



	<b>Experiment title: High pressure XAS investigation of a relaxor ferroelectric: <math>\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3</math></b>	<b>Experiment number:</b> 30 02 665
<b>Beamline:</b> BM30B          <b>Shifts:</b> 18	<b>Date of experiment:</b> from: 28-04-2004 to: 03-05-2004 and from: 08-09-2004 to: 13-09-2004 (test-time experiment)  <b>Local contact(s):</b> J.L. Hazemann	<b>Date of report:</b> 31-08-05          <i>Received at ESRF:</i> 06-09-05
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## Report:

It is of primary importance to analyse the local structure of relaxor ferroelectrics, and especially the cations shifts, which are at the origin of the outstanding properties of these materials. The aim of the proposed experiment was to perform EXAFS experiments under high pressure at the Pb L<sub>III</sub>-edge (13keV) and at the Nb K-edge (19 keV) in  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN), which is a canonical example of relaxor, widely studied by other techniques. In this compound, both the X-ray diffuse scattering and the Raman spectra are strongly affected by the application of high pressure <sup>[1]</sup>.

We had planned to use a diamond anvil cell to apply the pressure, like in a previous experiment on another relaxor compound  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  (NBT), where we succeeded in collecting meaningful EXAFS data at the Bi L<sub>III</sub>-edge (13.4 keV) up to 11.9 GPa<sup>2</sup>. It is known that diffraction processes within the two diamonds may spoil the EXAFS signal and that an adequate orientation of the cell has to be found, in order to minimize the amplitude of the glitches in the in the energy range of interest. With the diamonds used for the experiment on NBT, we could find such an orientation and collect EXAFS data in the range [13.3-13.9 keV]. However in the

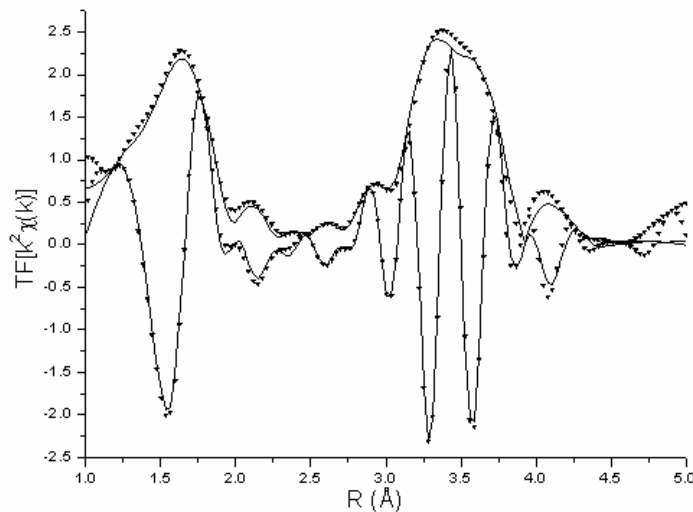
<sup>1</sup> J. Kreisel et al, Phys. Rev. B **65**, 172101 (2002) ; Phys. Rev. Lett **90**, 257601 (2003).

<sup>2</sup> ESRF experiment report HS2115.

present case, we could not find adequate experimental conditions neither at the Pb- L<sub>III</sub>-edge nor at the Nb K-edge. At the Pb L<sub>III</sub>-edge, which occurs at nearly the same energy as the Bi L<sub>III</sub>-edge, such a failure was rather unexpected. At the Nb K-edge, at 19 keV, the difficulties are still larger because the number of glitches increases with increasing energy, as it gets easier to meet diffraction conditions within the diamonds. After eliminating all causes of non-reproducibility linked with possible differences in the beam optics in the two experiments, it seems that the crystalline quality of the two diamonds or their relative crystallographic orientations are the key parameters to analyze. We tried several pairs of diamond without getting any noticeable improvement.

The remaining beam time has been used to study the EXAFS oscillations at the Zr K-edge in the BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> (BTZ<sub>x</sub>) system. The BTZ<sub>x</sub> relaxors (0.25 = x < 0.50) crystallize at any temperature in a cubic Pm-3m perovskite structure. Such an average structure cannot explain their observed outstanding properties. Moreover, contrary to the other relaxors which are compounds of fixed composition, BTZ<sub>x</sub> forms a solid solution from x = 0 up to x = 0.50. In the low substitution regime (x < 0.25), classical ferroelectric properties are reported. The EXAFS experiments were performed at room temperature in the transmission mode on 2 ferroelectric BTZ<sub>x</sub> samples (x = 0.05 and 0.20) and on 4 relaxors (x = 0.25, 0.30, 0.35, 0.40), in the transmission mode. In addition, BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> EXAFS spectra were also measured at 11 K for BaZrO<sub>3</sub> and at 11 K, 90 K and 150 K for BTZ35. The energy range [17.799–19.511 keV] was covered, using a Si(220) single crystal monochromator.

We performed the EXAFS data analysis in the R-range [1.15–4.52 Å], i.e. up to the fourth neighbours of Zr atoms, taking into account the multiple scattering paths which strongly contribute to the Fourier transform of the EXAFS signal between 3.0 and 4.0 Å. The quality of fits can be appreciated in Figure 1 for BTZ<sub>0.35</sub> at 10 K. The main results <sup>[3]</sup> are that, for all samples and at all temperatures, the Zr<sup>4+</sup> cations are located at the centre of the octahedra formed by their six oxygen first neighbours. Furthermore, the obtained Zr-O distance (2.099 Å) is very close to its value in BaZrO<sub>3</sub> and independent of the Zr/Ti ratio (x), while the average cubic lattice parameter increases linearly with x, as expected for a solid solution. Zr atoms thus tend to reproduce the same first neighbour environment as in BaZrO<sub>3</sub>, which is not polar. In the relaxor samples, the analysis of the further neighbours' contribution reveal departures from a perfect cubic structure. The oxygen atoms are ex-centred with respect to Zr-Zr bonds, but Zr, O, and Ti atoms are aligned. The shape of the ZrO<sub>6</sub> octahedra is thus affected by its chemical environment. A large distribution of Zr-Ba distances is observed. From these results, we can conclude that the origin of the relaxor behaviour in BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> is not linked with the ZrO<sub>6</sub> octahedron and must instead be linked to Ti<sup>4+</sup> or Ba<sup>2+</sup> displacements.



*Fig.1: Imaginary and modulus of the Fourier Transform of the EXAFS signal for BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub> at 10 K : experimental data (triangular dots) and fits (solid lines).*

<sup>3</sup> A publication on these results is written and should be submitted in a near future.