

Report for the proposal "HD-215" entitled "P-T local structure study of the off-center displacements of Zr in PbZr_{0.52}Ti_{0.48}O₃(PZT)"

J. Rouquette¹, A. Al-Zein^{1,2}, G. Fraysse¹, C. Levelut², G. Aquilanti³, M. Vaccari³, J. Haines¹

¹*Institut Charles Gerhardt Montpellier, UMR CNRS 5253, équipe C2M,
Université Montpellier II, 34095 Montpellier cedex 5, France.*

²*Laboratoire des Colloïdes, Verres et Nanomatériaux (LCVN), UMR CNRS 5587,
Université Montpellier II, 34095 Montpellier cedex 5, France. and*

³*European Synchrotron Radiation Facility, 6 rue Jules Horowitz, 38043 Grenoble cedex 09, France.*

Abstract: X-ray Absorption Spectroscopy appears as the technique of choice to probe the element selective Zr-shifts in the ferroelectric PbZr_{0.52}Ti_{0.48}O₃ (PZT) ceramics through the Ferroelectric-Paraelectric (*F-P*) transition. Contrary to what was reported in the literature, it has been possible to observe a very small polar displacement of the Zr-atom off-center (~ 0.06 Å) from centrosymmetric position based on the Extended X-ray Absorption Fine Structure (EXAFS) data and the Pre-edge Fine Structure (PEFS) analysis. It shows for the first time the implication of the Zr-atoms in the *F-P* phase transition and suggests that the cooperative small Zr-shifts (easily poled) under an applied electric field could be one of the keys for understanding the high electromechanical response, i.e. the piezoelectric effect, in this technologically important material.

PZT ceramics [1] are intensively used in technological applications (sensors and actuators, MEMS systems and high frequency devices) for more than fifty years due to their great electromechanical response. Although the Zr/Ti polar displacements macroscopically are suddenly

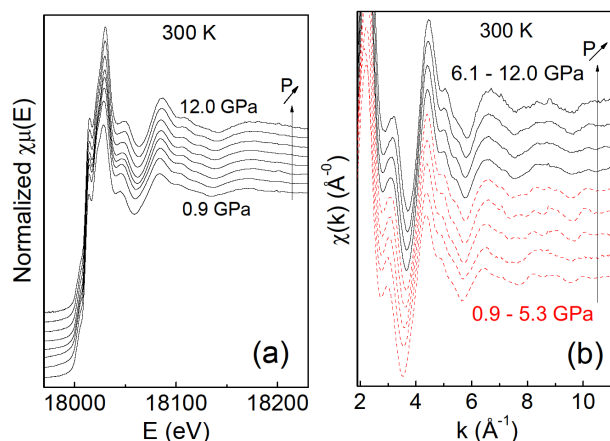


FIG. 1. a) Normalized XAS spectra obtained at 300 K between 0.9 GPa and 12 GPa, b) Extracted $\chi(k)$. Both signals are vertically shifted for clarity.

lost at the *F-P* phase transition above a critical pressure P_C and/or a critical temperature T_C , their individual atomic behavior is still unclear. The role of the Zr-shifts in PZT is of particular interest since it is known that the simple perovskite end-member lead titanate PbTiO₃ has relatively low piezoelectric properties.

High quality, high-pressure XAS data of PZT [2] were normalized to the jump at the absorption edge and the apparent small effect of pressure on the Zr *K* edge spectra can be seen, Figure 1a. Namely, the extracted $\chi(k)$ spectra, Figure 1b, evidence above 6.1 GPa a disappearance

