	Experiment title: Study of the temperature dependence of the local structure of the relaxor ferroelectric PLZT	**Experiment number**: HS-2727
Beamline:	**Date of experiment**: from: 11/05/2005 to: 17/05/2005	**Date of report**: 23/02/2006
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Report: the aim of the experiment is twofold:

1) studying the local structure of the relaxor ferroelectric $(Pb/La)(Zr/Ti)O_3$ (PLZT) near the Burns temperature T_B, at which the formation of polar clusters of nanometric size starts [1];

2) searching for a possible evidence of rotations of the O octahedra in the Ti-rich region of the PLZT phase diagram, where diffraction experiments indicate pure tetragonal distortion from the cubic perovskite structure [2], but dielectric, anelastic and NMR spectroscopies suggest the existence of an additional rotational instability of the octahedra [3].

PLZT is made relaxor by partially (up to 25%) substituting Pb^{2+} with La^{3+} in ferroelectric $PbZr_yTi_{1-y}O_3$ (PZT); this creates cation vacancies for charge compensation and therefore strong chemical, steric and charge disorder. We will refer to PLZT-V x/y/1-y, where x is the molar fraction of La in percent, y/1-y is the Zr/Ti ratio and V = A,B indicates whether the vacancies are in the A (Pb/La) or B (Zr/Ti) sublattice. The resulting state is a sort of polar glass called relaxor, where the ferroelectric transition at T_C transforms into a broad and frequency dispersive polar freezing at much lower temperature, and presents enhanced dielectric and electromechanical properties, attractive for applications [4]. Before freezing into the relaxor state at T_g, however, a condensation of fluctuating polar clusters of the size of tens of nanometers occurs at the Burns temperature $T_B >> T_f$, and in PLZT it is found that T_B is very close to T_C of the parent La-free ferroelectric material [1]. The analysis of the data is still underway and here only some preliminary results are shown.

Samples

We chose two compositions from the rombohedral and the tetragonal regions of the phase diagram of the parent PZT: **PLZT-B 9/65/35** belonging to the rombohedral region where Zr is displaced along <111> and the octahedra rotated about the same direction below $T_C = 625$ K in PZT 65/35 and **PLZT-A 22/20/80** belonging to the tetragonal region with atomic displacements along <100> below $T_C = 737$ K in PZT 20/80.

In view of the strong structural disorder, we also prepared samples of the corresponding La-free materials, **PZT 65/35** and **PZT 20/80**, whose structure is simpler and rather well characterized by diffraction experiments. These compositions serve as reference against which to compare the effect of the La susbtitution

and also as a more tractable starting point for the EXAFS analysis. Finally, samples have been prepared with the same nominal La substitution and Zr/Ti ratios but with exchanged sublattices for the cation vacancies: **PLZT-A 9/65/35** and **PLZT-B 22/20/80**.

PLZT was prepared and sintered exactly as for other samples we studied by dielectric, anelastic and NMR spectropies in previous works [3,5], the materials were then milled into powder down to the size of single grains, few μm, and heated in air at ~1000 K for reducing possible surface defects from milling. The powders were found single-phase within experimental error by X-ray diffraction. These powders were dispersed into boron nitride and pressed into circular pellets with appropriate densities and thicknesses (from 15 to 45 mg PLZT in 150 mg BN), in order to obtain $\Delta\mu = 1$ at the Pb L_{III} edge and ~0.19 at the Zr K edge; in this way it was possible to measure both edges during the same temperature run, still obtaining a good signal.

Experiment

Heating up to 800 K was accomplished by inserting the samples in a bag of graphite sheet in air through which electric current was driven. This method was very practical and preferred over the use of a furnace in vacuum, in order to avoid the possible risk of oxygen or lead oxide loss at high temperature.

The examined edges are: Zr K, Pb L_{III} in transmission and Ti K in fluorescence. The latter method was chosen in order to avoid the contribution from the La L edges, which unfortunately remained very intense; therefore, the Ti K acquisition was limited to the edge region, where symmetry-forbidden peaks allow the off-centre displacement of Ti to be estimated.

Ti-K XANES

The Ti-K spectra present peaks in the pre-edge region, which would be forbidden in a symmetric octahedral TiO_6 arrangement [6,7]. The area of the peak at 4967 eV, which we label B after [7], is proportional to the mean square displacement of the Ti ion with respect to the centre of the O octahedron, while peak C at 4970 eV is proportional to the average number of Ti atoms in the third coordination sphere around the absorbing Ti, and it is shifted to position C' at 4974 eV in case these positions are occupied by Zr ions [7].

