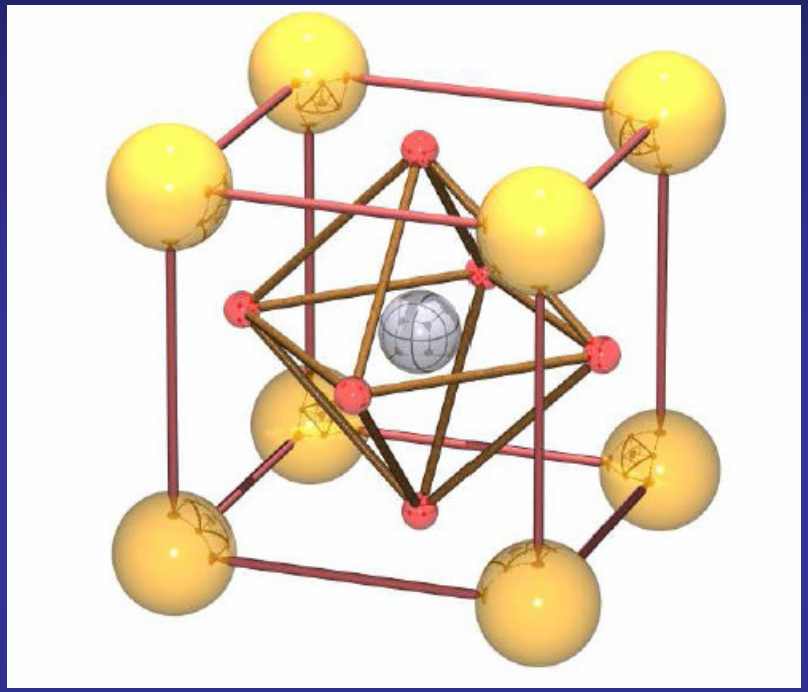
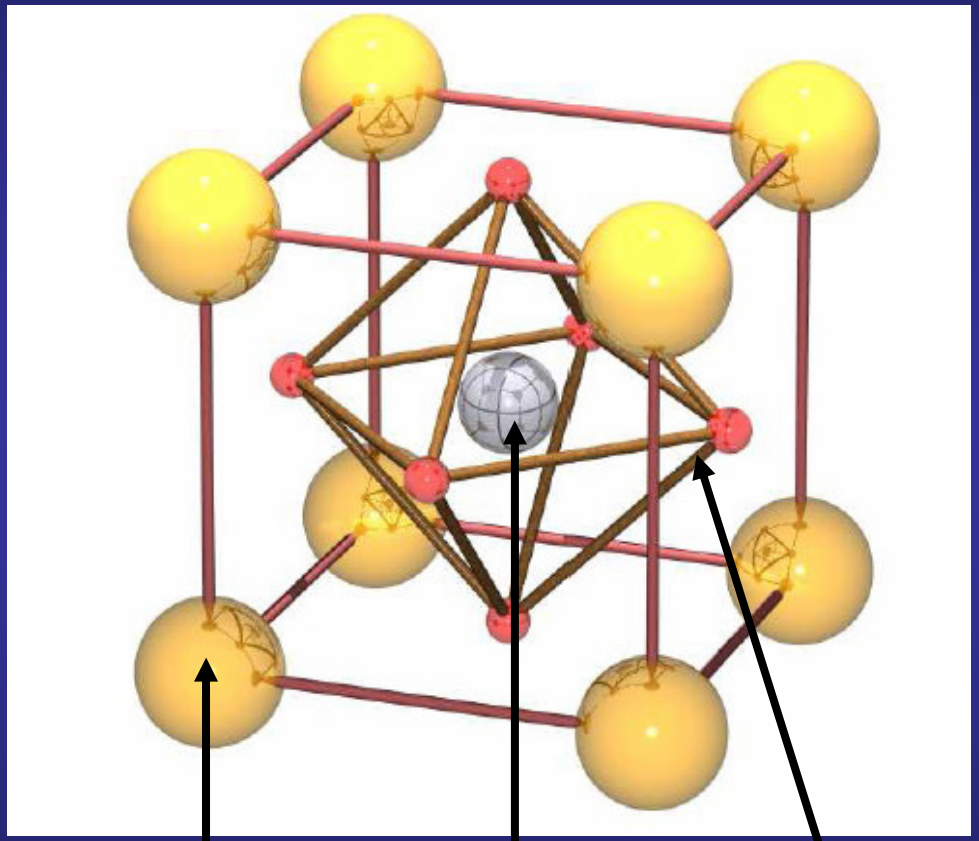
Convergence with respect the number of k-points: bulk $BaTiO_3$



