

Giant tetragonality, local octahedral distortions and chemical switching of the ferroelectric polarization in strained PbTiZrO_3 and BiFeO_3 thin films studied by X-ray photoelectron diffraction

Context and Subject

The fundamental property of ferroelectric (FE) materials is the electrically switchable spontaneous polarization below the Curie temperature. This has driven promising applications such as nonvolatile, low power consumption memories and chemical sensors. Surface structural changes in thin films can modify the ferroelectric state [Junquera2003] and thus the performance of these materials in such nanoscale devices.

The direction of the polarization in FE thin films is not only the result of a simple control through external electric field, since it usually results from the minimization of the electrostatic energy (driven by the equilibrium between short and long-range forces) in the whole sample. The presence of unscreened polarization charge creates an internal electric field, called the depolarizing field, which can partially or wholly cancel the polarization inside the material. This is particularly important in view of potential applications of FE thin films.

Surface charge can be screened through a variety of mechanisms including adsorbate species [Spanier2006, Krug2010], defects [Jia2004], free charge carriers from adjacent electrodes, surface structural changes such as rumpling and relaxation, and domain ordering which reduces the energy of the system by mutual screening of the depolarizing field in adjacent domains. [Shimada2010] Charge compensation of ferroelectric surfaces can involve extra or missing ions arising from interaction with the environment rather than electrons [Kalinin2004, Kim2010]. Ionic compensation can also stabilize the polarity of ultra-thin films [Liechtensteiger2005].

The chemical environment can interact strongly with the polarization orientation: on the one hand, the polarization orientation can influence surface chemical reactions (molecular adsorption depends on the polarization direction), and on the other hand, the chemical composition of the atmosphere (the oxygen chemical potential for instance) might induce preferential orientation of the polarization [Highland2011]. Indeed, it has been suggested that oxygen vacancies play a role in the stabilization of negative polarization, i.e. polarization pointing inwards the material.

X-ray Photoelectron Diffraction (XPD) combines the chemical sensitivity of core level photoemission with local order sensitivity around the emitting atom. The photoemission intensity is measured as a function of angle above the sample, [Osterwalder1991] giving information on interatomic distances, bond angles and chemical states. It is therefore ideally suited to measure the three dimensional surface distortions in the atomic structure of epitaxial FE films [Despont2006]. IRAMIS has recently installed a new, high angular resolution XPD experiment with fully automatic data acquisition system.

Experimental Method and Work Plan

The main experimental method to be employed is X-ray Photoelectron Diffraction in a set-up dedicated to XPD of functional oxides. The thesis work will be developed in two stages.

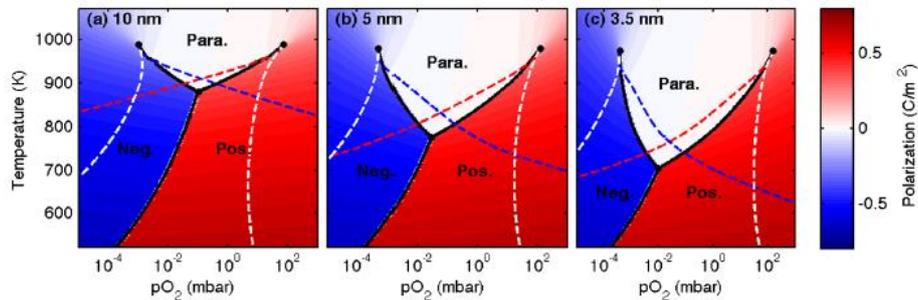


Figure Phase diagrams of ultra-thin PbTiO₃ films as a function of O₂ partial pressure showing the chemically induced switch between polarization states.

First high precision measurements of local atomic distortions in FE PbTiZrO₃ (PZT) thin films as a function of the oxygen partial pressure pO₂ during annealing will be carried out. The results will be directly compared with the state of the art X-ray diffraction data [Highland2012] in order to trace the phase diagram. These experiments will also benchmark the data acquisition and simulation techniques to be employed.

