ESRF	**Experiment title:** Critical diffuse scattering in antiferroelectric epitaxial thin films	**Experiment number**: HC-2616
Beamline: ID03	**Date of experiment**: from: 26/10/2016 to: 01/11/2016	**Date of report**: 01/03/2017
Shifts: 18	**Local contact(s)**: Jankowski Maciej	*Received at ESRF:*

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Report:

$PbZrO_3$ (PZO) is the prototype of antiferroelectric materials with a $T_C \sim 230°C$. In the form of epitaxial thin films the properties of PZO are substantially modified. On decrease of the film's thickness below a characteristic critical value (~ 20 nm) the ferroelectric phase becomes energetically preferred over the antiferroelectric one and size-driven antiferroelectric-ferroelectric (AFE-FE) transition takes place [1]. The purpose of current experiment was systematic investigation of the epitaxial strain effect in antiferroelectric thin films on enegetical balance between competing ferroelectric and antiferroelectric orderings.

$PbZrO_3/SrRuO_3/SrTiO_3$ and $PbZrO_3/Ba_{1-x}La_xSnO_3/MgO$ epitaxial heterostructures with different thickness of the PZO layer (d_{PZO} = 25–1000 nm) were studied. Films were grown by Prometheus group in University of Columbia, Berkeley, using pulsed laser deposition technique.

Usinggrazing-incidence X-ray scattering (GIXRD) we haveobtained the temperature and thickness dependence of integrated intensity ofsuperstructure reflections from PZO film and also diffuse scattering intensity distributions. Figure 1 shows temperature dependencesof Σ – superstructure (with coordinates (2¼ 0 ¼))and figure 2 shows temperature dependences of R – superstructure (with coordinates (½ ½ ½)).Black color line shows dependences obtained in work [2] corresponding toa single crystal PZO and red color line corresponds to dependences obtained for 50 nm PZO film in the current experiment. We can see strongly marked modification of temperaturedependences.It consists in much slower growth of superstructure intensity with decreasing temperature under T_C. And withdecrease of the film's thickness intensity growth becomes increasingly slower.We suggest that it can be connected with coexistence of ferroelectric and antiferroelectric phases.

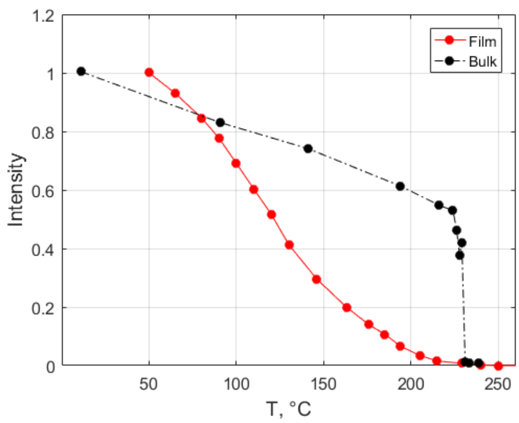

Figure 1. Temperature dependence of Σ – superstructure for 50 nm PZO film (red line) and single crystal PZO (black line)

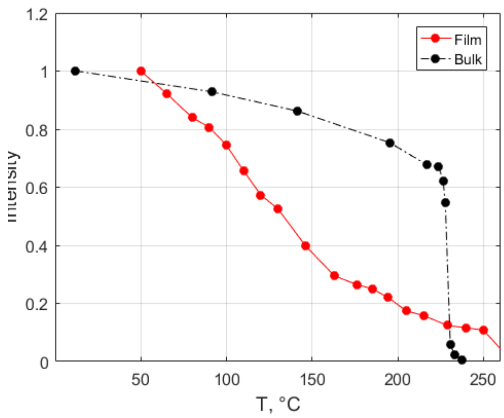

Figure 2. Temperature dependence of R – superstructure for 50 nm PZO film (red line) and single crystal PZO (black line)

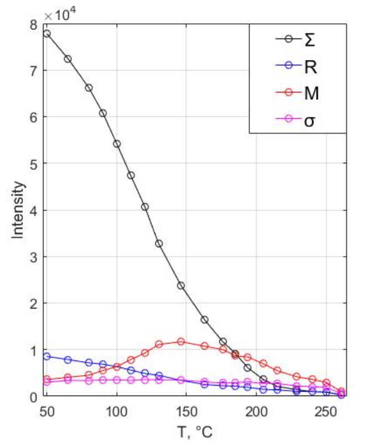

Figure 3.Temperature dependences of all superstructure reflections observed in the 50 nm PZO film

Figure 3 represents temperature dependences of all observed superstructures in the PZO film with thickness 50 nm.The existence of M – superstructures with a peak on their dependence was surprising because it has never been observed in pure PZO samples. But similar picture was observed in PZT single crystals with low concentration of lead titanate. It alsoshould be noted that M – superstructures arise earlier than Σ and R ones upon cooling. Our data clearly show that the structure behavior in PZO films is much more complicated than in single crystal samples and requires additional studies to make it clear.

We have successfully obtained diffuse scattering maps in the films with thickness down to d=25 nm. The anisotropy of the DS distributions are basically similar to those of bulk, but are characterized by enhanced signal at M-points which we suggest may be related to the formation of the corresponding superstructures at lower temperatures.

References:

[1] B. K. Mani et al., Critical Thickness for Antiferroelectricity in PbZrO3, Phys. Rev. Lett. 115, 097601 (2015).

[2] H. Fujishita and S. Hoshino,A study of structural phase transitions in antiferroelectricPbZrO3 by neutron diffraction,J. Phys. Soc. Jpn.,53(1), 226-234., (1984).