Why ferroelectricity? synchrotron radiation and *ab initio* answers

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An old question of solid state physics is being answered nowadays: the atomic-level understanding of ferroelectricity. Traditional ideas about ferroelectric phenomena relate with softening of optical phonons at the Brillouin zone origin and with "W-shaped" Landau free energy functions. Last decade experimental (synchrotron radiation, neutrons) and quantum-theoretical (Cohen, Resta, Spaldin) contributions have clarified detailed descriptions and explanations for atomic behavior leading to spontaneous polarization in perovskite and perovskite-related crystal structures. Work being performed by our interdisciplinary group on ferroelectricity is presented. Perovskite and Aurivillius ferroelectric phases are obtained by different methods. Fine details on crystal structures are investigated by means of synchrotron radiation at Stanford Synchrotron Radiation Laboratory. Electronic structures of considered phases are theoretically characterized by *ab initio* methods. High-resolution diffraction experiments demonstrate several symmetry break-downs in perovskite and Aurivillius phases. The structure-symmetry-polarization relationship is discussed for a number of representative cases. *Ab initio* explanation of ferroelectric polarization in perovskite structures is given. Energy calculation is performed by means of CASTEP code under GGA functional. Energy optimization leads to cubic-tetragonal symmetry break-down with off-centering cation displacements via second-order Jahn-Teller effect. Electronic structure is investigated with BandLab code, under LDA functional with LMTO method. Degeneracy of Ti 3d z^2 and Ti 3d (x^2+y^2) orbitals is the cause of cubic-perovskite deformation.

Keywords: Ferroelectricity; synchrotron radiation; ab initio calculations.

Una pregunta histórica de la física del estado sólido está encontrando respuesta en nuestros tiempos: la explicación a nivel atómico del origen de la ferroelectricidad. Las ideas tradicionales sobre fenómenos ferroeléctricos se relacionan con el "ablandamiento" de los fonones en el origen de la zona de Brillouin y con funciones en forma de "W" para la energía libre de Landau. Las contribuciones experimentales (radiación sincrotrónica, neutrones) y teóricas (Cohen, Resta, Spaldin) de la última década han esclarecido aspectos del comportamiento atómico que conducen a la polarización espontánea en estructuras perovskitas y asociadas. Se presenta el trabajo desarrollado por nuestro grupo interdisciplinario. Se obtienen fases ferroeléctricas perovskitas y Aurivillius por diferentes métodos. Se investigan detalles finos de las estructuras cristalinas mediante radiación sincrotrónica en el Laboratorio de Radiación Sincrotrónica de Stanford. Las estructuras electrónicas de las fases consideradas se caracterizan por métodos *ab initio*. Los experimentos de difracción en alta resolución demuestran ruptura de simetría en un número de sistemas perovskita y Aurivillius. Se discute la relación estructura-simetría- polarización. Se presenta una explicación *ab initio* de la polarización ferroeléctrica en perovskitas. La energía del sistema se calcula mediante el código CASTEP bajo un funcional GGA. La optimización de la energía conduce a la ruptura de simetría cúbica, con desplazamiento del catión Ti fuera del centro, vía una transformación Jahn-Teller de segundo orden. La estructura electrónica se investiga mediante el software BandLab, bajo un funcional LDA, con el método LMTO. La causa de la deformación de la perovskita es la degeneración de los orbitales Ti 3d z^2 y Ti 3d (x^2+y^2).

Descriptores: Ferroelectricidad; radiación sincrotrónica; cálculos *ab initio*.

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1. Introduction

Crystal and electronic structures of solid materials are crucial to understand and improve properties. Focusing attention on ferroelectricity, the experimental determination of crystal structure and symmetry and the theoretical calculation of crystal energy, band diagrams and densities of states (DOS) are of fundamental importance.

Our interdisciplinary group on Ferroelectricty, with participants from CIMAV, UACh and CCMC works on the synthesis and investigation of state-of-the-art ferro-piezoelectric ceramics, the application of high-resolution synchrotron radiation diffraction experiments to solve fine details of their structure-symmetry characteristics and the computer-aided theoretical calculation of electronic structures.

Here we report on our recent experimental and theoretical-computational activities, mainly dedicated to the study of perovskites and perovskite related so-called Aurivillius phases. We present some original results obtained by our group in both fields.

