ESRF	**Experiment title:** Polarized XAS and XMCD study of the pressure induced magnetoelectric phase transitions on multifferoic $TbMnO_3$	**Experiment number**: HC2580
Beamline:	**Date of experiment**: from: 13/04/2016 to: 19/04/2016	**Date of report**: 19/05/2015
Shifts:	**Local contact(s)**: Vera Cuartero	*Received at ESRF:*

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Report:

The application of high pressure on $TbMnO_3$ recently opened a breakthrough on the field of multiferroic magnetoelectric materials, showing magnetic ordering and a spontaneus electric polarization of the order of standard ferroelectrics for the first time [1]. In particular, the orthorhombic oxide $TbMnO_3$ is a widely studied multiferroic material, where a complex non-collinear magnetic ordering breaks the inversion symmetry of the system and triggers the appearance of spontaneous electric polarization P_s (~ 0.07 $\mu C/cm^2$) parallel to the **c** axis, below 27 K. The application of physical pressure induces a pressure-induced polarization-flop transition from **c** to **a** axis around 4.5 GPa and below 20 K [1]. The value of P_s under these conditions is the largest ever reported on a magnetic-driven ferroelectric, that is 1 $\mu C/cm^2$, comparable with standard ferroelectrics polarization values.

Low temperature and high pressure XAS measurements were performed on ID24 beamline at the ESRF [2] at the Mn K edge, using partially perforated diamond anvil cells with 600 μm cullet, compatible with the high-pressure cryostat. We loaded two different sets of single crystals, such that **E**||**a** and **E**||**c**, being **E** the direction of light polarization. We managed to explore the phase diagram points as depicted on figure 1.

In order to assert the right orientation of the crystals, polarized XAS spectra are measured at ambient conditions, as shown on figure 2 (a). This is in fully agreement with previously reported polarized XAS measurements in fluorescence yield on highly oriented big crystals [3]. In adittion, the **P**||**c** phase polarized XAS signals are almos equivalent to what it is observed on figure 1 (a) (not shown in this report). Figure 2 (b) shows the polarized XAS spectra on the **P**||**a** phase. The blue curve on the graph correspond to the X-ray Linear Dichroic (XLD) signal (**E**||**a** - **E**||**c**) and there are noticeable differences right above the edge in between the ambient (equivalent to **P**||**c** phase) and the **P**||**a** phase, indicating that the direction flipping and the enhancement of the electric polarization have an effect on the

anisotropic properties of Mn local enviroment and nearest neighbours arrangement projected along **a** and **c** axis. Figure 2 (c) shows show the Mn K edge XAS spectra at 5 K for a $TbMnO_3$ single crystal with **a** axis parallel to the light polarization vector for two pressure points, below and above the polarization-flop transition. Preliminarily, slight changes can be observed on both the pre-edge region, labelled as P, and the post-edge structures A and B. The increase on P structures intensity points towards variations on the occupation of 3*d* states of Mn but also to an enhancement of the hybridization of these states with the neighbouring 4*p* states above the transition, projected along **a** axis. Neither the edge position nor the white line intensity (first structure just right after the edge) change, indicating that Mn-O distances projected along **a** axis remain unchanged. However, there is a shift towards higher energies of A and B structures, which are related with the scattering process of the ejected photoelectron with further coordination shells, indicating a rearrangement of next-nearest neighbours.

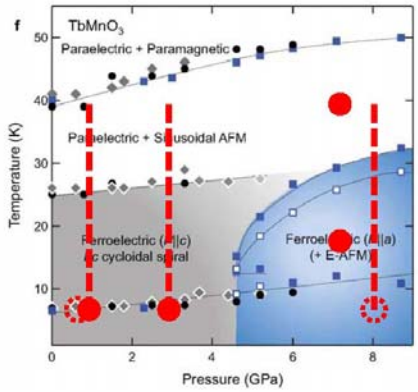

Fig. 1. P Vs. T phase diagram taken from reference [1]. The points explored on this experiment are marked in red (not filled points for **E**||**a** and filled points for **E**||**c**). The lines are a guide to indicate that several temperatures were explored above and below the ferroelectric phases.

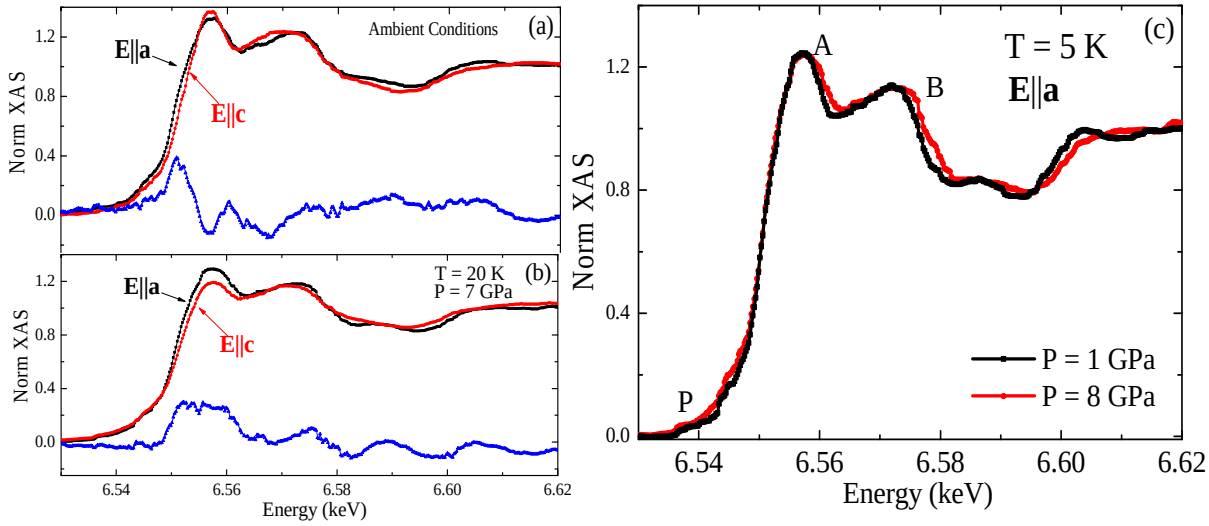

Fig. 2. Mn K edge polarized normalized XAS spectra for (a), (b) **E**||**a** (black) and **E**||**c** (red) at ambient conditions and 20 K and ~7 GPa respectively. The blue curve indicates the XLD signal (**E**||**a** - **E**||**c**) (c) **E**||**a** orientation at T = 5 K and at P = 1 GPa (black line) and P = 8 GPa (red line).

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[2] S. Pascarelli, O. Mathon, T. Mairs, I. Kantor, G. Agostini, C. Strohm, S. Pasternak, F. Perrin, G. Berruyer, P. Chappelet, C. Clavel and M. C. Dominguez, J. Synchrotron Rad. **23**, 353 (2016).
[3] M. C. Sanchez, et al., J. Phys. : Conf. Series **190** 012087 (2009).