameter
9 γ the most important deviation. As this parameter is found to be equal to zero in our
10 calculations, this structure can be considered as similar to the ideal perovskite structure. It will
11 be no more discussed in the following. For the orthorhombic structure, the atomic coordinates
12 in terms of the displacements u , v , and w from the special positions of the ideal cubic
13 perovskite structure are given in Table I. The non-zero values of these parameters indicate
14 local distortions which are consistent with octahedral tilting [30] although the tilt angles are
15 smaller than in SrZrO_3 . The variation of the cohesive energy as a function of volume is shown
16 in Fig. 1 for both ideal cubic and orthorhombic structures. The main result is that both
17 structures display similar cohesive energies (a difference of less than 1 meV/atom) at their
18 equilibrium volumes. It is also observed that the orthorhombic structure is more stable than
19 the cubic one at lower or higher volumes (higher or lower pressures). Our results obtained at
20 lower volumes are in agreement with general rules for predicting phase transitions in
21 perovskites due to octahedral tilting. Indeed, as mentioned in [32], if the octahedral are
22 completely rigid (as we find at lower volumes), the only way in which the unit-cell volume
23 can be reduced is by introducing tilts of the octahedral. It is mainly due to the fact that the
24 SrO_{12} polyhedra are more compressible than the TiO_6 octahedra. Therefore, the orthorhombic
25 structure which displays a tilt system is more favourable than the cubic one to pressure
26 effects. However, at higher volumes, the situation is quite different since our calculations
27 display important deformations of the TiO_6 octahedra with different values of Ti-O bond
28 lengths. In this case, general rules mentioned above cannot be applied and the behaviour of
29 SrTiO_3 as a function of pressure enters a new regime. We think that our results may serve as a
30 new approach to explain phase transitions in epitaxial SrTiO_3 films or by addition of
31 impurities which favour octahedral distortions. Another possibility for a local distortion is an
32 excess of Sr. It leads to the occurrence of the RP phases and it will be discussed in the next
33 section in further details.
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53

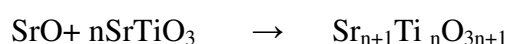
54
55 The calculated density of states (DOS) of TiO_2 and SrO references as well as SrTiO_3
56 in both cubic and orthorhombic structures are shown in Fig. 2a et 2b respectively. The two
57 DOS of SrTiO_3 are very similar with only a slight shift of the valence band (VB) towards
58 higher energies for the orthorhombic structure. The three peaks of the VB is made up
59 predominately of the O-2p states with a minor admixture from Ti 3d states in agreement with
60

1
2
3 other theoretical results [33-35]. The first major peak above the conduction band (CB) edge is
4 contributed mainly by Ti 3d states. This is followed with a more broadened Sr-4d peak (see in
5 Fig 2a DOS of SrO and TiO₂ taken as references). The calculated indirect gap is equal to 1.9
6 eV for both structures. The experimental band-gap energy is 3.2 eV in the cubic phase [1],
7 which implies that our value is underestimated as is typical in GGA calculations for oxides.
8 To understand more precisely how the bonding in the orthorhombic structure differs from the
9 bonding in the cubic one, we examine the charge density differences between the two
10 structures and the atomic one. Fig. 3 shows that the charge-density contour maps look similar.
11 However the charge transfer that occurs mainly from Ti and Sr atomic species towards the
12 oxygen atoms is much more important in the orthorhombic structure than in the perovskite
13 phase. Therefore, the Sr-O and Ti-O bonds are more ionic in the tilt system.

24 III. Sr_{n+1}Ti_nO_{3n+1} COMPOUNDS:

25
26
27
28 We first calculated the equilibrium structures of the Sr_{n+1}Ti_nO_{3n+1} compounds for n=1,
29 2 and 3. The initial structures were constructed computationally from experimental data and
30 then fully relaxed with respect to volume, cell shape and internal structural parameters. In
31 Table II, we report the calculated structural parameters for all structures as well as the
32 experimental data. As for the perovskite structure, the agreement between the calculated and
33 experimental parameters is very nice, the slight overestimation of the experimental data being
34 a well-known feature of GGA treatment.

