Ferroelectric topology and electronic structure of BaTiO$_3$(001)

Jelle Dionot[1,2]

Jointly supervised by
Grégory Geneste[3,4] and **Nick Barrett**[2]

[1]*Université Paris-Sud 11 – École Doctorale 107 "Physique de la Région Parisienne"*
[2]*Laboratoire d'Étude des Nanostructures et Imagerie de Surface (CEA-Saclay/DSM/IRAMIS/SPCSI)*
[3]*CEA/DAM – Île-de-France*
[4]*Laboratoire Structures, Propriétés et Modélisation des Solides (CNRS-UMR 8580 – École Centrale Paris)*
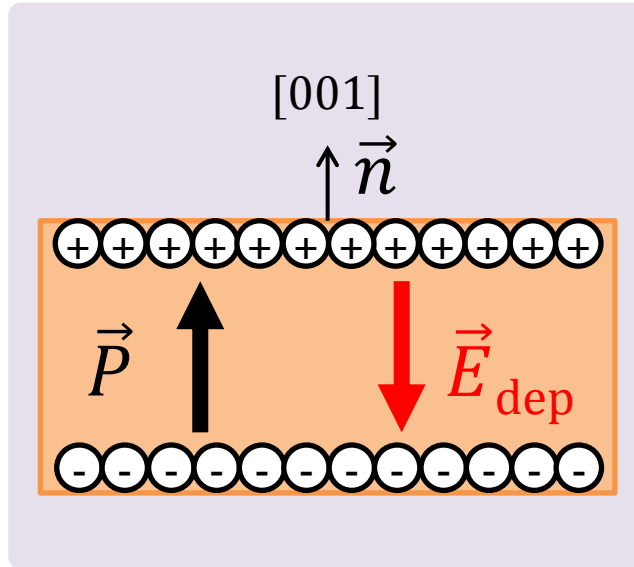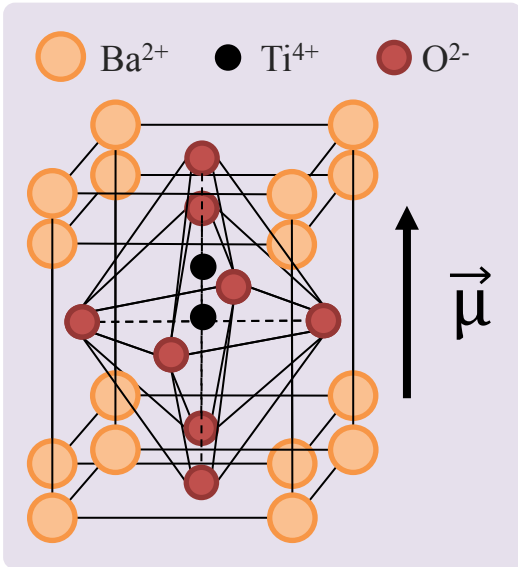
Outline

