ESRF	**Experiment title:** A direct insight into ferroelectricity under pressure by X-ray absorption spectroscopy	**Experiment number**: HC-5248
Beamline: ID24	**Date of experiment**: from: 04/07/2023 to: 10/07/2023	**Date of report**: 23/08/2023
Shifts: 18	**Local contact(s)**: Angelika Rosa	*Received at ESRF:*

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Report:

Objectives and workplan of the experiment:

From the proposal: *The approach is to use X-ray absorption spectroscopy as a short-range-based technique to probe the local environment of the Pb and Ti cations and look for direct proofs of off-cantering at high pressures, which can be accessed using EXAFS technique. […] We plan to perform in total* ***4 compression runs*** *(two absorber edges and two temperatures). […] We expect to obtain information on the local environment and coordination of Pb and Ti cations in* $PbTiO_3$ *up to 100 GPa at 15 K and RT.*

Changes in this workplan were made for several reasons.

1) Measurements at the Ti *K*-edge (~5 keV) in transmission mode was attempted at first; but turned out to be unsuccessful due to a too low number of counts. One day was used for an investigation of the problem by the local contact and beamline scientists. The conclusion was that the measurement should be possible, based on estimations of the expected absorption, using pair of thinner diamonds, so called mini anvils (1.2 mm instead of 1.6 mm for perforated one considered for this experiments). The Ti measurement was, therefore, abandoned for the sake of time for this session, but should be attempted again after deeper investigations when those new diamonds are available.

2) Measurement at the Pb L_3-edge at room temperature were then performed successfully up to ~84 GPa.

3) Considering the time needed for this experiment, decision was made to focus on it and abandon the low temperature runs. Overall, it is now clear that the programme (4 runs) was anyway too ambitious to fit into the allocated beamtime. This will be estimated more accurately in future proposals.

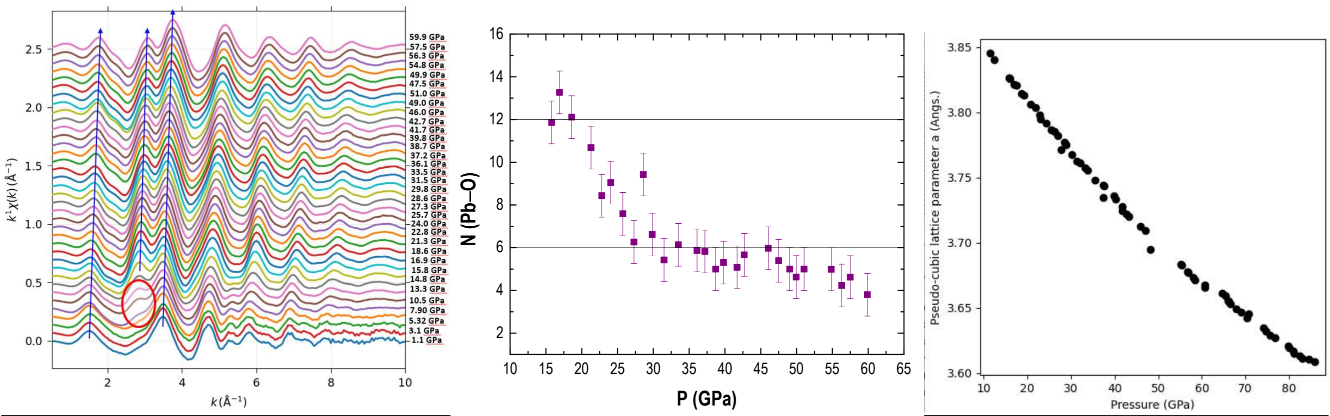
Results:

For the EXAFS measurement at the Pb L_3-edge (~15.03 keV), $PbTiO_3$ powder was loaded without any pressure transmitting medium in a pressure chamber with an indented thickness of 33-34 µm and a laser-drilled hole of 95 µm. The chamber was built from a Re gasket with an initial thickness of 200 µm. No medium was used to ensure that the thickness of the sample is optimized for the EXAFS measurement. The

NPDs were bevelled ones with an inner cullet of 200 and an external ring of 300 μm. Pressure was measured by X-ray diffraction on a gold chip placed in the high-pressure chamber and (at low pressures) by the fluorescence of a ruby chip placed on the back side of the cell. The maximum pressure reached was 84 GPa, i.e. higher than all high-pressure measurements reported in the literature. X-ray diffraction and EXAFS signals were measured at the centre of the high-pressure cell.

Data analysis is at a very early stage, but preliminary conclusions are as follows.

The EXAFS data acquired from ambient pressure to 84 GPa are displayed in figure (a). The signal is a bit noisy at first at low pressures before getting cleaner under the effect of compression. Also, in the low pressure range, the spectra show a very clear change that certainly reflects to transition from ferroelectric tetragonal towards cubic. Fits were performed from 15 GPa upwards. At 15-20 GPa, the analysis gives us a coordination of 12 (Figure (b)) for the pair-bond Pb-O, as expected for cubic $PbTiO_3$. Starting around 20 GPa, the coordination gradually goes down and stabilizes at a value of 6 at 25 GPa. We interpret this as the EXAFS signature of the first and well-established antiferrodistortive phase transition. A further modification seems to kick in around 50 GPa that will require further analysis.



<u>Figure:</u> *(a) EXAFS data (b) Pb-coordination (c) Pseudo-cubic lattice constant over the full pressure range.*

The setup used for XRD gave access to the (001) and (110) (pseudo-)cubic reflections over the full pressure range. We estimated a pseudo-cubic lattice parameter (see Figure (c)). No drastic change is observed but there could be a slight kink around 50 GPa that might correlate with the EXAFS data. It is not clear at this point what this corresponds to. In general, the strong non-hydrostatic conditions cause a significant broadening and the data quality do not allow to resolve the fine details of the expected cubic→tetragonal transition (splitting + superstructure) so that the XRD results will have to be taken with care. Nonetheless, they allow us to exclude the presence of a drastic phase transition in that range.

<u>Perspectives:</u>

It was agreed that the Ti measurement was worth pursuing and bears the most interesting promises to address the original problem. A follow-up proposal will be written to cover this part devoted entirely on Ti measurements. For the continuation, we will ask for mini anvil NPDs that should be appropriate with 1.2 mm of total thickness. A gain in the photon-flux of ~500-fold is foreseen using this thinner diamonds.

More generally, this first attempt clearly shows that this strategy is very promising for the study of ferroelectricity under very high pressure in general. $PbTiO_3$ is a model system; it would provide the most impactful demonstration and should certainly be focused on; but, as mentioned in the theoretical literature, high-pressure ferroelectricity *per se* should be ubiquitous in perovskites and other candidates could be investigated with other $3d^0$ *B* cations less challenging for EXAFS measurements (Zr, Hf…). Collaborations with theorists will be engaged to identify other potential candidates and submit future proposals along this line as well.