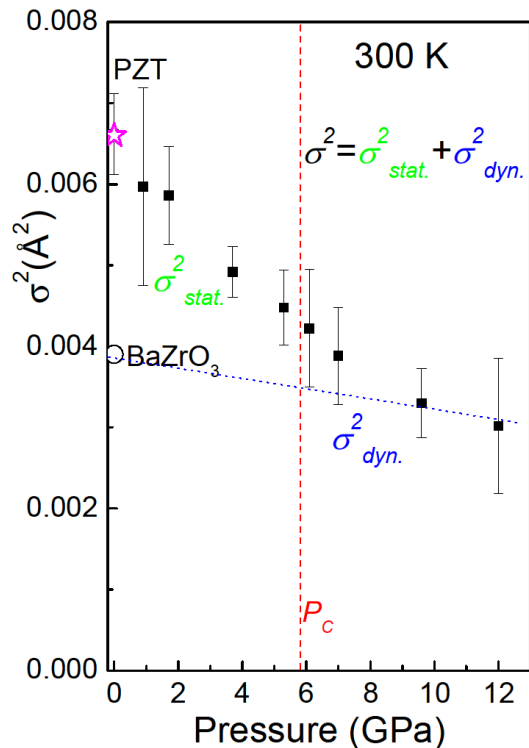


FIG. 2. Pressure behavior of the DWF for the Zr-O atom pairs at 300 K. Values reported in the literature for PZT [3] (*) and BaZrO₃ [4] (o) are also included. P_c (the dashed line) corresponds to the paraelectric transition [1]. The dotted line represents the decrease of $\sigma_{dyn.}^2$ with pressure.

of some high frequency contributions: in particular the split doubled features between $k = 6 \text{ \AA}^{-1}$ and $k = 7.5 \text{ \AA}^{-1}$ and between $k = 8 \text{ \AA}^{-1}$ and $k = 10 \text{ \AA}^{-1}$ merge into two single oscillations respectively. Based on these data, there might be a low pressure behavior below ~ 6.1 GPa, and a high pressure behavior above.

Figure 2 shows the pressure behavior of the experimental σ^2 for the Zr-O atom pairs at 300 K [2]; σ^2 accounts for the mean square displacement of the Zr-O distance. One can first note that the fitted ambient value is perfectly consistent with that reported in the literature [3] (the open star). Additionally, a noticeable decrease of σ^2 can be observed with increasing pressure with a change in the trend at ~ 7 GPa. At ambient

conditions, we can observe that the σ^2 of PZT is higher than that of BaZrO₃ (BZ) [4] where the Zr-atoms are known to be perfectly centrosymmetric. This can be attributed to the presence of static disorder in PZT, which is absent in BZ. At high pressure, the $\sigma_{dyn.}^2$ estimation of BZ perfectly fits the high pressure values of σ^2 for PZT indicating that pressure eliminates the static disorder for the Zr-atoms of PZT above 7 GPa and that the only contribution to the EXAFS DWF is dynamic above this pressure.

Figure 3a shows a smooth but observable decrease in the PEFS intensity [2] in the 0.9 GPa - 6.1 GPa pressure range. Above 6.1 GPa, the PEFS spectra overlap almost perfectly. Figure 3b shows the experimental and simulated XANES spectra obtained at 1.7 GPa and 7 GPa, which are consistent with a long range polar and non-polar state. All the features are correctly reproduced confirming that even a small Zr-shift can be observed in the PEFS signal.

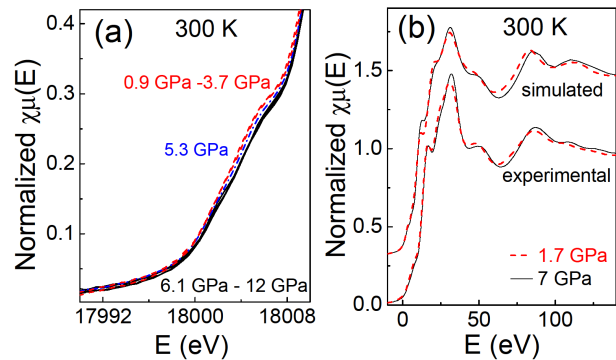


FIG. 3. a) High-pressure Zr K edge XANES spectra obtained at 300 K. Note the pressure evolution of the PEFS. b) Experimental and simulated XANES spectra at 1.7 GPa and 7 GPa. In b), the origin (0) corresponds to the Zr K edge.

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