- Ferroelectric properties of **single crystals**

- Physics and chemistry of **surfaces**
  - Stoichiometry
  - Doping
  - Strain

- **Experimental** and **theoretical** approaches
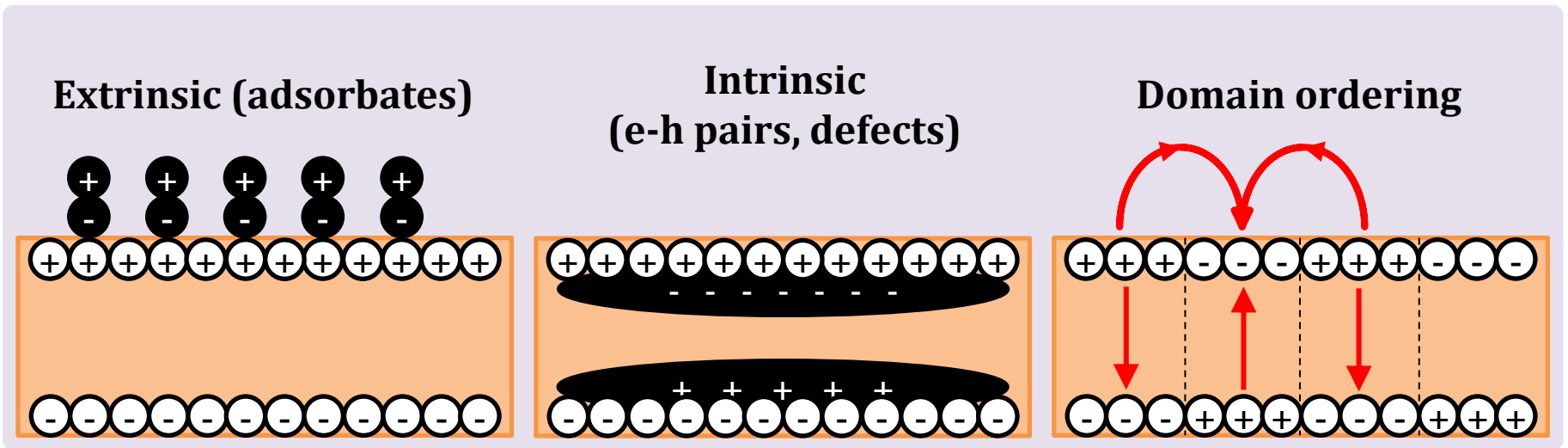 - Electron microscopy and spectroscopy
  - Ab initio simulation

Ferroelectric polarization screening on single crystal

Ba^{2+} Ti^{4+} O^{2-}

$\vec{\mu}$

[001]

$\uparrow \vec{n}$

$\vec{P}$ $\vec{E}_{\text{dep}}$

$$\vec{P} = \frac{\sum \vec{\mu}}{V}$$

$$\sigma = \vec{P}.\vec{n}$$

$$\vec{E}_{\text{dep}} = -\frac{\vec{P}}{\varepsilon\varepsilon_0}$$

Extrinsic (adsorbates)

**Intrinsic
(e-h pairs, defects)**

Domain ordering

Experimental approach:
Surface full-field imaging techniques
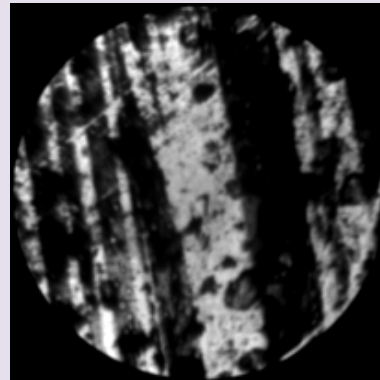
500 nm   **50 nm**   **5 nm**