35
36
37 The formation energies of the Ruddlesden-Popper (RP) Sr_{n+1}Ti_nO_{3n+1} phases were
38 calculated according to the following reaction:



40
41
42 Our results are reported in Table III as well as results obtained in the previous
43 theoretical studies. Our calculated formation energies are negative in agreement with the
44 general trend obtained in previous results. However our results give much more negative
45 formation energies (in excellent agreement with the experimental value of Sr₂TiO₄ [36]) and
46 also they provide a different structural hierarchy. We find a lower formation energy for
47 Sr₃Ti₂O₇ than for Sr₂TiO₄, in agreement with empirical based results [21, 24] but in opposite
48 to ab initio ones performed by Suzuki and Fujimoto [25]. Noguera [26] found values which
49 are much smaller than ours. Moreover our results show lower formation energy for Sr₄Ti₃O₁₀
50 even if the formation energy difference between Sr₄Ti₃O₁₀ and Sr₃Ti₂O₇ phases is smaller than
51 that between Sr₃Ti₂O₇ and Sr₂TiO₄. Let us mention that the formation energy of Sr₄Ti₃O₁₀
52
53
54
55
56
57
58
59
60

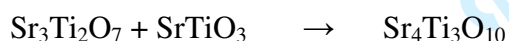
obtained by Udayakumar and Cormack [21] remains constant (in fact all the structures for $n \geq 2$ display a constant formation energy) while the formation energy given by Mc Coy et al. [24] is smaller than that of $\text{Sr}_3\text{Ti}_2\text{O}_7$. Quite surprisingly, Noguera [26] found a positive value for $\text{Sr}_4\text{Ti}_3\text{O}_{10}$. Because of the energy differences of the competing structures are small we also have performed a set of calculations using the local density (LDA) approximation since a general source of inaccuracy might be due to the approximations for the exchange-correlation energy functional. Both sets of calculations give similar results, the largest difference being smaller than 5 meV. The DOS of the three RP phases are shown in Fig. 4(a-c). Their shapes are roughly similar to that of SrTiO_3 , the additional structures in both VB and CB being due mainly to two kinds of inequivalent oxygen and strontium atoms, those belonging to the SrO double layers and those from the SrTiO_3 units.

Having negative formation energies is a necessary condition to study the feasibility of RP structures under thermodynamical equilibrium conditions but it is not a sufficient condition. Indeed since these phases correspond to different chemical compositions, one must also consider the reactions between them or in other terms to determine the ground states of the SrO- SrTiO_3 section. First we find that the following reaction:



has an exothermic reaction energy of -0.056 eV. Consequently, $\text{Sr}_3\text{Ti}_2\text{O}_7$ is more stable than the associated combination of Sr_2TiO_4 and SrTiO_3 .

The second reaction of interest is:



which displays a much smaller reaction energy of -0.016 eV. Such a result indicates that RP phases with n greater than 2 can be considered as metastable phases.

For compositions richer in SrO than $\text{Sr}_3\text{Ti}_2\text{O}_7$, the following reaction is:



is energetically favourable (-0.144 eV).

All our results suggest that equilibria in the SrO- SrTiO_3 system may be based on a series of three compounds, namely Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$ and SrTiO_3 . RP phases with $n > 2$ may form under special preparation conditions or if cation dopants were to be used. The inability to extract single phases of RP series for $n > 2$ and the possible appearance of these phases as mixed ones confirms the experimental view. For instance the observation by Tilley [23] of the coherent intergrowth of lamellae of different widths of the various RP ($n=3$ to 8) phases in a matrix of $\text{Sr}_3\text{Ti}_2\text{O}_7$ can be explained by the absence of a thermodynamic driving force for ordering the RP structure layers.

IV. SUMMARY AND CONCLUSIONS:

Ab initio calculations were performed to shed light on the structural aspects of phase equilibria in the Strontium-Titanium-Oxygen System. For SrTiO₃, the results of these calculations have revealed a strong competition between the perovskite structure and the orthorhombic one which is the first step to understand the occurrence of structural phase transitions in strained SrTiO₃ films. Our calculations have also offered a theoretical basis for the Ruddlesden-Popper phases. We found that only the RP Sr_{n+1}Ti_nO_{3n+1} phases with n=1 and 2 are ground states in the SrO-SrTiO₃ system. We believe that the results presented in this paper illustrate the usefulness of first-principles based calculations in elucidating complex structural behaviour in non-stoichiometric compounds.

