EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Local atomic order and Mbar pressure-temperature phase diagram of $BaZrO_3$ perovskite**	**Experiment number**: MA-5258
Beamline: BM23	**Date of experiment**: from: 13/04/2022 to: 19/04/2022	**Date of report**: 28/07/2023
Shifts: 18	**Local contact(s)**: Joao Elias FIGUEIREDO SOARES RODRIGUES	*Received at ESRF:*

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Report:

The main objective of this project was to probe the underlying mechanisms at short-range of the octahedral tilting-driven structural phase transition in $BaZrO_3$ using EXAFS data. We performed XAS measurements following the temperature-pressure phase diagram of $BaZrO_3$ perovskite in the 10–300 K and 0–1.2 Mbar ranges.

We have asked for this project 6 fresh NPDs with beveled Boehler-Almax design and height 1.6 mm and cullet sizes of 150/300 µm. At the ESRF, the proposal was accepted and 18 shifts of beamtime were granted in BM23. Three DACs equipped with NPDs were prepared, as follows: 1 LeToullec CuBe cell for low temperature with 150/300 µm NPDs, 1 conventional LeToullec cell for room temperature with 150/300 µm NPDs, and 1 LeToullec CuBe cell for low temperature with 200/300 µm NPDs. The latter one was loaded with neon gas, while the formers ones were considered for solid loading. In fact, we requested an exchange of one 150/300 µm pair for another 200/300 µm pair available at the BM23/ID24 stock.

We conducted EXAFS measurements at Zr *K*-edge (17.998 keV) under isothermal compression at two different temperatures: 15 K and 295 K. In run1, one 150/300 µm cell was solid loaded with $BaZrO_3$ and compressed up to 120 GPa. In run 2, we compared the temperature effect on the local atomic structure barium zirconate under pressure. For this purpose, a CuBe cell with 150/300 µm NPDs was solid loaded with $BaZrO_3$ and the DAC placed inside a helium-flow cryostat at 15 K. Later, the cell was compressed up to 120 GPa maintaining a fixed

temperature at 15 K. In run 3, we probed the effect of hydrostaticity on the local structure at 15 K. A third cell with 200/300 μm was loaded with a $BaZrO_3$ pellet (20×20×15 μm^3) and the neon as pressure transmitting medium.

Both ruby and gold foil were employed as pressure gauge. We used a helium-flow cryostat for diamond anvil cells developed in collaboration with and at the HP-ESRF sample environment. The temperature was monitored from a Pt-thermocouple mounted near the DAC [see in Fig. 1(a)]. The local atomic arrangement was probed using EXAFS measurements at the Zr *K*-edge up to *k*-range of 18 $Å^{-1}$. The beamline BM23 was operating with two fixed-exit Si(111) crystals combined with Pt-coated KB focusing mirror system inclined to 3 mrad for the harmonic rejection. The beam size was set to 3×3 μm^2 (FWHM). Fig. 1(a) depicts the setup employed for low temperature and high-pressure EXAFS acquisition in BM23.

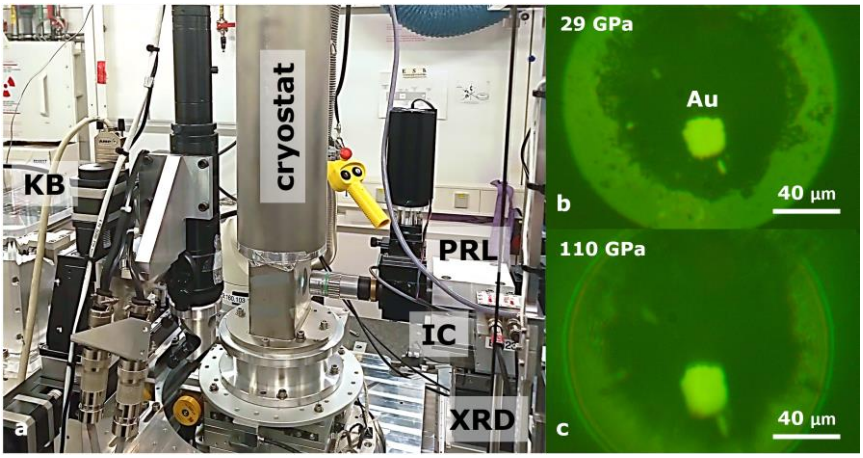

Figure 1. Experimental setup in BM23 considered for low temperature and high-pressure XAS data acquisition (a). Photographs of the gasket hole in run 2 (at 15 K) under 29 (b) and 110 (c) GPa.

