	Experiment title: **Ti and Nb K-edge XAFS study of the relaxor ferroelectrics PMN and BTZ in their non-polar state**	**Experiment number**: 30 02 795
Beamline: BM 30B	**Date of experiment**: from: 22/01/2008 to: 29/01/2008	**Date of report**: 02/09/2009
Shifts: 21	**Local contact(s)**: D. Testemale	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

C. Laulhé* , F. Hippert*

LMGP, Bâtiment INPG –Minatec

3 parvis Louis Néel

BP 257

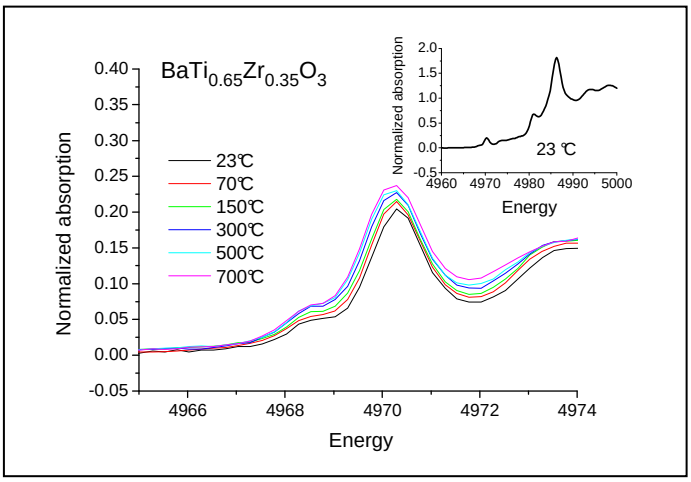
38016 GRENOBLE cedex 1 (FRANCE)

Report :

Relaxor ferroelectrics are characterized by a broad and frequency-dependent maximum of the dielectric permittivity as a function of temperature, instead of the sharp and frequency-independent divergence observed in classical ferroelectrics. They exhibit no long range polarisation but it is generally admitted that their peculiar dielectric behaviour is related to the dynamics of randomly orientated nano-scaled polar regions [1]. In relaxors with the ABO_3 perovskite structure, these regions arise from short-range correlated displacements of the A and/or B cations within their negatively charged oxygen cages. They are detected well above the temperature of the maximum of the dielectric permittivity (T_m) up to a temperature denoted T_{Burns}. The persistence of cation displacements above T_{Burns} is an open question, related to the debate on the nature (displacive or order-disorder) of phase transitions in classical ferroelelectrics such as $BaTiO_3$.

The aim of the experiment was to study cation displacements in two typical relaxors $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $BaTi_{0.65}Zr_{0.35}O_3$ (BTZ) through XAFS measurements below and above T_{Burns}. Due to the risk of a Pb pollution of the furnace, we decided to focuse on $BaTi_{0.65}Zr_{0.35}O_3$ (T_{Burns}= 300 K and T_m = 180 K at 1 kHz) and to compare its behaviour with that of $BaTiO_3$ and $SrTiO_3$ measured in the same experimental conditions. $BaTi_{0.65}Zr_{0.35}O_3$ has an average cubic perovskite crystallographic structure. EXAFS studies at the Zr K-edge have shown that the Zr atoms are located close to the centre of their oxygen octahedron [2]. By contrast, through the analysis of pre-edge features of the XANES spectrum at the Ti K-edge [3], we could establish that the Ti atoms are strongly displaced (by approximately 0.2 Å) in the temperature range [10 K – 300 K]. In order to get information on Ti displacements at higher temperature, we have measured XAFS spectra at the Ti K-edge from room temperature up to 700 °C.

Experiments have been performed in the transmission mode, using a Si(220) double-crystal monochromator. Pellets were made by mixing the sample powders with a boron nitride powder. The temperature evolution of the pre-edge part of the XANES spectra in $BaTi_{0.65}Zr_{0.35}O_3$ is shown in Fig. 1. A high intensity pre-peak centred at 4970 eV is detected in the whole temperature range.



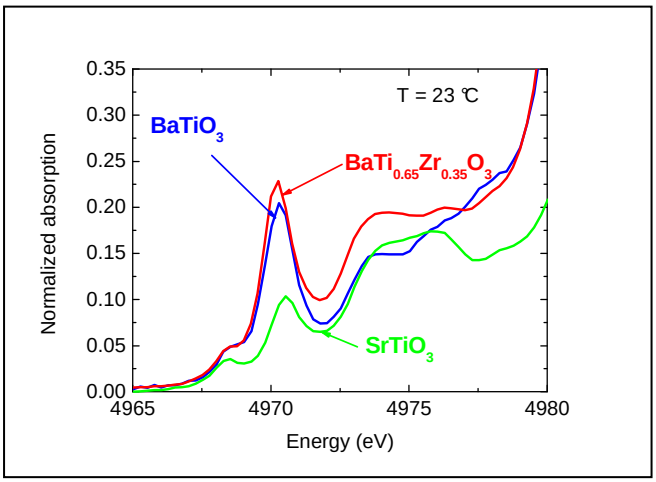


Fig.1: XANES spectra of $BaTi_{0.65}Zr_{0.35}O_3$ at the Ti K-edge. The spectra have been normalized so that the edge step is equal to 1

Fig.2: Comparison of XANES spectra at the Ti K-edge at 23°C in $BaTi_{0.65}Zr_{0.35}O_3$, $BaTiO_3$ and $SrTiO_3$.

Neglecting a quadrupolar contribution, this pre-peak results from the *p-d* hybridization that occurs when Ti atoms are displaced out of their centrosymmetric position. In a first approximation its area is proportional to the mean squared Ti displacement, which includes an eventual static displacement and the effect of atomic vibrations [4,5]. These two contributions cannot be easily separated. Nevertheless, at all temperatures up to 700 °C, the amplitude of the pre-peak measured in $BaTi_{0.65}Zr_{0.35}O_3$ is found to be much larger than that measured in $SrTiO_3$ and similar to that measured in $BaTiO_3$. One example is given in Fig. 2. Since the only contribution to the pre-peak in the paraelectric $SrTiO_3$ comes from atomic vibrations, we can conclude qualitatively that appreciable (non vibrational) Ti displacements persist in the $BaTi_{0.65}Zr_{0.35}O_3$ relaxor up to 700°C, that is well above T_{Burns}.

EXAFS analysis (in progress) is expected to provide additionnal information on the evolution of the Ti-O distance distribution as a function of temperature. However the extraction of EXAFS oscillations is made difficult by the restricted available k- range imposed by the the presence of the Ba LIII-edge at 5245 eV.

[1] L.E. Cross, Ferroelectrics **76**, 241 (1987).
[2] C. Laulhé, F. Hippert, J. Kreisel, *et al.*, Phys. Rev. B **74**, 014106 (2006).
[3] C. Laulhé *et al.*, experiment report no 30 02 764.
[4] B. Ravel, E. A. Stern, Physica B **208-209**, 316 (1995)
[5] R. V. Vedrinskii *et al.*, J. of Phys.: Condens. Matter **10**, 9561 (1998).