ACKNOWLEDGMENTS:

We acknowledge Laboratoire de Physique et Modélisation des Milieux Condensés for computational resources on the PC cluster PHYNUM (CIMENT, Grenoble).

REFERENCES:

- [1] M. Cardona, Phys. Rev. A **140**, A651 (1965)
- [2] V.E. Henrich, Rep. Prog. Phys. **48**, 1481 (1985)
- [3] J.G. Bednorz and K.A. Muller, Phys. Rev. Lett. **52**, 2289 (1984)
- [4] F. Gervais, B. Claes, and P. Odier, Mater. Res. Bull. **22**, 1629 (1987)
- [5] H.P.R. Frederikse, W.R. Thurber, and W.R. Hosler, Phys. Rev. A **134**, A442 (1964)
- [6] U. Balachandran and N.G. Error, J. Solid State Chem. **39**, 351 (1981)
- [7] U. Balachandran and N.G. Error, J. Electrochem. Soc. **129**, 1021 (1982)
- [8] B. Odekirk, U. Balachandran, N.G. Error, and J.S. Balkemore, Mater. Res. Bull. **17**, 199 (1982)
- [9] K.H. Kim, K.H. Yoon, and J.S. Choi, J. Phys. Chem. Solids **46**, 1061 (1985)
- [10] J.F. Schooley, W.R. Hosler, and M.L. Cohen, Phys. Rev. Lett. **12**, 474 (1964)

- 1
2
3 [11] J.F. Schooley, W.R. Hosler, E. Amber, J.H. Becker, M.L. Cohen, and C.S. Koonce, *Phys.*
4 *Rev. Lett.* **14**, 305 (1965)
5
6 [12] C.S. Koonce, M.L. Cohen, J.F. Schooley, W.R. Hosler, and E. R. Pfeiffer, *Phys. Rev.*
7 **163**, 380 (1967)
8
9 [13] M. Ziese, *Rep. Prog. Phys.* **65**, 143 (2002)
10
11 [14] H. Dulli, E.W. Plummer, P.A. Dowben, J. Choi, and S.H. Liou, *Appl. Phys. Lett.* **77**, 570
12 (2000)
13
14 [15] C.N. Borca, B. Xu, T. Komesu, H-k Jeong, M.T.Liu, S.H. Liou, and P.A. Dowben, *Surf.*
15 *Sci. Lett.* **512**, L346 (2002)
16
17 [16] Y. Lu, X.W. Lee, G.O. Gong, G. Xiao, A. Gupta, P. Lecoeur, J.Z. Sun, Y.Y. Wang, and
18 V.P. Dravid, *Phys. Rev. B* **54**, R8357 (1996)
19
20 [17] T. Obata, T. Manako, Y. Shimakawa, and Y. Kubo, *Appl. Phys. Lett.* **74**, 290 (1999)
21
22 [18] J.M. De Teresa, A. Barthelemy, A. Fert, J.P. Contour, F. MONTaigne, and P. Seneor,
23 *Science* **286**, 507 (1999)
24
25 [19] F. He, B.O. Wells, Z-G Ban, S.P. Alpay, S. Grenier, S.M. Shapiro, Weidong Si, A. Clark
26 and X.X. Xi, *Phys. Rev. B* **70**, 235405 (2004)
27
28 [20] S.N. Ruddlesden and P. Popper, *Acta Crystallogr.* **11**, 54 (1958)
29
30 [21] K.R. Udayakumar and A.N. Cormack, *J. Am. Ceram. Soc.* **71**, C-469 (1988)
31
32 [22] K.R. Udayakumar and A.N. Cormack, *J. Phys. Chem. Solids* **50**, 55 (1989)
33
34 [23] R.J.D Tilley, *J. Solid State Chem.* **21**, 293 (1977)
35
36 [24] M.A. McCoy, R.W. Grimes, and W.E. Lee, *Philos. Mag. A* **75**, 833 (1997)
37
38 [25] T. Suzuki and M. Fujimoto, *J. Of Appl. Phys.* **89**, 5622 (2001)
39
40 [26] C. Noguera, *Phil. Mag. Lett.* **80**, 173 (2000)
41
42 [27] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6** (1996) 15; *Phys. Rev. B* **54** (1996)
43 11169;
44
45 [28] G. Kresse and D. Joubert, *Phys. Rev. B* **59** (1999) 1758
46
47 [29] J.P. Perdew and Y. Wang, *Phys. Rev. B* **45** (1992) 13244
48
49 [30] A. Ahtee, M. Ahtee, A.M. Glazer and A.W. Hewat, *Acta. Cryst. B* **32**, 3243 (1976)
50
51 [31] J.A.M. van Roosmalen, P. van Vlaanderen, and E.H.P. Cordfunke, *J. Of Solid State*
52 *Chemistry* **101**, 59 (1992)
53
54 [32] R.J. Angel, J.Zhao and N.L. Ross, *Phys. Rev. Lett.* **95**, 25503 (2005)
55
56 [33] G. Fabricius, E.L. Peltzer y Blanca, C.O.Rodriguez, A.P. Ayala, P. de la Presa, and A.
57 Lopez Garcia, *Phys. Rev. B* **55**, 164 (1997)
58
59 [34] S-Di Mo, W.Y. Ching, M.F. Chisholm and G. Duscher, *Phys. Rev. B* **60**, 2416 (1999)
60

