



	Experiment title: XAFS study of lead-free relaxors $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ at the Ti K-edge	Experiment number: 30 02 764
Beamline: BM 30B	Date of experiment: from: 17/05/2006 to: 21/05/2006	Date of report: 15/08/2006 <i>Received at ESRF:</i> 22/08/2006
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Report :

Relaxors form a special class of ferroelectrics. Their dielectric permittivity shows a broad, frequency-dependent maximum as a function of temperature, which is not related to a structural phase transition as is the case in classical ferroelectrics. It is generally admitted that the peculiar behavior of relaxors is related to an intrinsic *local* structure, that consists of nano-scaled polar regions distributed in the sample [1]. In the perovskite structure of $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ (BTZ), these polar regions are due to local cations shifts within negative-charged oxygen cubo-octahedral cages (Ba^{2+} cations) or octahedral cages (Zr^{4+} and Ti^{4+} cations).

We have applied XAFS techniques to study directly these local displacements. Previous studies of the Zr K-edge EXAFS oscillations revealed that the Zr^{4+} cations are located at the centre of their oxygen octahedra in BTZ relaxors ($0.27 \leq x \leq 0.50$), within the accuracy of the analysis [2]. **The aim of the present experiment was to investigate the Ti displacement in BTZ as a function of x, starting from the well-known ferroelectric BaTiO_3 .**

The Ti K-edge XAFS spectra were measured at 10 K, 90 K, 150 K, and 300 K on increasing temperatures for BaTiO_3 and BTZ with $x = 0.05, 0.20, \text{ and } 0.35$, in the fluorescence mode. Samples were pellets made of BTZ powders mixed with graphite powder (0.01 mole of BTZ for 1 mole of C). The surface of the pellets was oriented at approximately 45° to the incident x-ray beam and the detector. A Si(220) double-crystal monochromator was used. The acquisition time was about 30 min per spectrum, and a total of 3 spectra per sample and temperature was necessary to obtain satisfactory statistics.

The fluorescence spectrum of BTZ ($x = 0.35$) is shown as an example in figure 1. The absorption first increases at the Ti K-edge (~ 4970 eV). The second jump of the absorption (~ 5245 eV), which is due to the Ba LIII-edge, limits the available k-range for the analysis of Ti EXAFS oscillations. Hence, we focused on the analysis of the XANES spectra. A selected set of normalized spectra is shown on figure 2.