Objectives

- study the convergence of the different phases of bulk $BaTiO_3$ with respect the number of k-points

Perovskite oxides ABO_3: prototypes of ferroelectric materiales



$BaTiO_3$

First ferroelectric without hydrogen bonds

First ferroelectric with a paraelectric phase

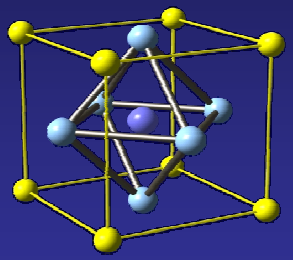
First ferroelectric with more than one ferroelectric phase

Very simple (5 atoms per unit cell)

$\Rightarrow$ lot of theoretical models

Phase transitions of $BaTiO_3$ as a function of the temperature

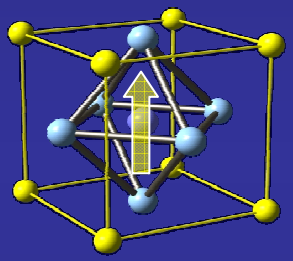
High T



Cubic

Paraelectric

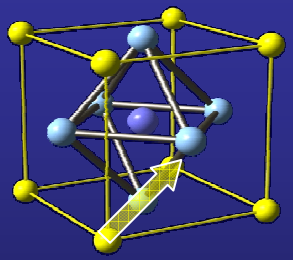
130 ºC



Tetragonal

P along [001]

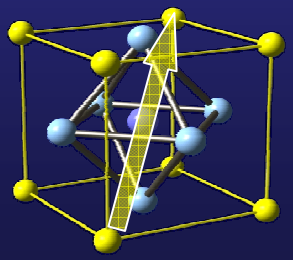
5 ºC



Orthorhombic

P along [110]

-90 ºC



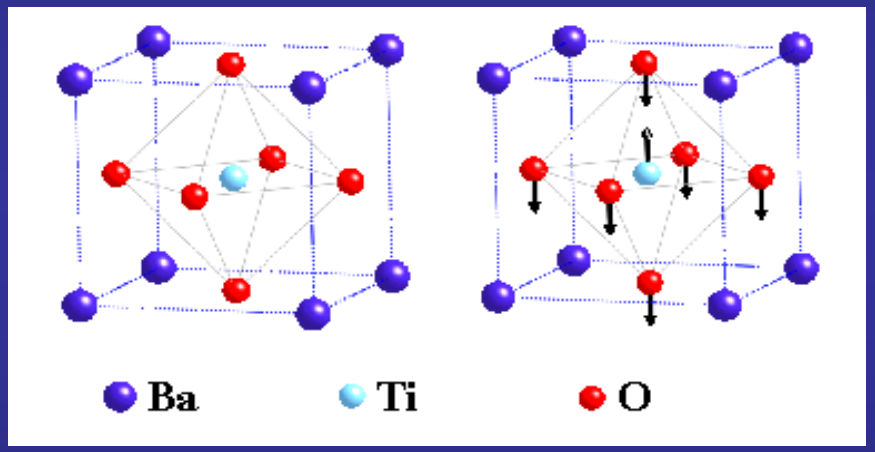
Rhombohedral

P along [111]

Phase transitions from cubic to tetragonal, pattern of cooperative polar atomic displacements

