ESRF	**Experiment title:** **XAFS investigation of the local structural anisotropy induced by an applied electrical field in ferroelectrics.**	**Experiment number**: HS-3771
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Report:

Nowadays, it is still object of research whether perovskite ABO_3 systems belong to the order-disorder or to the displacive ferroelectric phase transition classes. Due to the importance of working out information about the dipole moment formation in ferroelectrics, the XAFS (X-ray Absorption Fine Structure) technique was proposed to detect changes in the local atomic structure induced by an externally applied electric field. As well as Standard EXAFS data, Quick EXAFS measurements before and after the application of the electric field were undertaken for improving sensitivity. In order to measure at different relative orientations between the photon polarization vector $\vec{\varepsilon}$ and the electrical field vector $\vec{E}$, two sample holders were built. The first of them, consisting of two metallic electrodes with a gap of 2 mm, allowed a maximum electric field of 10 kV/cm and positions $\vec{E} \perp \vec{\varepsilon}$, $\vec{E} \| \vec{\varepsilon}$; and the second, consisting of two aluminum foils separated by the 0.5 mm sample thickness, permitted a maximum electric field of 40 kV/cm and positions $\vec{E} \perp \vec{\varepsilon}$, $\vec{E} \angle \vec{\varepsilon}$.

EXAFS measurements were recorded in transmission mode on powder samples at the BM29 beam line, which was monochromatized by a Si (111) double-crystal. The samples chosen for this proposal were standard ones: $KNbO_3$, ferroelectric at RT (Room Temperature) and $SrTiO_3$, paraelectric at RT.

Differenciating the data measured with and without electric field, the derivative effect, which mainly appears at the edge energy, is reduced as the spectra accumulation increases. However, Standard measurements do not give enough energy reproducibility to detect subtle changes in absorption fine structure as measurements with and without electric field are quite separated in time. This trouble is overcome with Quick EXAFS, as we manage to subtract spectra measured much closer in time (13 seconds for collecting each complete spectrum) and averaging enough number of these pair measurements to minimize the statistical noise.

Fig. 1 shows the average of Quick EXAFS difference spectra for $KNbO_3$ at the Nb K-edge and $SrTiO_3$ at the Sr K-edge measured with the second sample holder. The pair of measurements with and without electric field was repeated 800 times for $KNbO_3$ and 300 times for $SrTiO_3$. Both measurements were carried out with the maximum electric field and thus for an electric field increase ΔE = 40 kV/cm. Fig. 2 shows the average of Quick EXAFS difference spectra for $SrTiO_3$ at the Sr K-edge measured with the second sample holder for different electric field increases ΔE = 40, 20, 5, 0 kV/cm. For all values of the electric field, each pair of measurements was repeated 100 times.

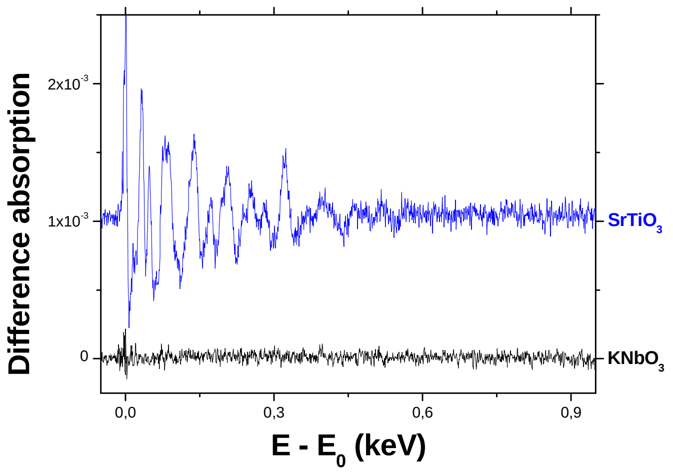

Figure 1. Average of Quick EXAFS difference spectra for $KNbO_3$ at the Nb K-edge and $SrTiO_3$ at the Sr K-edge, both for ΔE = 40 kV/cm.

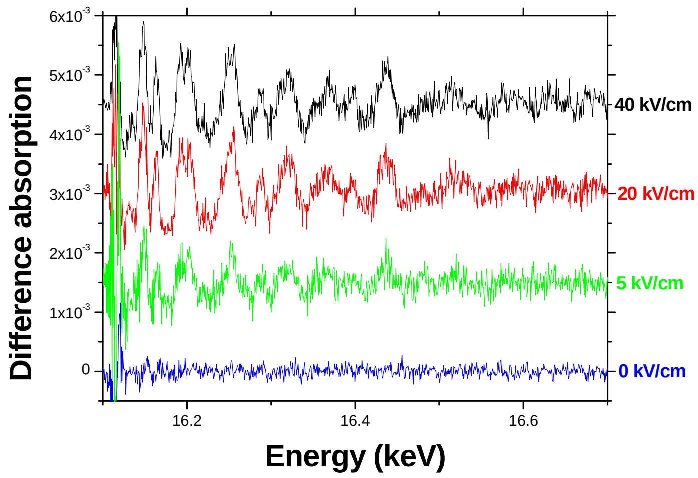

Figure 2. Average of Quick EXAFS difference spectra for $SrTiO_3$ at the Sr K-edge for ΔE = 40, 20, 5, 0 kV/cm, as shown on the right.

According with these results, no difference is found for $KNbO_3$ with a noise level of $\pm 0.5 \cdot 10^{-4}$. On the other hand, the average of Quick EXAFS difference spectra for $SrTiO_3$ yields a signal which is of similar amplitude for E = 40, 20 kV/cm and becomes slightly smaller for E = 5 kV/cm. It has been found out that this difference signal is in phase with the corresponding EXAFS signal weighed by k^2 and therefore, it represents changes to the Debye-Waller factor $\Delta\sigma^2$ as modelled in [1]. It turns out that in agreement with our result for Quick EXAFS measurements $5 \cdot 10^{-5}\,\text{Å}^2 < \Delta\sigma^2 < 1 \cdot 10^{-4}\,\text{Å}^2$, we detect temperature changes of about 5 K.

No structures were found for either $KNbO_3$ or $SrTiO_3$ using the first sample holder, and results obtained for $SrTiO_3$ with the second sample holder are the same for 90 and 45° between $\vec{E}$ and $\vec{\varepsilon}$.

Given that, in terms of $\Delta\sigma^2$, we are in the same order of magnitude than results obtained in [1]; we can confirm that in this first test, it has been checked that Quick EXAFS at the high quality performance BM29 beam line is a valid technique for the measurement of tiny atomic displacements on the local scale induced by external perturbations.

[1] M. P. Ruffoni, R. F. Pettifer, S. Pascarelli, A. Trapananti and O. Mathon, J. Synchrotron Rad. (2007). 14, 421-425.