ESRF	**Experiment title:** Uncovering the mechanism behind the giant strain response and the low strain hysteresis of lead-free $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ ferroelectric materials.	**Experiment number**: MA-4727
Beamline: BM25 Spline	**Date of experiment**: from: 13 April 2021 at 08:00 to: 17 April 2021 at 08:00	**Date of report**: 10 June 2021
Shifts: 12	**Local contacts**: Dr. Jesús LOPEZ SANCHEZ and Dr. Juan RUBIO ZUAZO	*Received at ESRF:*

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Report

Brief summary

Experiments aimed to investigate the accountable mechanism for the giant strain response and the low strain hysteresis of lead-free $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ (BZCT) piezoceramic system with tailored microstructure. High-resolution XRD measurements on poled and unpoled samples with different grain sizes were performed to obtain complete information about phases coexistence and field-induced phase transformations in the BZCT system. Due to the restrictions for external users at ESRF, experiments had to be done remotely, which forced us to make some modifications to the initially proposed experiment. However, the obtained results allow fulfilling the proposal objectives. The user team followed the experiments remotely as planned with the BL staff.

Experiments description

A set of BZCT samples were sent to the BL staff for experiments, which are detailed below:

- HR-XRD patterns (two-theta up to 100º) were collected for unpoled, morphotropic phase boundary (MPB) BZCT with grain sizes of 5, 7, 10, 15, and 25 μm (5 samples) to elucidate the composition of crystallographic phases.
- HR-XRD patterns (two-theta up to 100º) were collected for unpoled, tetragonal BZCT with grain sizes of 5 and 25 μm (2 samples) as a pure crystallographic phase reference and to reveal the grain size effect on the phase stabilization. In addition, a rhombohedral BZCT sample was also measured (as a pure crystallographic phase reference of the system).
- Five representative reflexions (i.e., 220, 222, 400, 440, and 444) were selected to determine, with very high resolution, the peak splitting depending on the orientation for poled and unpoled MPB BCZT samples with different grain sizes (8 samples). This set of experiments was designed to reveal the field-induced phase transformations in the BZCT system.
- HR-XRD patterns were collected for unpoled tetragonal and MPB compositions as a function of temperature to evidence the phase transitions occurrence in the BZCT system.

Since all planned experiments on the BZCT system were carried out before all beamtime finished, one shift was used to test HR-XRD measurements on multiferroic $BiFeO_3$-$PbTiO_3$ thin films, which had been previously sent to BL staff. Two representative areas (unpoled and poled) of the films were selected for XRD measurements; both experiments were carried out successfully. As a result of this test, a new proposal concerning the study of field-induced phase transformations in $BiFeO_3$-$PbTiO_3$ thin films will be sent for the next run.
All XRD measurements were performed in reflection mode with a beam energy of 17 keV.

Preliminary results

Rietveld analysis is in progress to evaluate the composition of crystallographic phases of MPB BZCT ceramics for different grain sizes.
HR-XRD patterns of poled samples show an apparent grain size effect on phase stabilization (Figure 1), suggesting that the outstanding properties exhibited for MPB BZCT with moderate grain size are related to phase transformations mechanisms rather than typical mechanisms of domain wall motion.

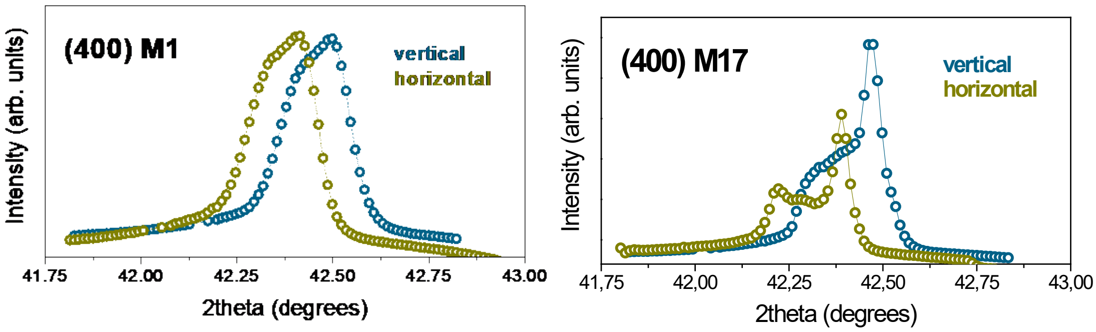

Figure 1. 400 reflexion paralel (vertical) and perpendicular (horozontal) to poling direction for poled 5 μm (M1) and 25 μm (M17) MPB BCZT samples.

Phase transformation in temperature is revealed by analyzing the HR-XRD 1D pattern. For example, Figure 2 shows the evolution of the 400 reflection from the rhombohedral phase (at -50 ºC) to the tetragonal phase (at 50 ºC) to the cubic phase (at 100 ºC).

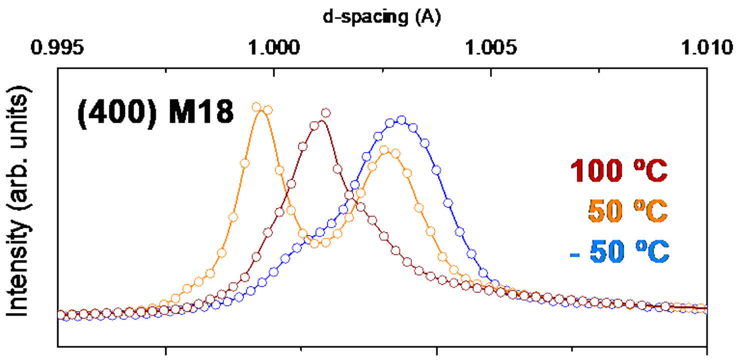

Figure 2. 400 reflexion for unpoled 25 μm MPB BCZT sample (M18) at different representative temperatures.

At present, the data processing continues through the peak fit analysis of significative reflections. Variables such as peak position, FWHM, and integrated intensity are being analyzed to find correlations with the macroscopic properties of the different samples. The results reveal an extensive MPB zone with the coexistence of three crystallographic phases. Results will be published in the near future.

The extensive MPB zone observed in the temperature experiment and the phase stabilization observed in the poled/non-poled samples experiment is strong evidence of a possible electric-field-induced crystallographic transformation. The following experimental proposal is focused on this electric-field-induced crystallographic transformation. An experiment with an in-situ applied electric field at different temperatures will be proposed to study this phenomenon.