1
2
3 [35] I. N. Yakovin and M. Gutowski, Phys. Rev. B **70**, 165319 (2004)
4

5 [36] D.R. Lide, *CRC Handbook of Chemistry and Physics 72nd edition* (Boston,
6
7 Massachusetts: CRC Press)
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Peer Review Only

1
2
3
4
5 Figure Captions:
6
7
8

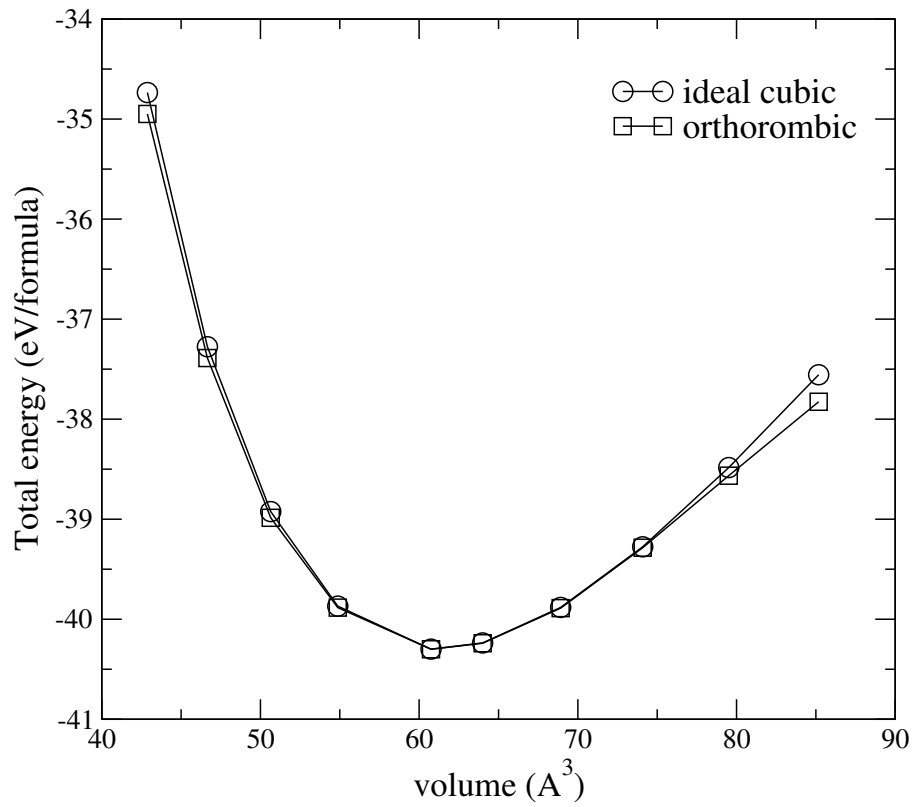
9 Figure 1: Calculated cohesive energy as a function of the volume for the perovskite and
10 orthorhombic structures.
11

12
13 Figure 2: Total electronic DOS for: a) for TiO_2 (full line); SrO (dotted line) b) SrTiO_3 :
14 full line , perovskite structure; dotted line orthorhombic structure.
15
16
17