2. High resolution diffraction experiments

All the synchrotron radiation experiments reported here were performed at the powder diffractometer, beamline 2-1, of Stanford Synchrotron Radiation Laboratory (SSRL).

2.1. Pr-doped strontium titanate

Strontium titanate, $SrTiO_3$, is a prototype of room-temperature cubic perovskite. It becomes tetragonal and ferroelectric at approximately T $\sim$ 30 K. Doping this perovskite with small amounts of praseodymium converts it in a room-temperature ferroelectric [1]. Ferroelectricity implies neces-

sarily a cubic symmetry break-down. However, careful conventional x-ray diffraction experiments do *not* show the expected symmetry transformation.

A sample with composition $Sr_{0.9}Pr_{0.1}TiO_3$ was examined under high-resolution diffraction at SSRL. The specimen was mounted on a zero background holder and data was collected in reflection geometry at 10 KeV (1.240 Å) from 15 to 95° in 2θ. The scanning step was 0.01° in 2θ. Rietveld analysis of the experimental spectrum was performed by means of software FULLPROF [2, 3]. Figure 1 shows the experimental and calculated diffraction patterns. The zoom shows splitting of peak (2, 0, 0) into a doublet (0, 0, 2)/(2, 0, 0). This splitting demonstrates that symmetry is not cubic, but tetragonal. Structure refinement was based on a *P4mm* symmetry model. Convergence was satisfactory, with agreement factors: $R_p = 12.1$; $\chi^2 = 1.96$. Table I contains the refined structure parameters.

This case study shows how synchrotron radiation solves a structure-properties paradox.

2.2. Aurivillius phases

Figure 2 describes schematically the family of so-called Aurivillius phases (AP). Crystal structure resembles a "sandwich". The "bread" is formed by bismuth oxide layers. The "mass" consists of n ($n = 1, 2, \ldots$) perovskite layers. The figure shows AP with $n = 2$, 3 and 4. AP are ferroelectric, with their spontaneous dipole generally parallel to the bismuth

TABLE I. The crystal structure of $Sr_{0.9}Pr_{0.1}TiO_3$. Space group: *P4mm*. Cell parameters (Å): $a=b=3.90187(7)$; $c=3.90720(7)$.

Atom	x	y	z	Occ.
O1	0.5000	0.5000	0.0000	1.000
O2	0.5000	0.0000	0.5000	2.000
Sr	0.0000	0.0000	0.033(3)	0.895(7)
Pr	0.0000	0.0000	0.033(3)	0.105(7)
Ti	0.5000	0.5000	0.533(3)	1.000

FIGURE 2. The crystal structure of Aurivillius phases with n = 2, 3 and 4.

oxide layers and with a (technologically interesting) high Curie temperature.

AP tend to crystallize in plate-like shape, with the plate face parallel to the bismuth oxide crystal planes. Figure 3 shows a scanning electron micrograph of a powder sample with composition $Bi_8Ti_3Fe_4O_{24}$, an AP with $n = 7$. The specimen was obtained at CIMAV by the molten salts synthesis method [4].

