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ESRF

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*http://193.49.43.2:8080/smis/servlet/UserUtils?start*

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The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| | | |
|---|---|---|
| ESRF | **Experiment title:**<br>In situ studies of the temperature-dependent strain in $PbTiO_3$-based ferroelectric superlattices | **Experiment number**:<br>02-02-674 |
| **Beamline**:<br>D2AM | **Date of experiment**:<br>from: 25/08/06 to: 31/08/06 | **Date of report**:<br>23/10/06 |
| **Shifts:**<br>12 | **Local contact(s)**:<br>Nathalie BOUDET | *Received at ESRF:* |


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## Report:

Experimental research of ferroelectric oxide superlattices is recently attracting a lot of attention not only because of their promising technological application but also because of the fundamental understanding of ferroelectricity at the nanoscale. Thus by combining suitable materials, strains are introduced at the interfaces between layers leading to a change of the Curie temperature and of the tetragonality **[1-3]**. Our research activity is focused on superlattices based on the typical perovskite ferroelectric $PbTiO_3$ (PT). PT is considered as a perovskite-type ferroelectric material and undergoes a cubic paraelectric –tetragonal ferroelectric transition around 490°C. This material exhibits also a very large tetragonality at room temperature (c/a = 1.066) making its study very interesting. In a film form, the c-polarization axis is aligned either normal to the interface (c-domains) or parallel to the interface (a- domains). The use of substrate whose lattice constants are far from PTO ones, induces the formation of periodic 90° domain structure (a/c domains) with domain wall making an angle of 45° with respect to the (001) film surface plane as shown on figure 1.

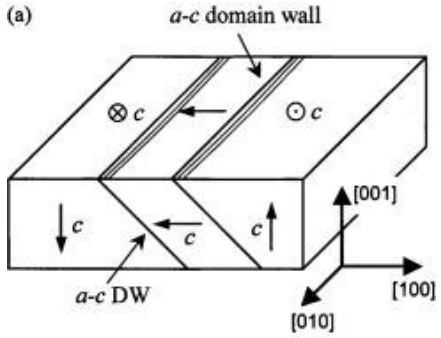


***Figure 1 :*** *Schematic drawing of the a-c domain wall structure observed in epitaxial $PbTiO_3$* ***[4]***

It's well established that the formation of such structure results from strain relaxation during the phase transition and is thickness dependent. And since the ferroelectric properties are closely linked to domain structures, it's essential to study its formation during the phase transformation and its evolution.

In situ high temperature X-ray diffraction appears to be among the best suitable techniques to carry out such study because it allows **real time observation**. Thus we have used synchrotron X-ray for in situ monitoring the evolution of the domain structures as a function of temperature through studies performed both in and out of plane. The energy fixed at 16 Kev allows us a complete structural characterization of the domain structure. On the one hand, the out-of- plane structure has been studied by recording the diffraction profiles from L = 2 to L = 6 on a 1D detector. On the other hand, the in-plane structure have been investigated by recording a reciprocal space mapping about the (0KL) nodes in a asymmetric modes on a 2D detector allowing fast data acquisition versus temperature. Since it was the first time that high temperature stage was used on the 7-circle diffractometer beamline BM2-D2AM, it had been necessary to select a sample already studied as a function of temperature to make a data comparison. We choose a 100nm PT thin film deposited on MgO substrate for its a/c domain structure and for its Curie temperature around the bulk one allowing us a complete study of the domain structure evolution. All synchrotron measurements have been performed during heating of the thin film up to 600°C, which is the maximum temperature before damaging the sample.

Concerning (00L) lines, each order shows two peaks: one is assigned to the diffraction of the c-domains and the other is related to the a-domains. We have reported on figure 2, the temperature dependence of the lattice parameters a (of the a-domains) and c (of the c-domains), deduced from classical X-ray measurements (ECP), and from synchrotron X-ray measurements (ESRF). Thanks to the good signal-to-noise ratio of the synchrotron radiation, lattice parameters have been calculated from several orders (from L = 2 to L = 6) whereas for classical X-ray measurements these parameters have been deduced only from the order L = 2 owing to the weakness of the signal at superior orders.

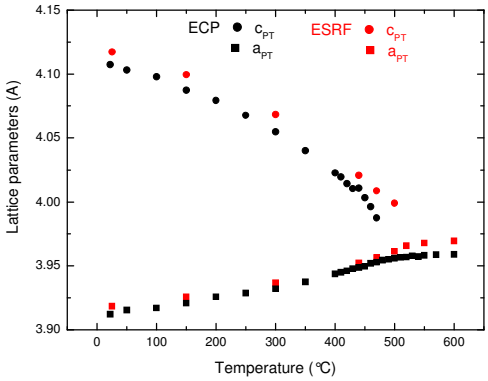


***Figure 2** : Temperature dependence of the lattice constants a-axis and c-axis of PT thin film deduced from ECP measurements (black symbols) and ESRF measurements (red symbols)*