Optical microscopy
Domain ordering

Polarized Light

DIC
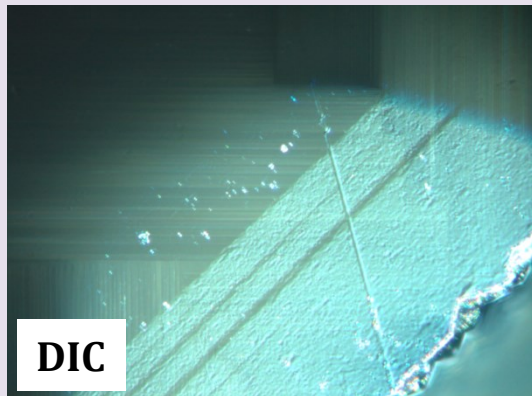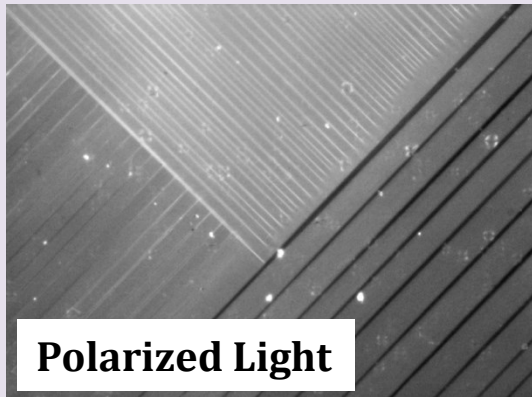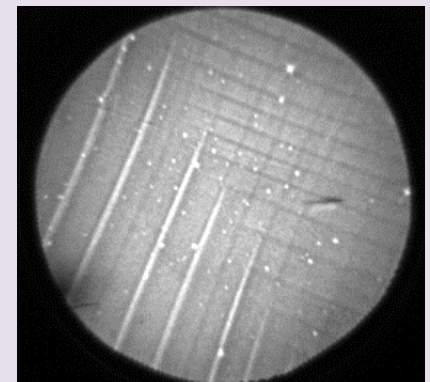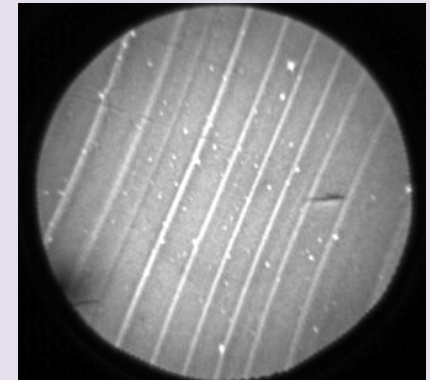
PEEM
Photoemission threshold
Work function
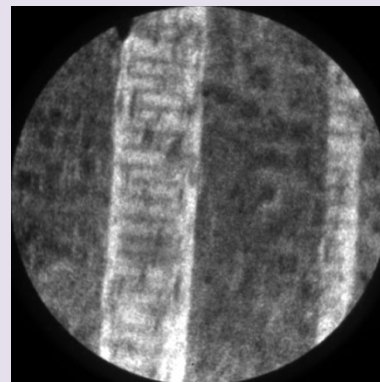
LEEM
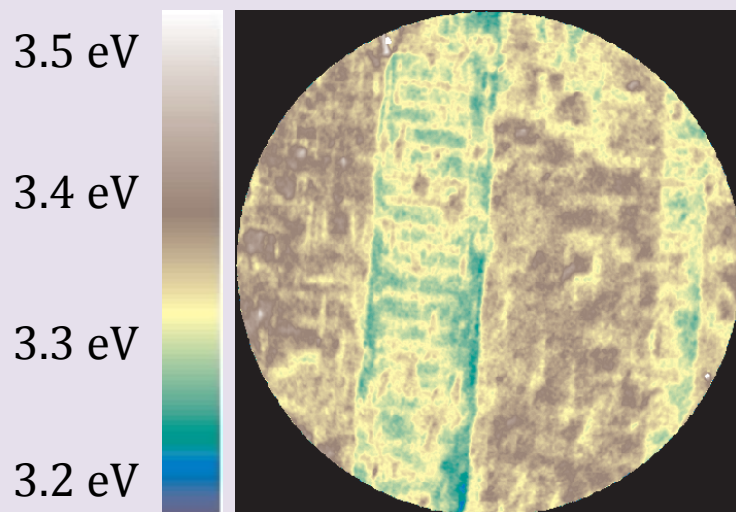Surface Potential
Phase Transition