18
19 Figure 3: Charge density difference $\rho_{\text{self}}(\mathbf{r}) - \rho_{\text{at}}(\mathbf{r})$ between bulk and free atom in a) cubic
20 and b) orthorhombic SrTiO_3 . Both compounds display a depletion of charge on Ti and Sr
21 sites and a gain of charge on oxygen sites with respect to the electronic configuration of
22 the atoms (the maximum is added under brackets in arbitrary units). The transfer of charge
23 is drastically increased as the TiO_6 octahedrons are tilted in the orthorhombic structure.
24
25
26
27
28
29

30 Figure 4: Total electronic DOS for: a) Sr_2TiO_4 ; b) $\text{Sr}_3\text{Ti}_2\text{O}_7$; c) $\text{Sr}_4\text{Ti}_3\text{O}_{10}$
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

I



view Only

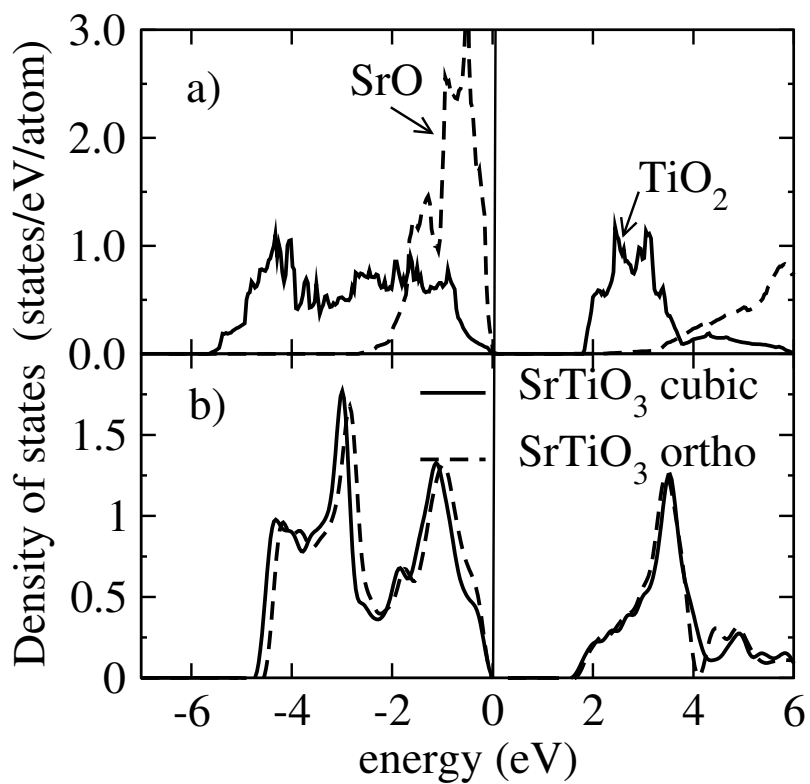
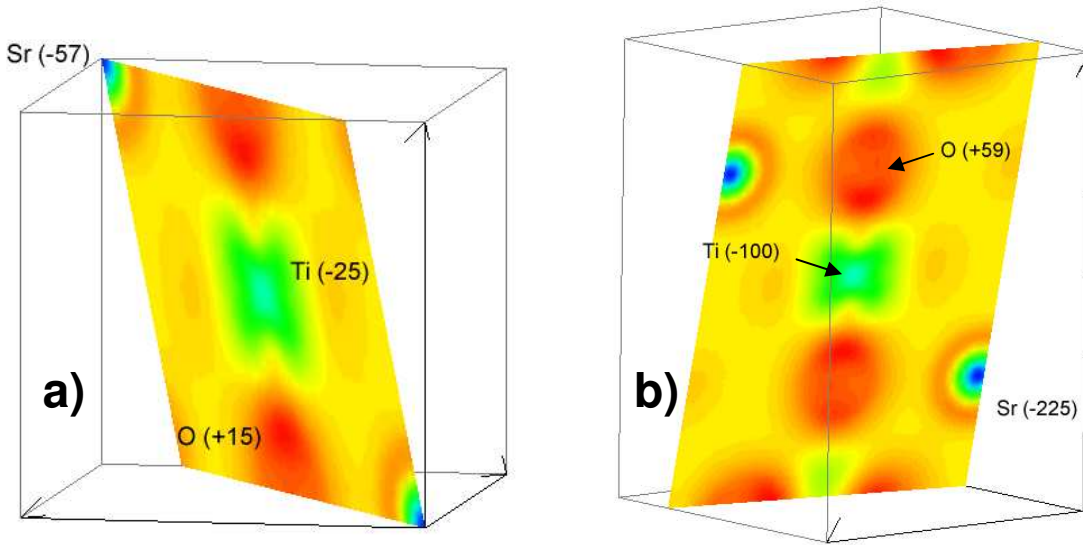