An important event in AP is their tetragonal $\rightarrow$ orthorhombic (or lower) symmetry transformation occurring at the Curie point Tc. At T > Tc, crystallographic axes *a* and *b*, both parallel to the bismuth oxide layers, show the same magnitude. Under the ferroelectric transformation T $\leq$ Tc, *a* becomes slightly larger than *b* and the crystal changes to orthorhombic (or lower, if inter-axial angles change). The
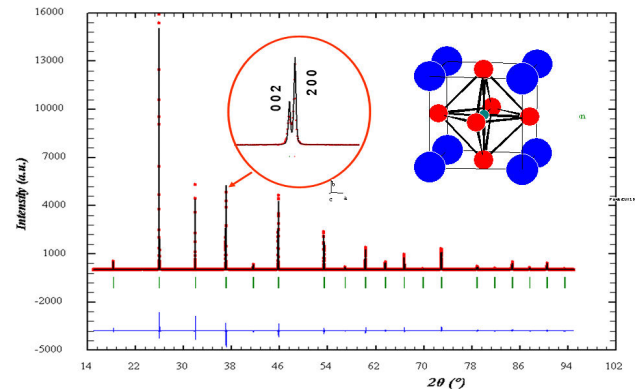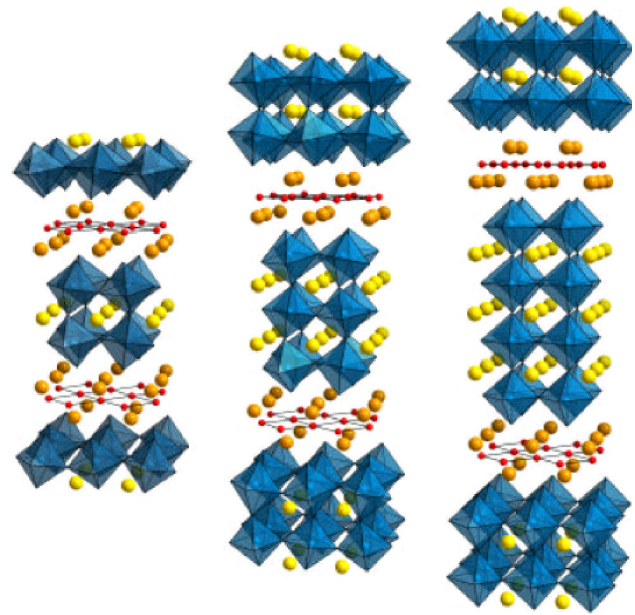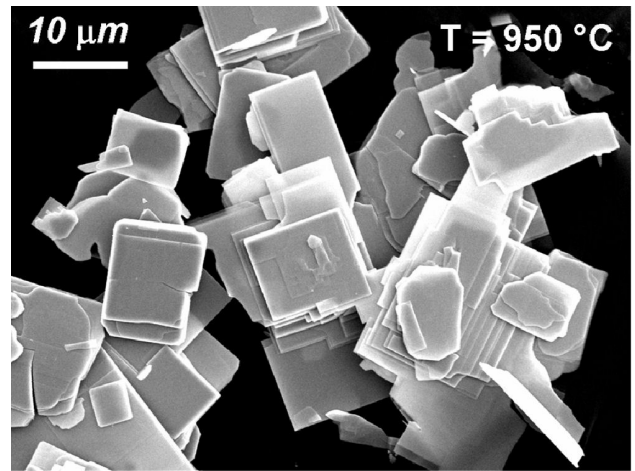

FIGURE 1. Observed (points) and calculated (continuous curve) diffraction patterns for $Sr_{0.9}Pr_{0.1}TiO_3$. Curve in the bottom is the difference spectrum. The insets represent a zoom of the (0,0,0/2,0,0) doublet and the perovskite unit cell.

FIGURE 3. Crystal morphology of (n = 7) Aurivillius compound $Bi_8Ti_3Fe_4O_{24}$, prepared by molten salts synthesis.

diffractometric problem, then, is to detect this (sometimes subtle) symmetry breakdown. We illustrate the scenario by means of a case study: The characterization of pure and Nb-doped ($n = 3$) bismuth titanate, $Bi_4Ti_3O_{12}$, abbreviated BIT.

A BIT sample, prepared by the molten salts method, was examined at SSRL under similar conditions as those mentioned for doped $SrTiO_3$. The high resolution diffraction pattern is shown in Fig. 4.

A similar specimen, with 2 % of Ti atoms substituted by Nb, was also investigated. Nb is added to increase electrical resistivity, a technological requirement.

Is tetragonal symmetry break-down detected? Does a very small amount of Nb produce observable changes in the diffraction pattern of BIT?

The insets in Fig. 4 demonstrate the positive answers to the stated questions. Doublet (2, 0, 0)/(0, 2, 0) is clearly resolved. This proves orthorhombic (or lower) symmetry. Doublets transform slightly when the material is doped. The peaks produced by the doped sample are faintly displaced to smaller angles. The numerical values of the corresponding lattice parameters are shown in Table II.

The observation of a small increase in cell parameter is consistent with the larger radius of the Nb atom, as compared with that of Ti. The $(a - b)$ parameter difference also changes very slightly:

$$(a - b)_{\text{BIT}} = 0.0387 \, \text{Å} \quad (a - b)_{\text{Nb - doped BIT}} = 0.0369 \, \text{Å}$$

The Aurivillius BIT case illustrates the capability of synchrotron radiation to detect extremely fine structural changes produced by subtle chemical variations.