At first glance, these two evolutions are quite similar since as the temperature increases the two parameters of the tetragonal phase (a and c) merge towards a single value of the cubic phase. Nevertheless, some differences have to be underlined. First, there is a vertical shift of the value of the lattice parameters between the two experiments. This shift can be explained by a difference between the sample adjustments. But the most striking feature comes from the shift between the two Curie temperatures deduced. From ECP data, we assign a Curie temperature of **470°C** whereas ESRF data allow us to determine a transition between **500°C and 520°C**. These two values of Curie temperatures cannot be attributed to a difference in the temperature sensor measurements since the evolution versus temperature of the lattice parameter of MgO substrate deduced from classical and synchrotron experiments are the same. To explain this shift, we have to remind that the evolutions of lattice parameters are deduced from the order L = 2 for classical measurements and from L = 2 to L = 6 for synchrotron measurements. Thus when the temperature increases, the two peaks get closer and it appears easier to separate two peaks very close at L = 6 than at L = 2. **This experiment demonstrates the importance of recording the diffractions profiles over several orders for an accurate determination of $T_C$.**

In order to investigate the in-plane structure, reciprocal space mapping (RSM) have been performed around the (043) node in asymmetric mode. We present on figure 3, the RSM maps obtained at room

temperature with the 2D detector. The left figure clearly exhibits two separated nodes : the intense one corresponds to the c-domains contribution whereas the weak one comes from the a-domains diffraction. Due to the presence of the a-domains structure, one would expect to see a splitting of this node depending of c-polarization axis direction in the plane ([100] or [010]). The broadening of the c node on the right could suggest the existence of such node. This figure exhibits also a large trail behind the c-domains node and as shown on the right figure, a second mapping centred on the bottom of this node demonstrates unambiguously the presence of a third node quite unexpected. The intensity of this unknown node comparable with the a-domain one seems to indicate that it is a node related to the a-domains diffraction.

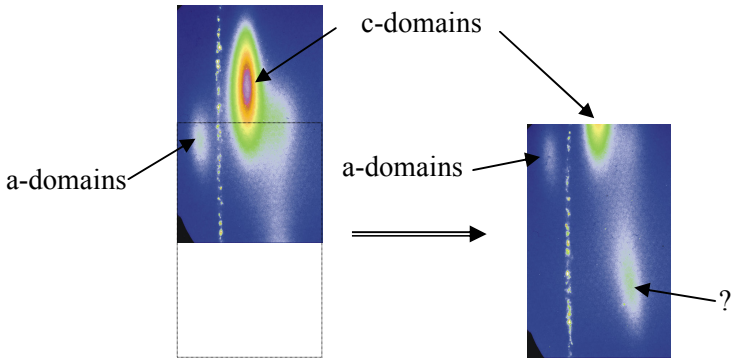


***Figure 3 :*** 2D images at room temperature around 043 node of the PT thin film showing the unexpected node (?)

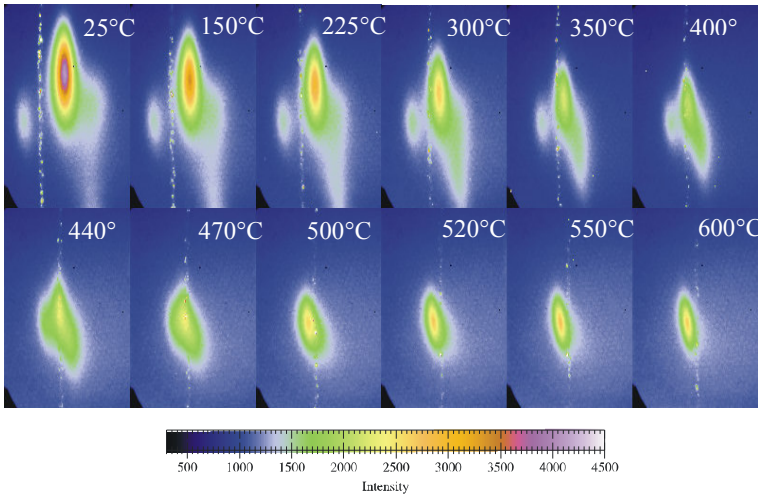


***Figure 4 :*** 2D images centred on the 043 node of the PT thin film as a function of the temperature showing the bringing closer of the three nodes.

Figure 4 shows 2D images of the 043 diffraction nodes of PT film as a function of temperature. As the temperature increases, the three nodes (a-domains, c-domains and the unknown node) get closer and finally merge toward a single node. The occurrence of this single node can be understood as the manifestation of the phase transition from tetragonal symmetry to a cubic one. We estimate the Curie temperature around **520°C** which is in good agreement with the temperature deduced from 00L lines. The evolution of the unknown node with temperature strongly suggests that this node corresponds to a-domains and only intense strains can explain the position of this node on the 2D images. Studies are now in progress to convert the 2D images in (HKL) maps in order to determine the in-plane lattice parameters of these three nodes as a function of temperature. Thanks to the determination of lattice constants along the three crystallographic directions and by structures strains considerations, it will be possible to explain the occurrence of such node.

**References :**

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