Figure 3:



Peer Review Only

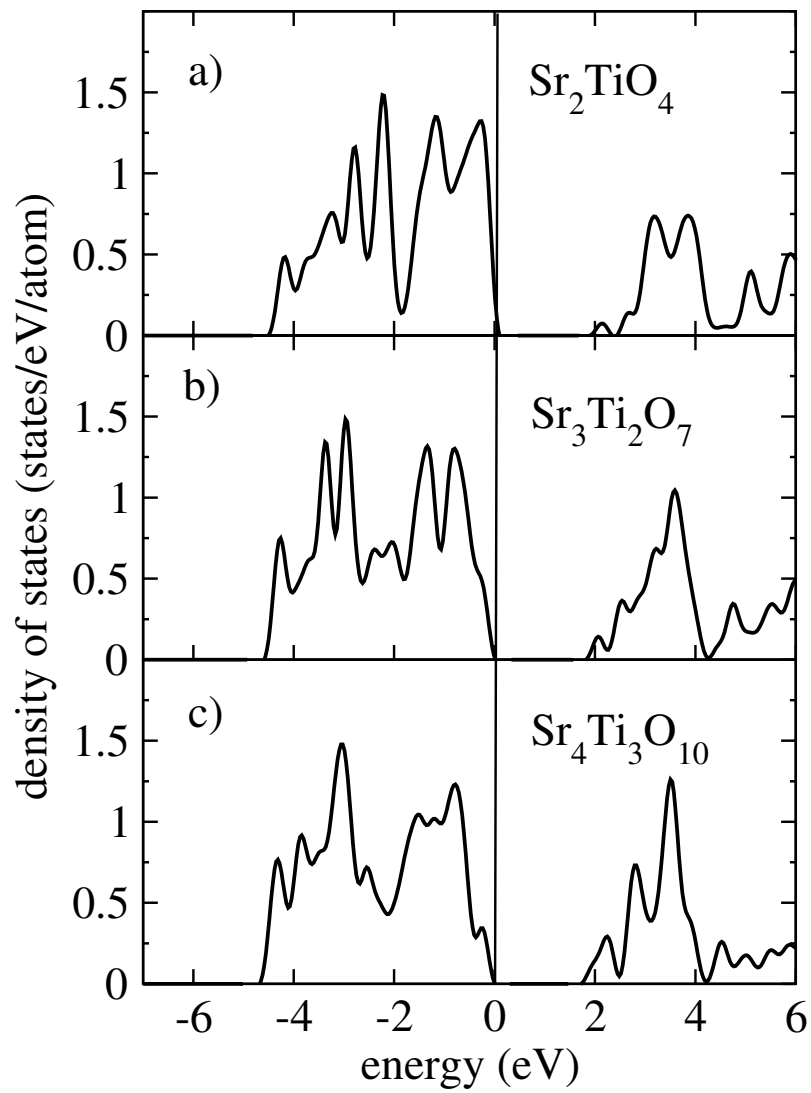


Table I: Space group and calculated lattice parameters (in Å), oxygen positions (in direct coordinates) and crystallographic structures of SrTiO₃ (experimental and prototypes), compared to experimental values [under brackets]. u, v, w indicate possible displacements from the ideal cubic perovskite positions according to space group Pbnm. Oxygen atoms are small red balls, Ti are grey balls embedded in the octahedrons of oxygen and Sr are the blue balls.