TABLE II. cell parameters for BIT = $Bi_4Ti_3O_{12}$ and for 2 % at Nb-doped BIT

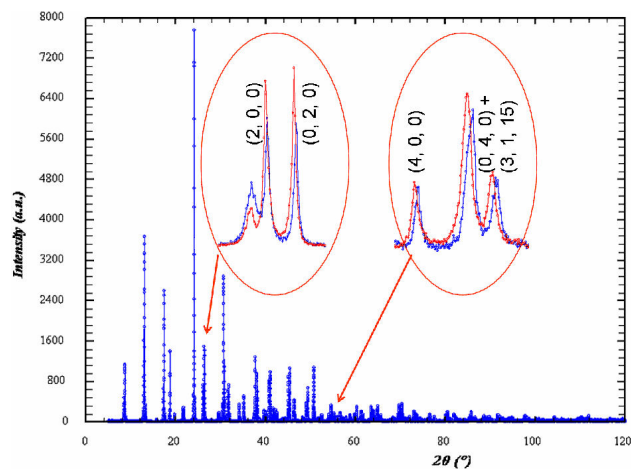|	BIT	Nb-doped BIT
a (Å)	5.4470(1)	5.4488(1)
b (Å)	5.4083(1)	5.4119(1)
c (Å)		32.8082(4)

FIGURE 4. High resolution diffraction patterns for pure and doped BIT. The slightly more intense peaks are from the doped phase.
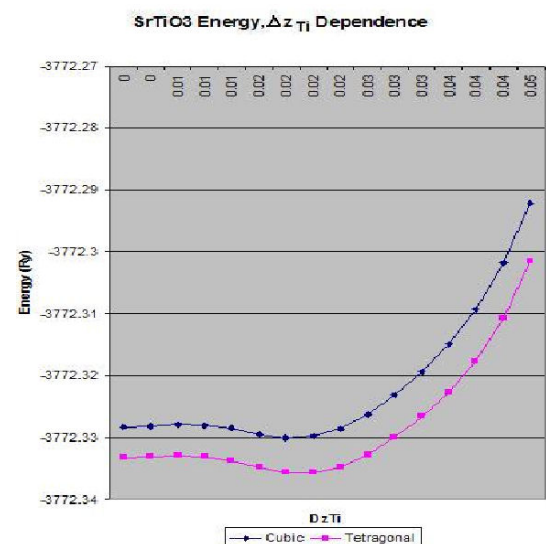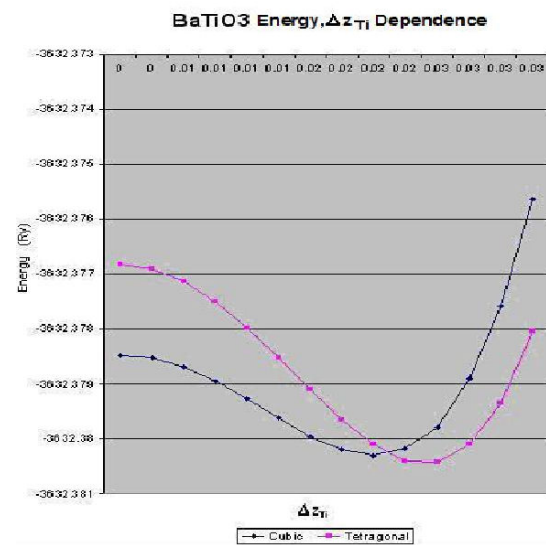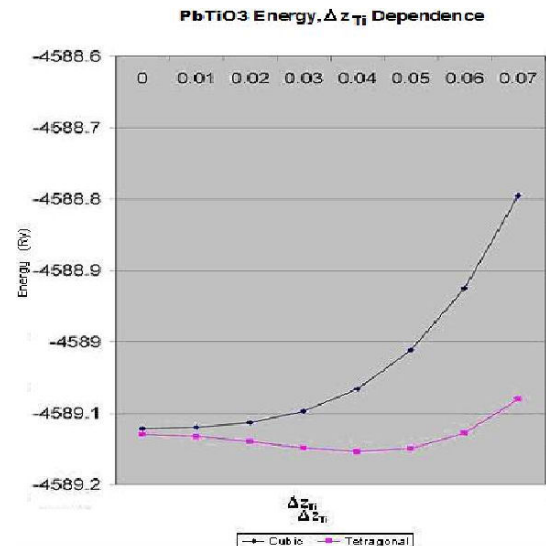

FIGURE 5. Perovskites energy as a function of titanium atom off-centering. (Observe the differences among vertical scales. Tendency to produce tetragonality may be represented as follows: Pb>Ba>Sr).