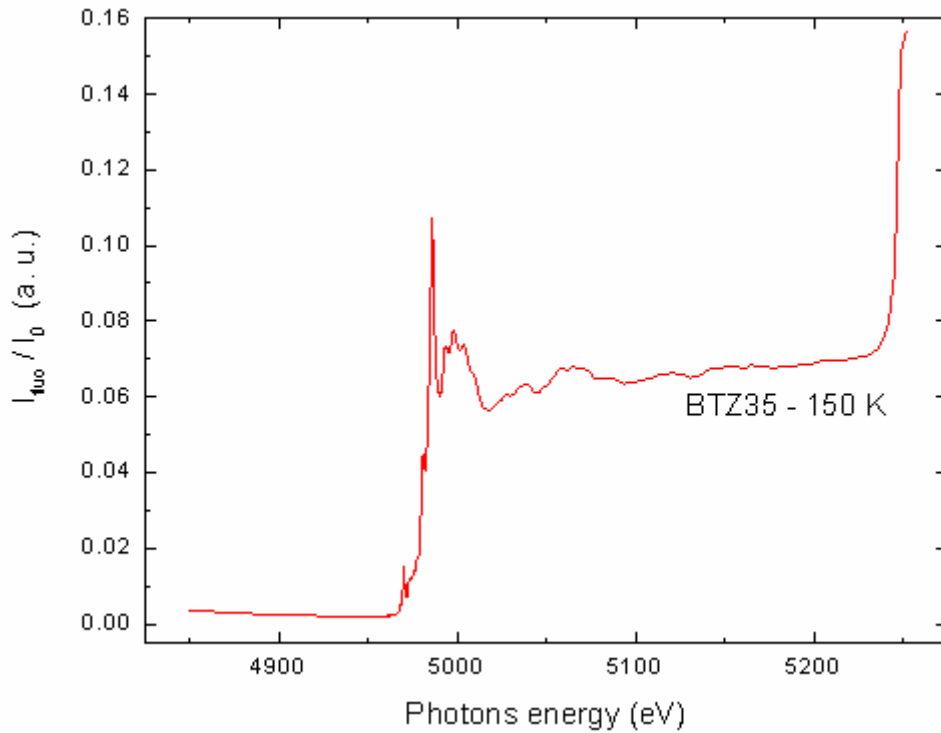


Fig.1: Fluorescence X-ray absorption spectrum of BTZ ($x = 0.35$) at 150K, at the Ti K-edge.

As previously reported by the authors of ref [3], the BaTiO_3 Ti XANES spectra present several peaks. The peak centred at 4969 eV (shown by an arrow on figure 2) is due to the Ti displacement from the centre of its oxygen octahedron. The area of this peak is proportional to the mean-square of the latter displacement [3, 4]. Ravel's EXAFS study of BaTiO_3 [3] gives a Ti off-centring equal to 0.19 Å at low temperatures.

We observed the peak at 4969 eV in all BTZ samples and at all studied temperatures. Qualitatively, its area is independent of x (see figure 2) and temperature. This striking result shows that the local displacement of Ti atoms is the same in the well-known ferroelectric BaTiO_3 and in all BTZ samples, whether ferroelectrics ($x = 0.05$ and 0.20) or relaxor ($x = 0.35$).

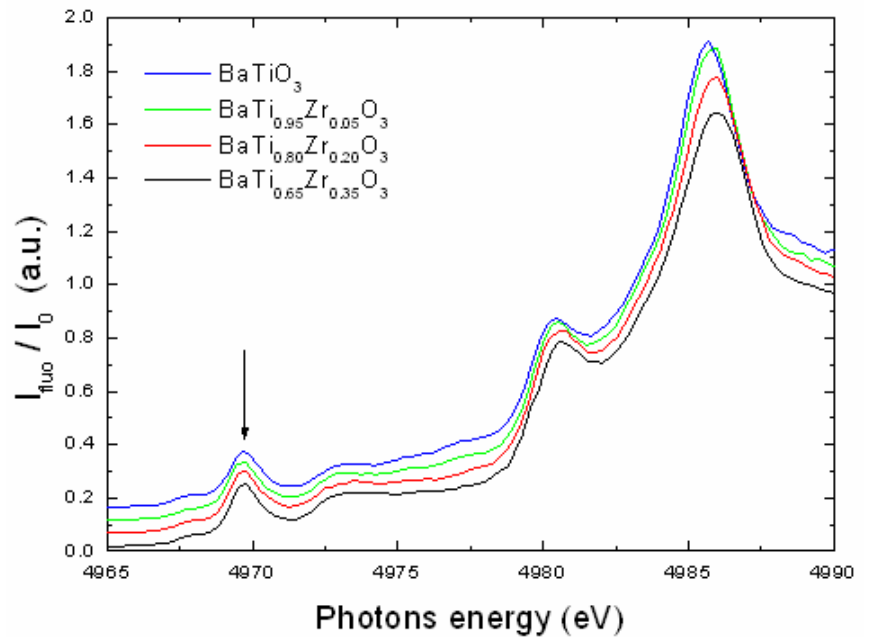


Fig. 2 : Comparison between the normalized XANES spectra of BaTiO_3 and BTZ with $x = 0.05, 0.20,$ and 0.35 at 150K. The spectra were vertically shifted for sake of clarity. The measurement step is 0.25 eV.

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