Spectromicroscopy in real and reciprocal space (chemistry and band structure)
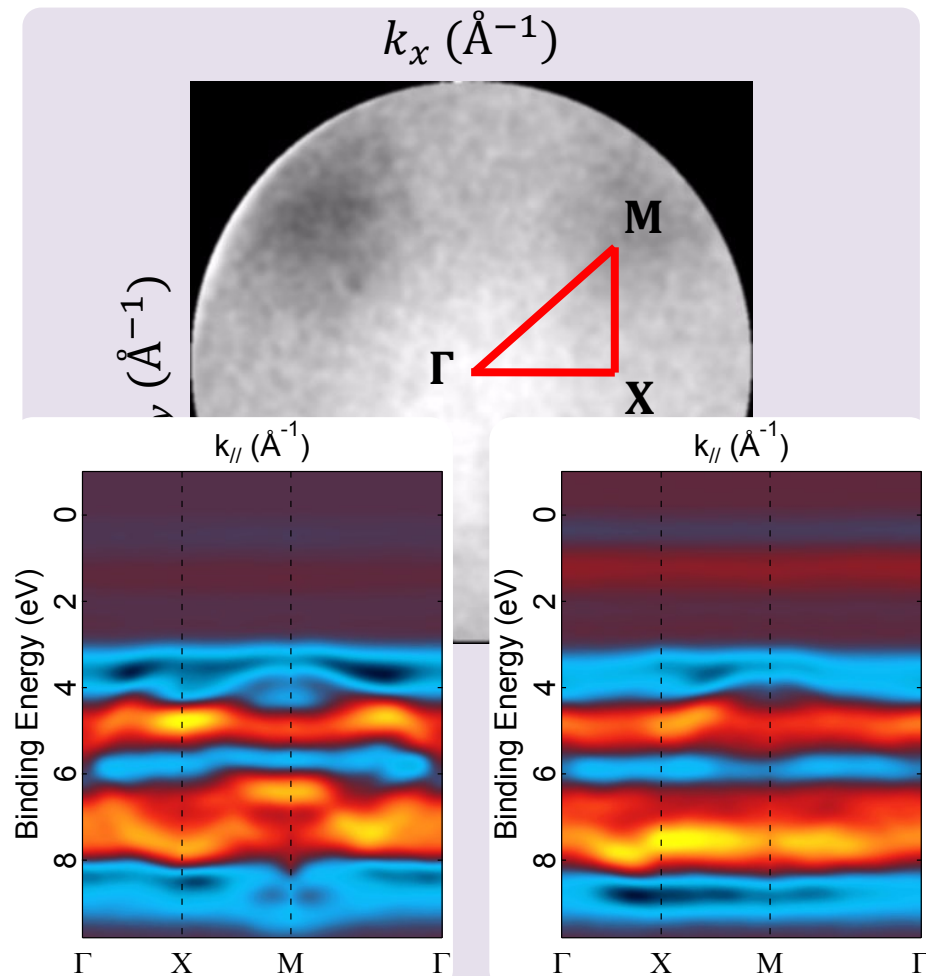
Real-space imaging

Work function variations
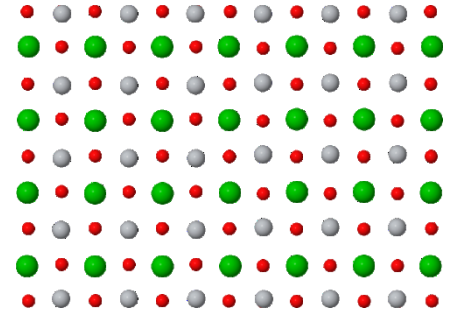*Surface charge differences in ferroelectric domains*

3.5 eV

3.4 eV

3.3 eV

3.2 eV

Direct surface chemistry
Core level imaging

Reciprocal-space imaging

k_x (Å^{-1})

k_y (Å^{-1})

M

Γ

X

$k_{//}$ (Å^{-1})

$k_{//}$ (Å^{-1})

Binding Energy (eV)

0

2

4

6

8

Γ   X   M   Γ

Binding Energy (eV)

0

2

4

6

8

Γ   X   M   Γ

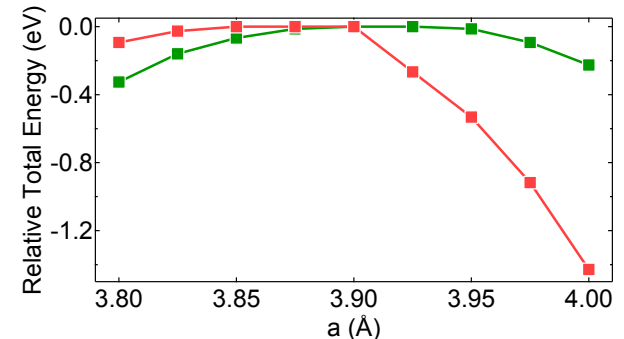# Theoretical approach: simulation

- Free standing slabs (~130 atoms)
  - **Surface**
    - **Compensation of internal depolarizing fields**

