ESRF	**Experiment title:** **Antiferroelectric nanodomain mapping in epitaxial PbZrO3 thin films**	**Experiment number**: HC 3496
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Report:

Our experiment focused on the development of a novel technique for studying nanodomain configurations in ferroic materials in the form of epitaxial thin films, to complement the existing and more conventional methods (electron diffraction and piezo-response force microscopy), which have their important limitations, such as the need of polar samples in the case of PFM, or the demand for high-vacuum and charge issues in electron-related techniques. However, more importantly, they are less flexible in probing the volume distribution of the domains because of limitations of angular maneuvering with electron probe and purely-surface oriented character of PFM. X-ray nanoscopy allows circumventing some of those obstacles and provides a non-destructive approach for characterizing domain configurations of films and its changes when external stimuli are applied, such as high temperatures or electric fields.

The idea of the new method is to scan the surface of the film with an ultra-sharp-focused synchrotron X-ray beam and monitor the intensities of superstructural reflections that uniquely correspond to distinct antiferroelectric domain orientational states.

We have tested a 1000 and 50-nm-thick $PbZrO_3$ epitaxial film, grown at UC Berkeley. The experiment was carried out at the beamline ID01 – ESRF. Measurements were made at room temperature, where the material mainly resides in the antiferroelectric phase and T= 200 C, where it resides in a mixed ferro- and antiferroelectric state. Since domains are smaller than the beam, a statistical approach is imperative for a characterization of the domain distribution inside the volume of interaction between beam and sample.

Technically, we have measured the spatial distributions of the diffraction signal by translating the sample using piezo-stage, while keeping the angular geometry intact. The scanning has been done over the area of 6 by 6 microns, while the beam size was optimized to 60 by 100 nm. Each time we have configured the angles so that the diffraction conditions for a particular superstructural reflection was met. Namely, we have studied the reflections that correspond to the out-of-plane antiferroelectric modulations represented by reduced wavevectors (in pseudocubic reference frame) (0.25, 0, 0.25), (0.25, 0, -0.25), (0, 0.25, 0.25), (0, -0.25, 0.25), which correspond to the four of the six symmetry-allowed orientational domain states of the Pbam antiferroelectric unit cell. The remaining two orientational states were found to be systematically absent due to the strain energy minimization related to the epitaxial lattice mismatch. The measurements have been done in the KMAP regime for obtaining the information about the distribution of the domains with respect to small spontaneous tilts.

Intensity distributions do not have regular patterns, contrasted to bulk samples, and have a rather chaotic spatial domain distribution, with no visible traces of domain walls oriented in usual high-symmetry directions (Fig. 1). Domains have sizes smaller than the spot size (about 100 nm), which is clearly evident from the intensity histograms in (Fig. 2). Heating up to 200 C results in a decrease in density of antiferroelectric domains, which we interpret as an increase of the density of ferroelectric domains in a two-phase state.

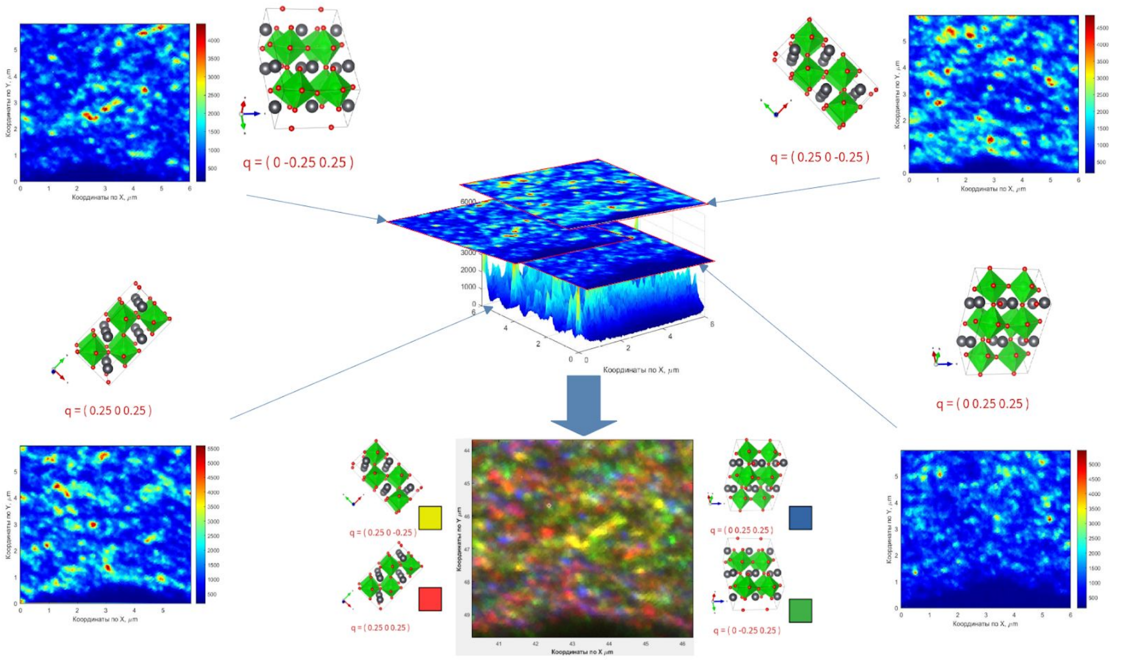

Fig. 1. Piezo-stage scans of the four different reflections that correspond to the four existing domain orientations. An overlap of them allows an approximate reconstruction of the domain structure, on the level of statistical prevalence of particular domains in particular areas of the film.

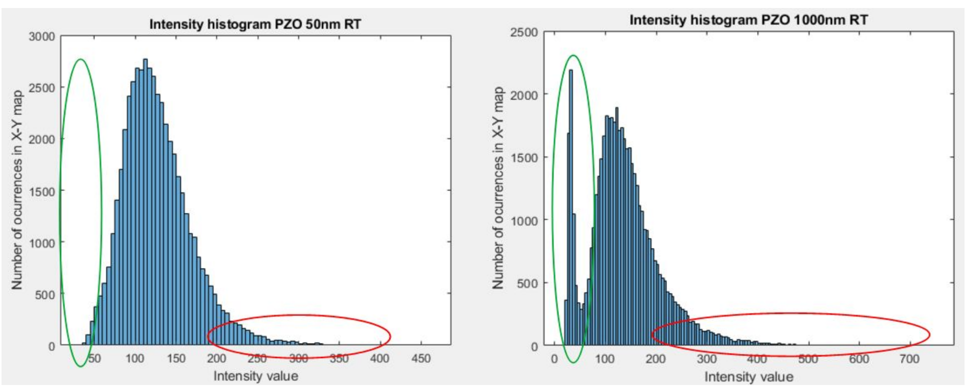

Fig. 2. Intensity histograms obtained for PbZrO3 samples with thicknesses of 50 and 1000 nm. Green ovals highlight the areas of zero occurrences of intensity values below a particular threshold, which indicates the unusually small size of the antiferroelectric domains. Red ovals denote the distribution tails, which correspond to the dense clusters of domains of a particular type, presumably - large domains of particular orientation.