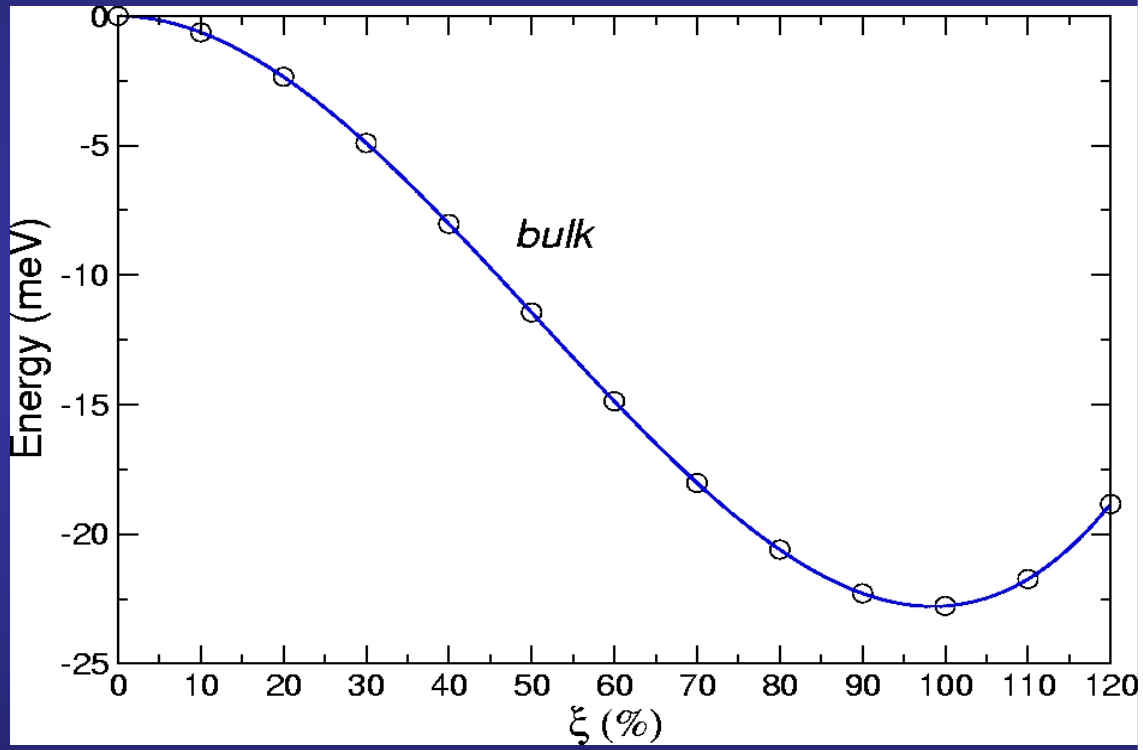
Paraelectric

Up



$\xi = 0$

$\xi = 1$



Continuum evolution of ξ

Sign of the quadratic coefficient critical

$A > 0 \Rightarrow$ parabola (paraelectric ground state)

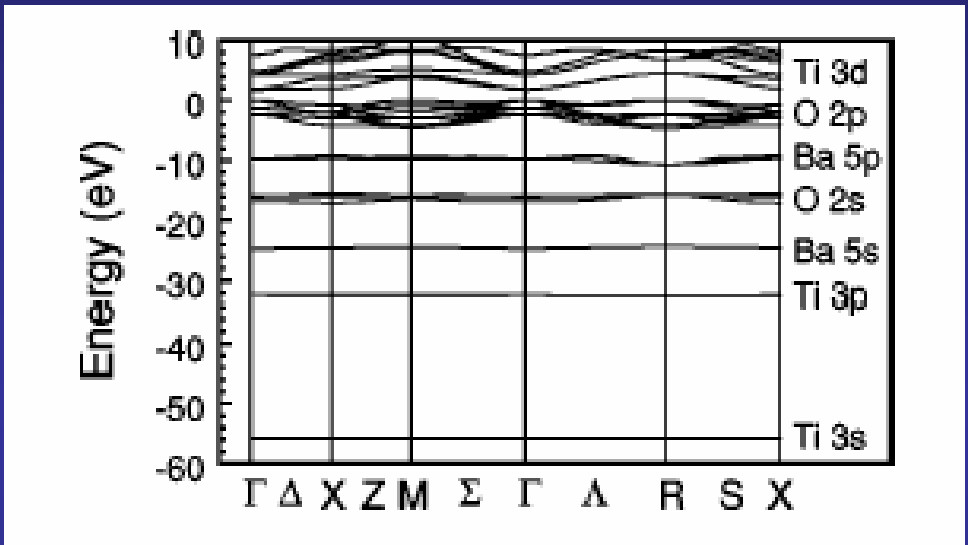
$A < 0 \Rightarrow$ double well (FE ground state)

