ESRF	**Experiment title:** Incommensuration and short-period antiferroelectricity in $PbZrO_3$ ultrathin films	**Experiment number**: HC-3213
Beamline: ID03	**Date of experiment**: from: 14/12/2017 to: 18/12/2017	**Date of report**: 01/03/2018
Shifts: 12	**Local contact(s)**: Maciej Jankowski	*Received at ESRF:*

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Report:

Antiferroelectric (AFE) materials have attracted considerable research interest in the recent years because of their potential applications in sensors, actuators, charge storage devices and also electrocaloricrefrigeration devices [1,2].AFE thin films demonstrate significant improvement of its energy storage characteristics and giant electrocaloric effect due to energetically competing ferroelectric and AFE ordering. The aim of our experiment was studying of the evolution of newly discovered phases on decreasing the film thickness down to several unit cells where theory and macroscopic experiments suggest the domination of ferroelectric structures instead of AFE ones.

$PbZrO_3$ thin film samples were grown using pulsed laser deposition technique at the University of California, Berkeley on the $SrTiO_3$ substrate with $SrRuO_3$ bottom electrode as buffer layer.The thicknesses of the studied films were 100, 50 and 5 nm, the thickness of the $SrRuO_3$ layer is 20 nm. This range of thicknesses covers the most interesting region, where AFE-ferroelectric phase competition in 100 and 50 nm films changes to stabilisation of the ferroelectric phase in 5 nm film. The pseudocubic main axes of the films were coincident with the ones of the substrate, oriented along the [001] direction.

In our experiment we used grazing-incidence X-ray scattering (GIXRD) to study picture ofbragg splitting, in-plane lattice strain and superstructure reflections presented in films.On the basis of this data set we will be able to characterize the phase states, presented instudied PZO thin films. At first,we have measured the temperature dependences for superstructure peaks, existed in PZO films. We investigated a set of reflections which was selected to cover all the possible domain orientations. Apart from the superstructure reflections characteristic to the antiferroelectric phase, we identify the reflections with pseudocubic coordinates of the form(H+0.5, K+0.5, L) or so-called M-points. This indicates the presence of structures having orthorhombic symmetry as aneffect of anti-phase Pb atoms displacements, which are apparently similar to the ones previouslyproposed for the rhombohedral high-temperature phase in $PbZr_xTi_{1-x}O_3$. For these structures, inthe films only the domain orientations with displacements parallel to the surface are observed incontrast to the antiferroelectric domains where the parallel to surface Pb displacements are absent(figure 1). These results have been published [3]. In the 5 nm film we haven't observed any superstructure reflections which indicates on the absense of anti-polar ordering. But we detected a phase transition into ferroelectric phase from the temperature dependences of bragg peaks intensity. This phase transition takes place at T ~ 320 °C.In order to measure temperature dependences of bragg intensity with high accuracy, we had to find experimentally optimal incidence angle at which the signal-to-noise ratio is maximal.

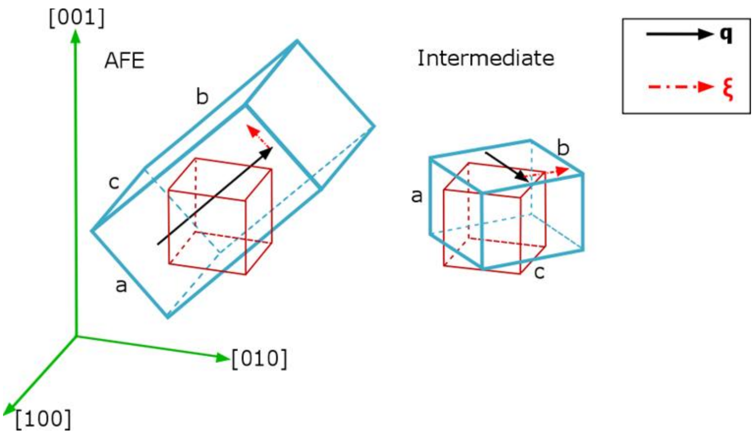

Figure 1. Depiction of AFE and intermediate orthorhombic structure illustrating their orientation with respect to the film normal. Solid black and dotted red arrows here represent the vectors: **q** – modulation wavevector direction and ξ – displacement vector, respectively.

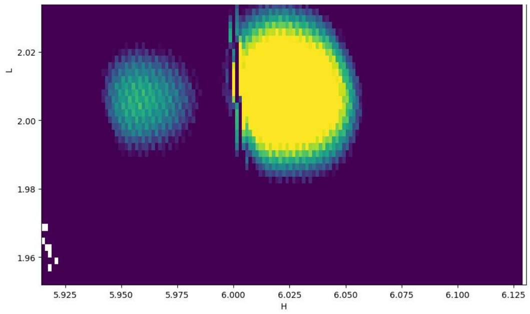

Figure 2. Bragg splitting of the (6 0 2) bragg peak in the 5 nm film.

We have measured picture of braggs splitting for wide range of temperatures in all investigated films. Example of bragg splitting presented at figure 2 for (6 0 2) peak in the 5 nm film. Now we are working onphase statescharacterisation of investigated films. On the basis of collected data we can make a preliminary assumption that the symmetry of the 5 nm film is rhombohedral or monoclinic.We also roughly estimated stress values in the films from the shift of the film peaks position relative to the substrate peaks position.The obtained values are in good agreement with values obtained in the work *Chaudhuri et al. (2011)*, determined from the Raman peak shifts.

References:

[1] H. Liu and B. Dkhil, Z. Kristallogr. 226 (2011).
[2] Glazkova-Swedberg E., et al. Computational Materials Science 129, 44-48 (2017).
[3] G. A. Lityagin, D. A. Andronikova, Iu. A. Bronwald, M. A. Kniazeva, M. Jankowski, F. Carla, R. Gao, A. Dasgupta, A. V. Filimonov, R. G. Burkovsky, "Intermediate phase with orthorhombic symmetry displacement patterns in epitaxial $PbZrO_3$ thin films at high temperatures", Ferroelectrics /accepted, in press/ (2017).