3. *Ab initio* calculations on Perovskites.

Numerical modeling have become an important tool to understand the behavior of materials and *ab initio* calculations result an ideal method to understand the quantum origin of the properties observed in the macroscopic world. Experimental methods can tell us that something is happening but *ab initio* calculations can explain why.

Our group has been interested in multiferroic materials and one such a property present in this kind of materials is ferroelectricity. We have calculated the electronic structure of $PbTiO_3$, $BaTiO_3$ and recently $SrTiO_3$. Our goal is to understand the origins of ferroelectricity in perovskites (ABO_3). Theoretical background for the calculations that follow can be found in the papers by Cohen [5], Resta [6] and Spaldin [7].

The software used was the CASTEP code under a GGA (PBE) functional as well as the BandLab code under LMTO with LDA functional.

Energy dependence on the titanium atom position has been analyzed for each titanate. Results are plotted on Fig. 5. Blue lines corresponds to the energy of the (pseudo) "cubic" perovskite, when the position of the titanium atom is changing on the z direction. The pink line corresponds to the tetragonal case. It is observed that all three materials are tetragonal and that an energy minimum exists out of the central position in the cell. All the structures were calculated with *P4mm* space group. The cell parameters used on this analysis are shown in Table III. These parameters were taken from experimental reports, except for cubic $PbTiO_3$. For this case, the values were obtained by optimizing the structure in CASTEP.

The electronic structure of $PbTiO_3$ is shown in Fig. 6 for cubic and tetragonal structures. The Ti 3d e_g orbitals are shown on green and red colors. The structure deformation from cubic to tetragonal eliminates the energy degeneracy shown on the red ellipse. This effect is known as a Jahn-Teller deformation. In this case, Ti 3d z^2 is the orbital with lowest energy. This is the origin of ferroelectricity in some perovskites.

A similar effect is observed in $BaTiO_3$ and Fig. 7 shows its electronic band structure. Here changes in the energy of the Ti 3d z^2 orbital are less pronounced, resulting in a smaller crystal deformation along the c direction.

Calculations for SrTiO3 are shown in Fig. 8. Smaller but visible changes on the Ti 3d z^2 orbital are observed in the red circles.

TABLE III. Cell parameters (in Å) used in the analysis.

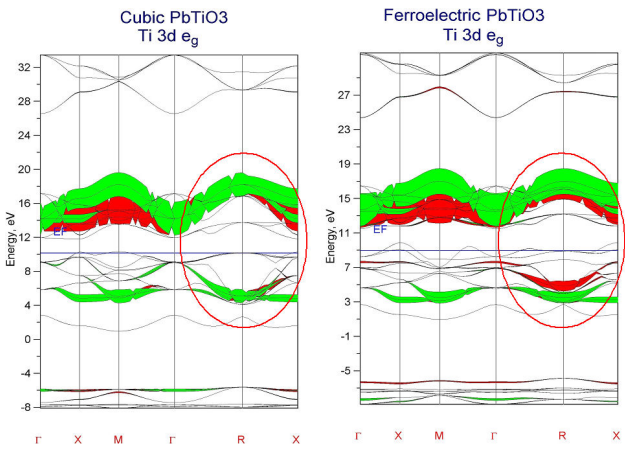|	PbTiO3	BaTiO3	SrTiO3
Cubic	a = b = c = 3.8927	a = b = c = 4.0094	a = b = c = 3.9
Tetragonal	a = b = 3.9005,	a = b = 3.997,	a = b = 3.9002,
	c = 4.1565	c = 4.0314	c = 3.9007

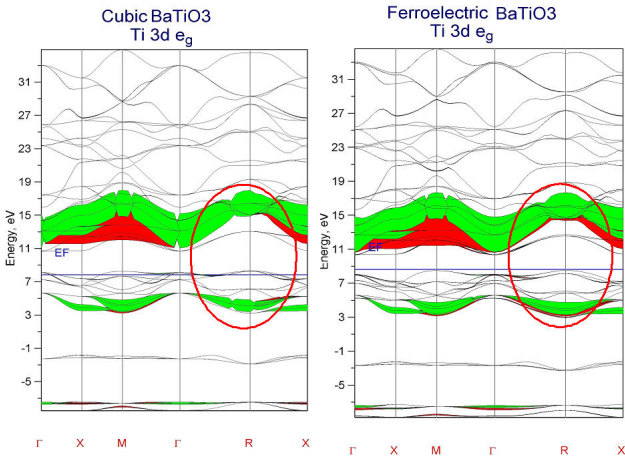FIGURE 6. $PbTiO_3$ bands diagrams. Electronic structure.