We performed temperature scans of the pre-edge Ti-K region at compositions PZT 20/80, PLZT A 22/20/80, PZT 65/35 and PLZT B 9/65/35 from room temperature up to 70-100 K above T_B.
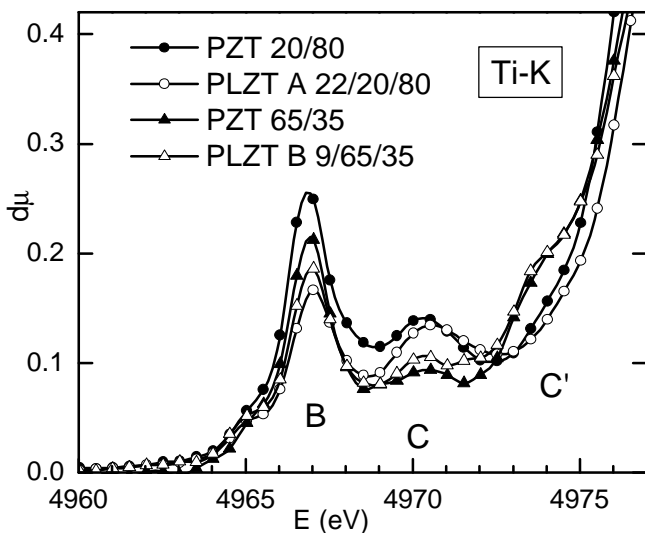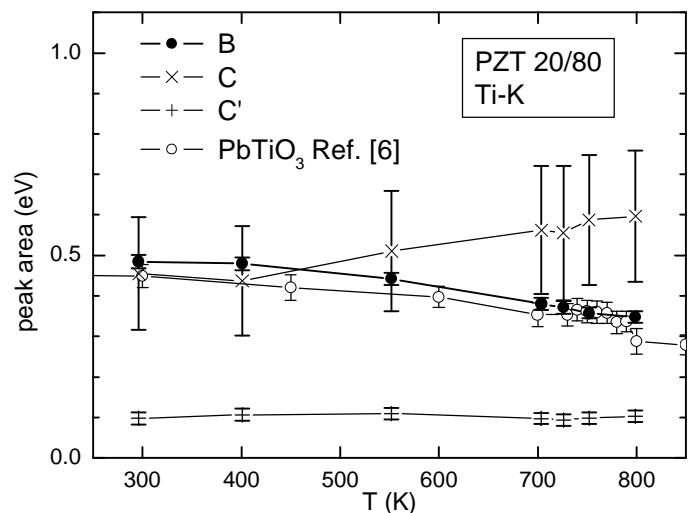

Fig. 1

Fig. 2

Figure 1 compares the spectra of the four samples at 295 K. The height of peak B is maximum for the strongly tetragonal PZT 20/80 and smaller for PZT 65/35, as expected from diffraction experiments. The addition of La clearly reduces the mean Ti off-centre displacement; in fact, although both PLZT samples are cubic from XRD, the reduction of peak B is much stronger in the sample with higher La substitution. Figure 2 presents the areas of the three peaks in PZT 20/80 as a function of temperature, compared with that of peak B in $PbTiO_3$ (=PZT 0/100) from [6]. In agreement with the theoretical analysis [7], the areas of peaks C and C' are constant within experimental error, while the off-center displacement of Ti increases on cooling well outside experimental error, with a steeper slope around $T_C \sim 740$ K.

Zr-K and Pb-L$_{III}$ EXAFS

Up to now preliminary first-shell analysis has been carrier out on the Zr-K spectra, but we are starting an analysis including larger atomic clusters and multiple scattering contributions based on FEFF for the paths calculation.
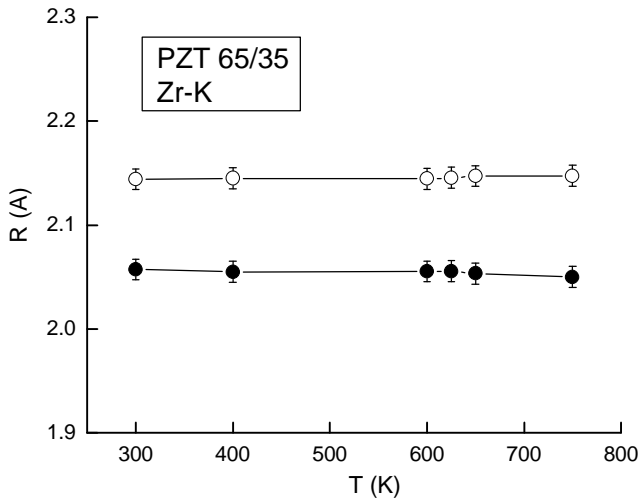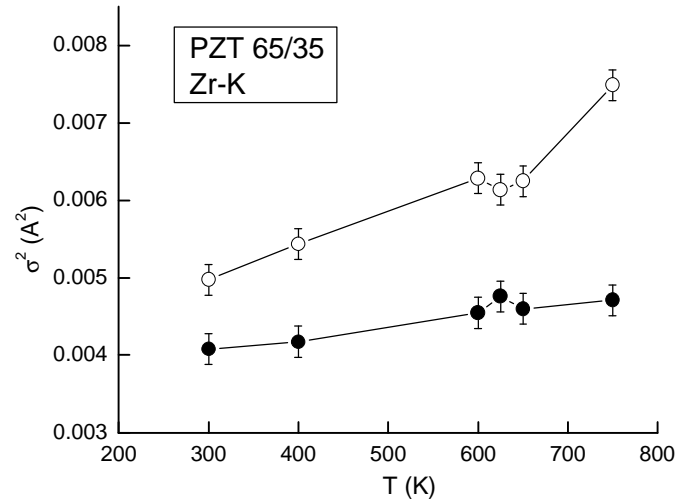

Fig. 3

Fig. 4

Figures 3 and 4 present the two Zr-O distances and respective σ^2 from first-shell analysis of PZT 65/35, arising from the shift of Zr along <111> with respect to the octahedron center. As already noted for PbTiO$_3$ [8], the Zr-O distances are already splitted above the Curie temperature, $T_C = 625$ K in this case, indicating a transition with strong order/disorder nature. On the other hand, σ^2 presents a sharp maximum exactly at T_C, likely due to the displacive component of the transition.

The analysis of the La-substituted samples on the Zr-K edges is underway and we hope that the Pb-L$_{III}$ spectra will provide clues not only on the temperature dependence of the atomic displacements but also on the possible existence of rotations of the octahedra induced by La.

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