Data analysis is currently in progress. However, the XANES region for run 3 is represented in Fig. 2(a). The Fourier transform EXAFS oscillations at 15 K from 0–30 GPa can be seen in Fig. 2(b), which attested the high-quality XAS data thanks to the provided nano-polycrystalline diamond anvils from GRC Ehime University (Japan). We expect to provide a detailed scenario on the local environment of $BaZrO_3$ and how the pressure can be considered to promote the antiferrodistortive instabilities in this compound. The X-ray absorption data are in common agreement to recent high-pressure single-crystal X-ray diffraction data collected at the ESRF beamline ID15B (expt. HC-5258).

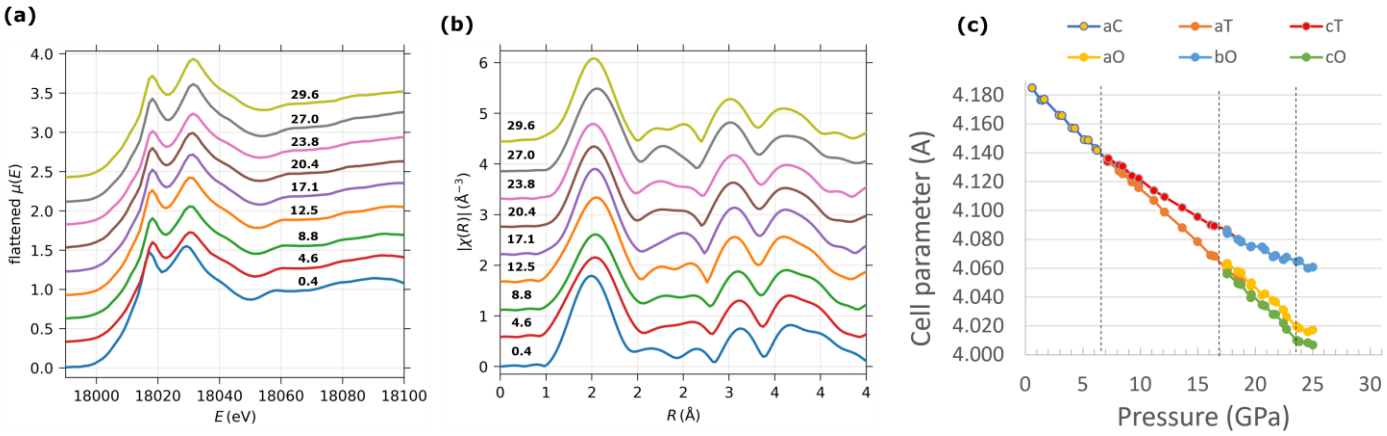

Figure 2. Zr *K*-edge XANES (a) and the Fourier transform EXAFS oscillations χ(*R*) at 15 K from 0 up to 30 GPa (run 3) (b). The $BaZrO_3$ sample loaded in Boehler-Almax NPD diamonds of 200/300 μm culet size with

neon as the pressure transmitting medium. Lattice parameters of $BaZrO_3$ single-crystal refined from SXRD data obtained in ESRF beamline ID15B.

References

Currently, we are planning to report our findings in this project in a joint publication, as cited below:
J.E. Rodrigues, A.D. Rosa, G. Garbarino, T. Irifune, T. Shinmei, J.A. Alonso, O. Mathon. *Evidences for local antiferrodistortive instabilities in $BaZrO_3$ induced under high-pressure*. To be submitted for Nature group journal *npj Quantum Materials*.