- 2 supercell terminations
  - **BaO**
  - **TiO$_2$**

- Density Functional Theory based on minimization of **total energy of the system at 0 K**

Out-of-plane polarization with uncompensated depolarizing field

Barium

Titanium

Oxygen

$\vec{\mu}$

$$\vec{P} = \sum_j Z_j w_j \vec{u_j}$$

BaO termination

Theoretical approach: simulation

Out-of-plane polarization with uncompensated depolarizing field

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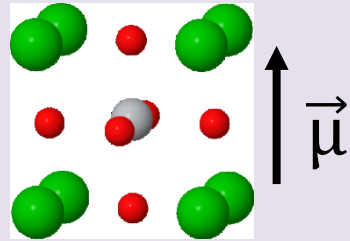
Barium

Titanium

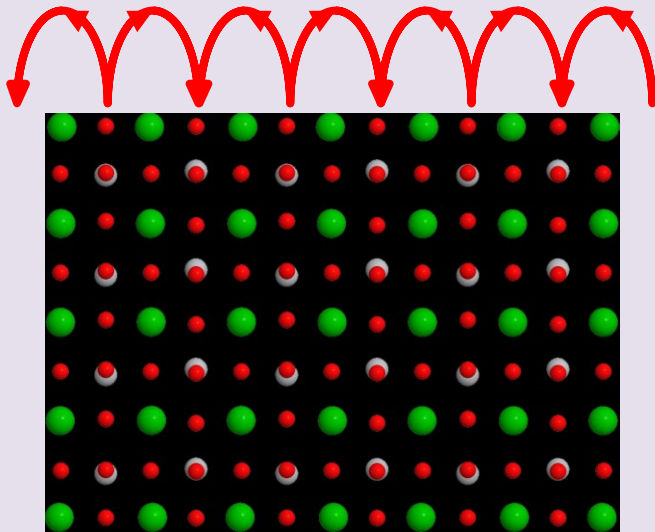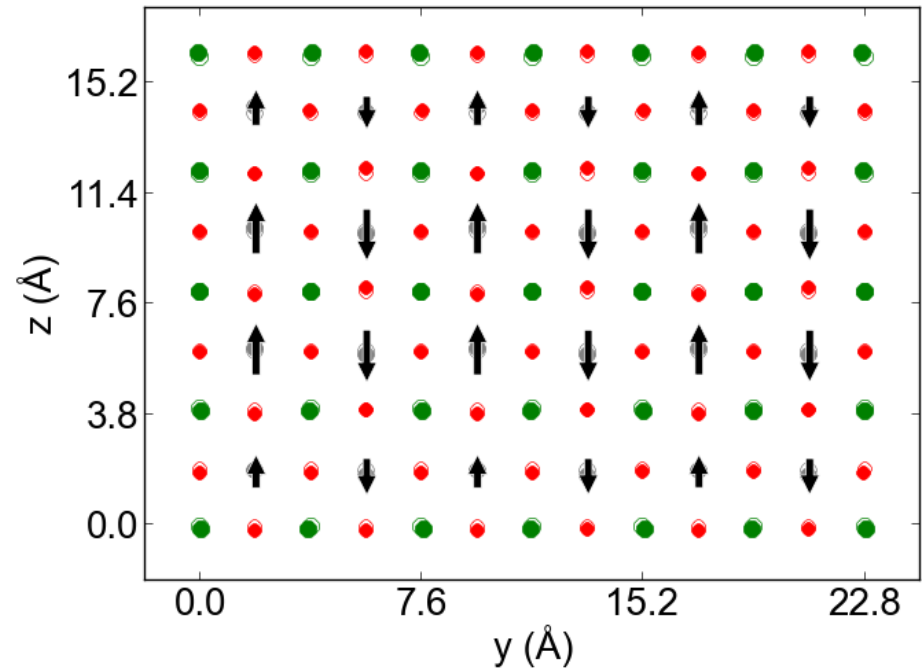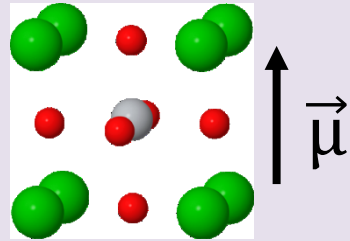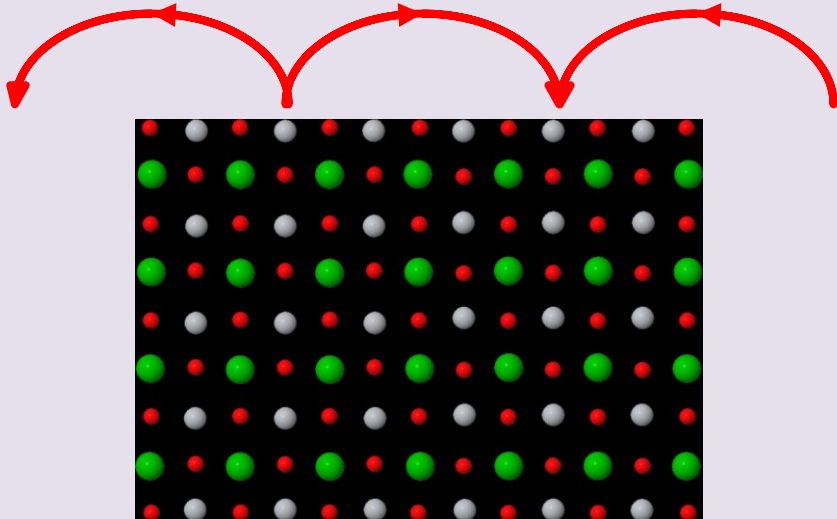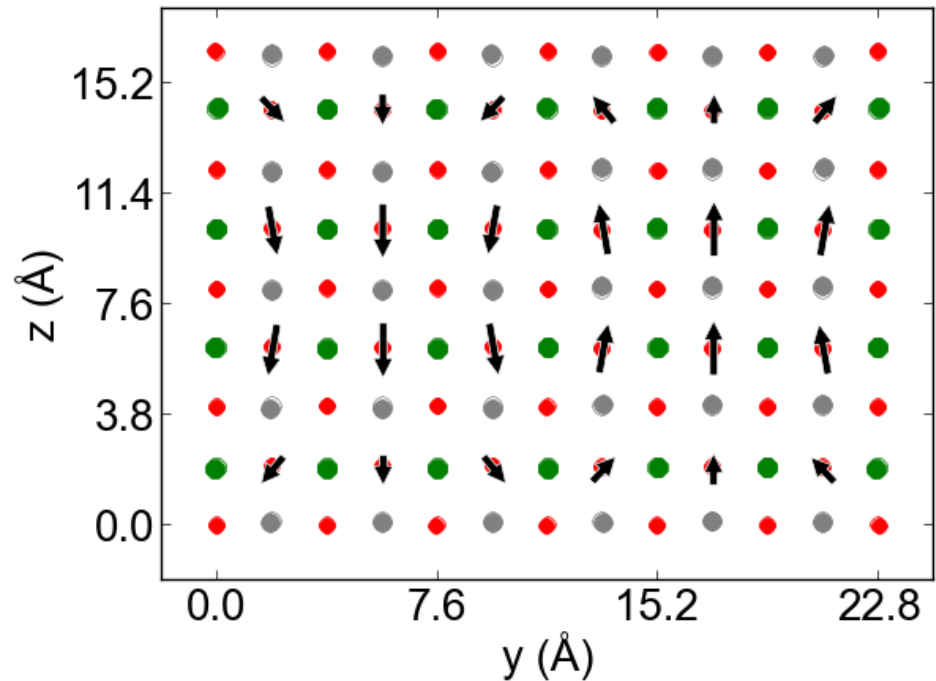Oxygen