Assuming only polarization along z

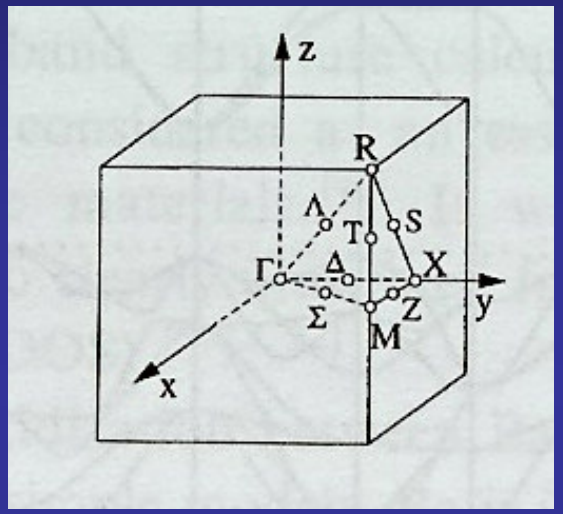
$$U(\xi) = A\xi_z^2 + B\xi_z^4 + C\xi_z^6 + D\xi_z^8 + \cdots$$

Bulk $BaTiO_3$ is a band insulator: Expt. gap 3.2 eV

LDA (DFT) band structure



High-symmetry lines in the 1BZ



Rather ionic material: well-separated sets of bands (see the exercise on band-structure MgO)

Each band:

- Located in the same energy regions than the different orbitals of the isolated atoms
- Marked dominant character $\Rightarrow$ labeled by the name of the main atomic orbital

Some covalent features

Ph. Ghosez *et al.*, Phys. Rev. B, 58, 6224 (1998)

Ph. Ghosez *et al.*, Ferroelectrics, 220, 1 (1999)

Structural relaxation of the cubic bulk $BaTiO_3$ phase

To keep the symmetry during the relaxation, we have to impose some constraints.

Write the following lines in the constr.f file (in Src directory)

```
! Symmetrize the stress tensor for a cubic structure

      stressav = ( stress(1,1) + stress(2,2) + stress(3,3) ) / 3.0d0

      stress(1,1) = stressav
      stress(1,2) = 0.0d0
      stress(1,3) = 0.0d0

      stress(2,1) = 0.0d0
      stress(2,2) = stressav
      stress(2,3) = 0.0d0

      stress(3,1) = 0.0d0
      stress(3,2) = 0.0d0
      stress(3,3) = stressav

! Symmetrize the forces for a cubic structure

      fa(1,:) = 0.0d0
      fa(2,:) = 0.0d0
      fa(3,:) = 0.0d0
```

Recompile the code

Structural relaxation of the cubic bulk $BaTiO_3$ phase

Starting from a cubic symmetry…

```
LatticeConstant       4.00 Ang   # Experimental lattice constant of cubic bulk BaTiO3
%block LatticeVectors
  1.00  0.00  0.00
  0.00  1.00  0.00
  0.00  0.00  1.00
%endblock LatticeVectors

AtomicCoordinatesFormat   Fractional
%block AtomicCoordinatesAndAtomicSpecies
   0.0   0.0   0.0         1
   0.5   0.5   0.5         2
   0.5   0.5   0.0         3
   0.5   0.0   0.5         3
   0.0   0.5   0.5         3
%endblock AtomicCoordinatesAndAtomicSpecies
```

Structural relaxation of the cubic bulk $BaTiO_3$ phase

…Run the Conjugate Grandient Minimization with the previously imposed constraints

```
#
# Molecular dynamics and relaxations
#

MD.TypeOfRun       CG                      # We are going to perform a
                                           #   Conjugate Gradient (CG) minimization
MD.VariableCell    .true.                  # Is the lattice relaxed together with
                                           #   the atomic coordinates?
MD.NumCGsteps      50                      # Number of CG steps for
                                           #   coordinate optimization
MD.MaxForceTol          0.01 eV/Ang        # Tolerance in the maximum
                                           #   atomic force
MD.MaxStressTol         0.0001 eV/Ang**3   # Tolerance in the maximum
                                           #   stress in a MD.VariableCell
                                           #   Conjugate Gradient optimization

%block GeometryConstraints
  routine constr
%endblock GeometryConstraints
```

In this example, we have performed those minimizations for you.
They have been performed at different k-points samplings.

siesta < BaTiO3.cubic.222.fdf > BaTiO3.cubic.222.out

Structural relaxation of the bulk tetragonal $BaTiO_3$ phase

To keep the symmetry during the relaxation, we have to impose some constraints.