FIGURE 7. $BaTiO_3$ bands diagrams. Electronic structure.
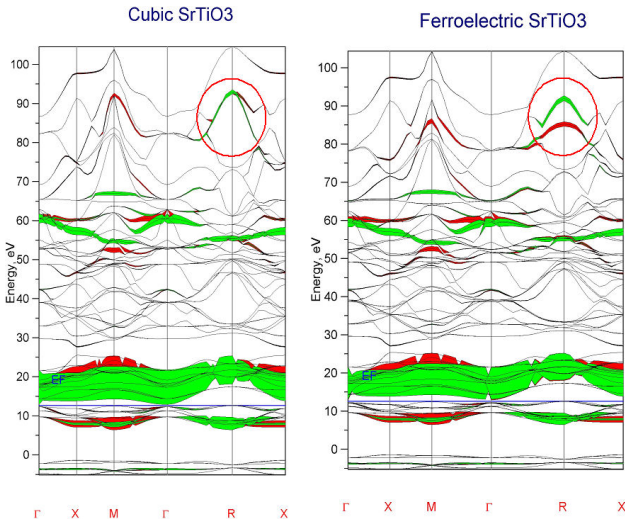

FIGURE 8. $SrTiO_3$ bands diagrams. Electronic Structure.

A larger deformation for one perovskite is due to a stronger bonding A^+ - O (A stands for Pb^{+2}, Ba^{+2} or Sr^{+2}). This bonding is observed in the overlap shown in the Density of States (DOS) in Figs. 9 to 11 for $PbTiO_3$, $BaTiO_3$ and $SrTiO_3$, respectively.
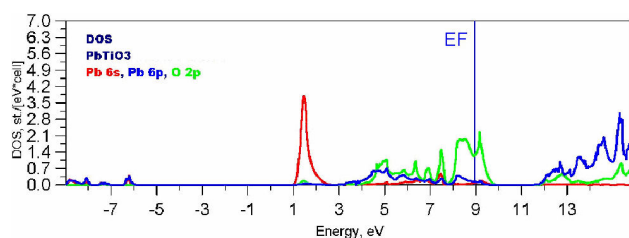
FIGURE 9. Contribution to the DOS of the Pb-O bonding.
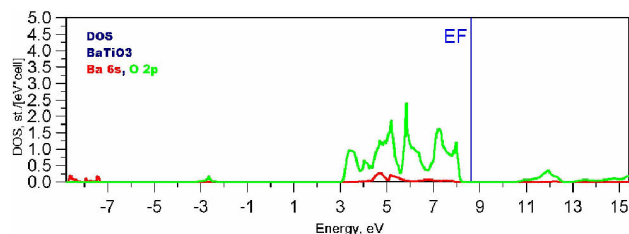

FIGURE 10. Contribution to the DOS of the Ba-O bonding.

The analyzed results comply well with the experimental properties of these materials. The $PbTiO_3$, $BaTiO_3$ and $SrTiO_3$ are ferroelectric and its origin has been interpreted as
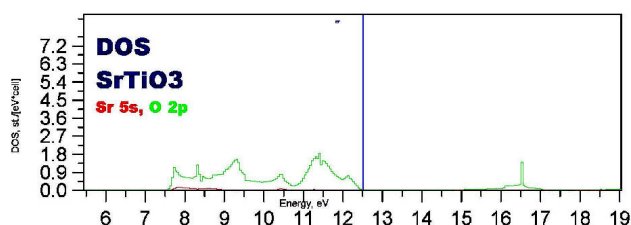

FIGURE 11. Contribution to the DOS of the Sr-O bonding.

Jahn-Teller deformations. We conclude that *ab initio* calculations are –in practice- useful tool to predict the properties of ferroelectric materials.

Acknowledgements

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