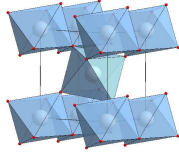
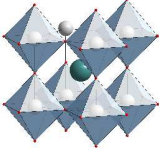
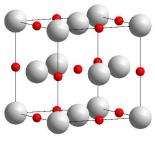
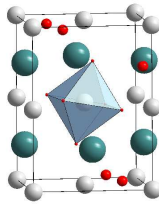
TiO ₂ (rutile)	SrTiO ₃ (perovskite)	SrO (NaCl)	SrTiO ₃ (orthorhombique)																
P4/mnm	Pm-3m	Fm-3m	Pbnm																
(a=b=4.65) [a=b=4.59] (c=2.96) [c=2.95]	(a=b=c=3.93) [a=b=c=3.91]	(a=b=c=5.21) [a=b=c=5.16]	(a=b=5.66) (c=7.98) [no exp.]																
$\pm(u,u,0)$ $\pm(u+\frac{1}{2}, \frac{1}{2}-u, 0)$ (u=0.305) [u=0.305]	$(\frac{1}{2}, 0, 0)$ $[\frac{1}{2}, 0, 0]$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$	<table> <thead> <tr> <th></th> <th>u</th> <th>v</th> <th>w</th> </tr> </thead> <tbody> <tr> <td>Sr</td> <td>0.001</td> <td>0.004</td> <td>0.0</td> </tr> <tr> <td>O(1)</td> <td>-0.029</td> <td>-0.001</td> <td>0.0</td> </tr> <tr> <td>O(2)</td> <td>+0.009</td> <td>0.009</td> <td>0.015</td> </tr> </tbody> </table>		u	v	w	Sr	0.001	0.004	0.0	O(1)	-0.029	-0.001	0.0	O(2)	+0.009	0.009	0.015
	u	v	w																
Sr	0.001	0.004	0.0																
O(1)	-0.029	-0.001	0.0																
O(2)	+0.009	0.009	0.015																
																			

Table II: Space group and calculated lattice parameters (in Å), oxygen positions (in direct coordinates) and crystallographic structures of the RP $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ phases with $n=1, 2$ and 3 (under parenthesis), compared to experimental values [under bracket, Ref. 20]. The defect structures can be formed from SrTiO_3 by removing a (001) sheet of TiO_6 octahedra and shearing the layer above by $\frac{1}{2}[111]$. Oxygen atoms are small red balls, Ti atoms are grey balls embedded in the octahedrons of oxygen and Sr are the blue balls.

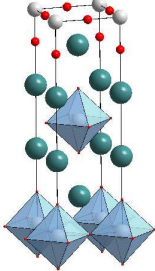
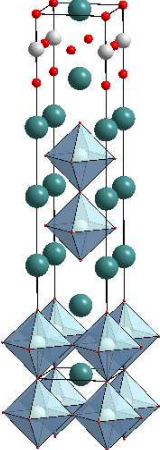
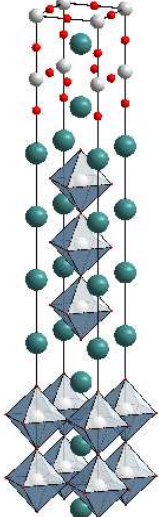
Sr_2TiO_4	$\text{Sr}_3\text{Ti}_2\text{O}_7$	$\text{Sr}_4\text{Ti}_3\text{O}_{10}$
I4/mmm	I4/mmm	I4/mmm
($a=b=3.92$) [$a=b=3.88$] ($c=12.66$) [$c=12.60$]	($a=b=3.93$) [$a=b=3.90$] ($c=20.48$) [$c=20.38$]	($a=b=3.94$) [$a=b=3.90$] ($c=28.35$) [$c=28.10$]
(0 0 z) (0 0 -z) ($\frac{1}{2}$ 0 0) (0 $\frac{1}{2}$ 0) ($z=0.158$) [$z=0.151$]	($z_1=0.096$) [$z_1=0.094$]	($z_1=0.069$) [$z_1=0.068$]
		

Table III: Cohesive energies (E_c) of the RP $Sr_{n+1}Ti_nO_{3n+1}$ phases with $n=1, 2$ and 3 and their formation energies (E_f) from: $SrO+nSrTiO_3 \rightarrow Sr_{n+1}Ti_nO_{3n+1}$

	E_c (eV/atom)		E_f (eV)				
	Present work	Ref. [36]	Ref.[21]	Ref. [24]	Ref.[25]	Ref.[26]	
SrO	6.097						
SrTiO ₃	8.059						
Sr ₂ TiO ₄	7.527	-0.200	-0.24	-0.11	-0.15	-0.158	-0.04
Sr ₃ Ti ₂ O ₇	7.753	-0.252		-0.14	-0.21	-0.144	-0.10
Sr ₄ Ti ₃ O ₁₀	7.844	-0.269		-0.14	-0.19		+0.02