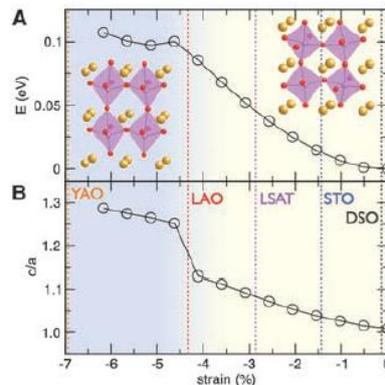


Figure Calculation of the rhombohedral to pseudo tetragonal phase as a function of strain [Zeches2009]

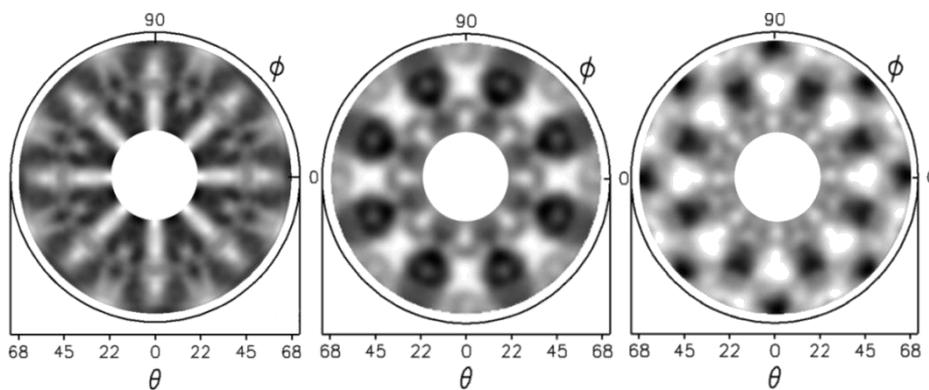
The second main part of the thesis work will apply the knowledge gained in XPD methodology to a thorough investigation of the local atomic distortions in the giant pseudo-tetragonal phase of BiFeO₃ (T-BFO) thin films grown on substrates with high misfit strain [Béa2009, Zeches2009, Infante2011]. The giant tetragonal like phase in compressively strained BFO films is in fact a monoclinic polymorph [Béa2009] and is predicted to display polarization up to 150 $\mu\text{m}/\text{cm}^2$. This is a huge value which, if switchable, would be of great interest in a variety of piezoelectric and ferroelectric applications. However, experimental results show polarizations half the predicted value. It is thought that the polarization enhancement due to the strong elongation along the c-axis is offset by rotations of the oxygen octahedra around the Fe cations. In order to quantify these effects it is mandatory to probe the local atomic structure around the metal cations. A second challenge is that the very strong

pseudo-tetragonality might shift the coercive field beyond breakdown making device manufacture impossible. However, the chemical switching of the polarization found in PZT [Highland2011] offers an alternative route to reversibly control the ferroelectric polarization.

The XPD analysis will be done as grown in order to determine precisely off-centering and the anti-ferrodistortive displacements of the oxygen octahedra. The chemical potential of the same films will also be studied as function of the partial pressure $p(\text{O}_2)$.

The longer term aim of these studies is to validate the use of the pseudo T-BFO in future high polarization ferroelectric devices.

PZT samples will be epitaxially grown on SrRuO_3 and LaSrMnO_3 electrodes in the group of Cristian Teodorescu at the National Institute of Materials Physics (Magurele, Romania). BFO T-phase films will be grown by the UMPPhy CNRS/Thalès (Stéphane Fusil)



Ba 3d, Ti 2p and O 1s XPD patterns obtained from single crystal $\text{BaTiO}_3(001)$.

The XPD experimental results will be interpreted thanks to simulations using either EDAC (single/multiple scattering, plane waves) or MSCD codes (curved wave multiple scattering). The simulation work will be done in collaboration with Alexandre Pancotti of the University of Goias (Brazil).

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