Write the following lines in the constr.f file (in the Src directory)

```
! Symmetrize the stress tensor for a tetragonal structure

      stressav = ( stress(1,1) + stress(2,2) ) / 2.0d0

      stress(1,1) = stressav
      stress(1,2) = 0.0d0
      stress(1,3) = 0.0d0

      stress(2,1) = 0.0d0
      stress(2,2) = stressav
      stress(2,3) = 0.0d0

      stress(3,1) = 0.0d0
      stress(3,2) = 0.0d0

! Symmetrize the forces for a tetragonal structure

      fa(1,:) = 0.0d0
      fa(2,:) = 0.0d0

      fav = ( fa(3,4) + fa(3,5) ) / 2.0d0

      fa(3,4) = fav
      fa(3,5) = fav
```

Recompile the code

Structural relaxation of the bulk tetragonal $BaTiO_3$ phase

Run the Conjugate Grandient Minimization starting from a tetragonal structural, that might come from a sligthly distorted cubic phase.

Use the same fdf entries as before for the CG minimization

```
LatticeConstant      3.942581 Ang
%block LatticeVectors
  1.00  0.00  0.00
  0.00  1.00  0.00
  0.00  0.00  1.010
%endblock LatticeVectors

AtomicCoordinatesFormat   Fractional
%block AtomicCoordinatesAndAtomicSpecies
   0.0   0.0   0.000        1
   0.5   0.5   0.512        2
   0.5   0.5  -0.015        3
   0.5   0.0   0.490        3
   0.0   0.5   0.490        3
%endblock AtomicCoordinatesAndAtomicSpecies
```

In this example, we have performed those minimizations for you. They have been performed at different k-points samplings

siesta < BaTiO3.tetra.222.fdf > BaTiO3.tetra.222.out

Despite the fact of being a band insulator, a good sampling in k is required to reproduce the right order of the phases

$2 \times 2 \times 2$ Monkhorst-Pack mesh

Cubic:	-3597.825482 eV
Tetragonal:	-3597.825483 eV
$\Delta\left(E_{\text{tetra}} - E_{\text{cubic}}\right)$:	0.00 meV

$4 \times 4 \times 4$ Monkhorst-Pack mesh

Cubic:	-3597.416802 eV
Tetragonal:	-3597.420217 eV
$\Delta\left(E_{\text{tetra}} - E_{\text{cubic}}\right)$:	-3.41 meV

$6 \times 6 \times 6$ Monkhorst-Pack mesh

Cubic:	-3597.400231 eV
Tetragonal:	-3597.410000 eV
$\Delta\left(E_{\text{tetra}} - E_{\text{cubic}}\right)$:	-9.77 meV

$8 \times 8 \times 8$ Monkhorst-Pack mesh

Cubic:	-3597.399473 eV
Tetragonal:	-3597.410330 eV
$\Delta\left(E_{\text{tetra}} - E_{\text{cubic}}\right)$:	-10.86 meV

At least $6 \times 6 \times 6$ Monkhorst-Pack mesh to achieve good convergence (< 1 meV) of the double-well depth energy

These numbers have been obtained with siesta-3.0-b, compiled with the g95 compiler and double precision in the grid.

Numbers might change slightly depending on the platform, compiler and compilation flags

Convergence of the structural properties with respect the sampling in reciprocal space

Phase	Atom	Position
Tetragonal	Ba	(0.0, 0.0, 0.0)
	Ti	(0.5, 0.5, 0.5+Δ_{T-Ti})
	O_1	(0.5, 0.5, 0.0+Δ_{T-O1})
	O_2	(0.5, 0.0, 0.5+Δ_{T-O2})
	O_3	(0.0, 0.5, 0.5+Δ_{T-O2})

Monkhorst-Pack mesh	a (Å)	c (Å)	c/a	Δ_{T-Ti}	Δ_{T-O1}	Δ_{T-O2}	$\Delta(E_{\text{tetra}} - E_{\text{cubic}})$ (meV)
$2 \times 2 \times 2$	3.947	3.947	1.000	0.000	0.000	0.000	0.000
$4 \times 4 \times 4$	3.942	3.974	1.008	0.012	-0.015	-0.010	-3.41
$6 \times 6 \times 6$	3.938	3.997	1.015	0.016	-0.022	-0.015	-9.77
$8 \times 8 \times 8$	3.939	3.991	1.013	0.015	-0.020	-0.014	-10.86
Experiment	3.986	4.026	1.010	0.015	-0.023	-0.016	

Experimental numbers from G. Shirane *et al.*, Phys. Rev. 105, 856 (1957)

Typical understimation of the volume by LDA, but nice internal coordinates

At least $6 \times 6 \times 6$ Monkhorst-Pack mesh to achieve good convergence of the structural properties