$\vec{\mu}$
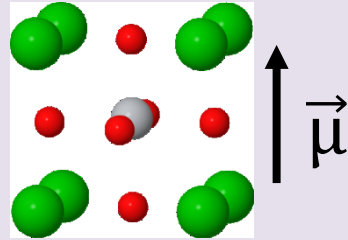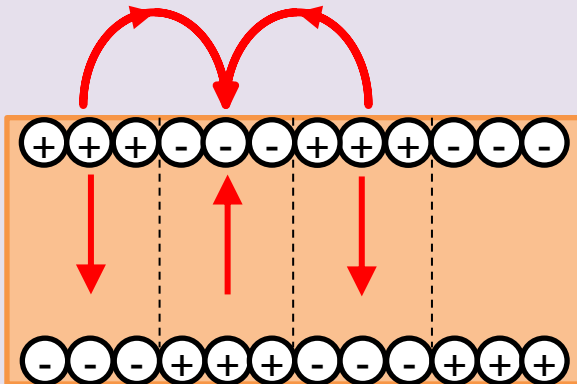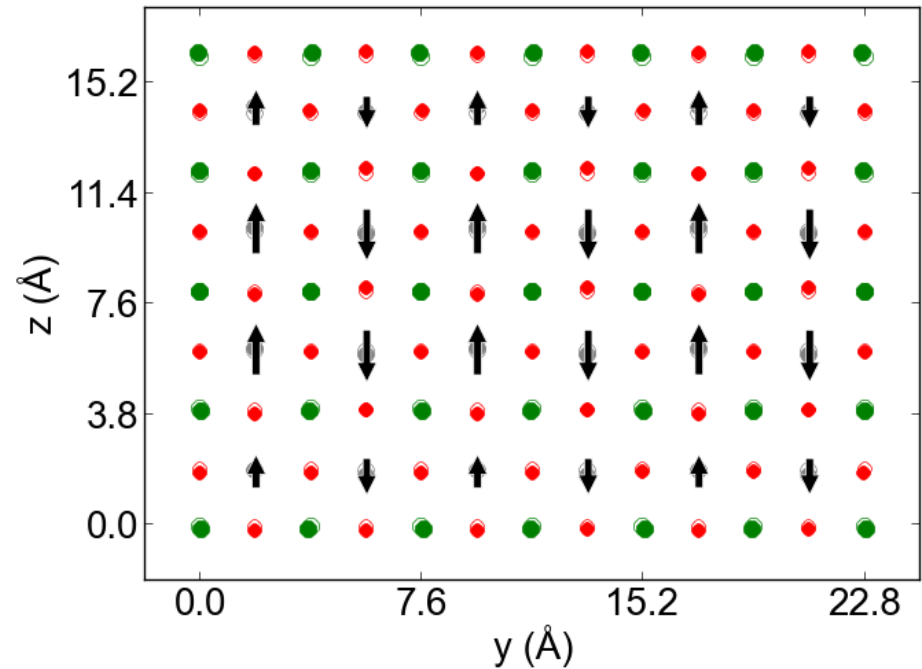
$$\vec{P} = \sum_j Z_j w_j \vec{u_j}$$

TiO$_2$ termination

Experiments & Calculations

Experiments

Oxygen vacancies stabilize **inward** out-of-plane polarization

Surface band structure of doped $BaTiO_3$

PRL **111**, 127602 (2013)

Calculations

Strain-polarization coupling

Surface relaxation and rumpling

Thank you for your attention!

So far so good!

Jelle Dionot

Pénultième année de thèse

Bât 462, P^e 6