



	Experiment title: Extension of X-ray spectroscopy under high pressure to low Z elements	Experiment number: MI - 757
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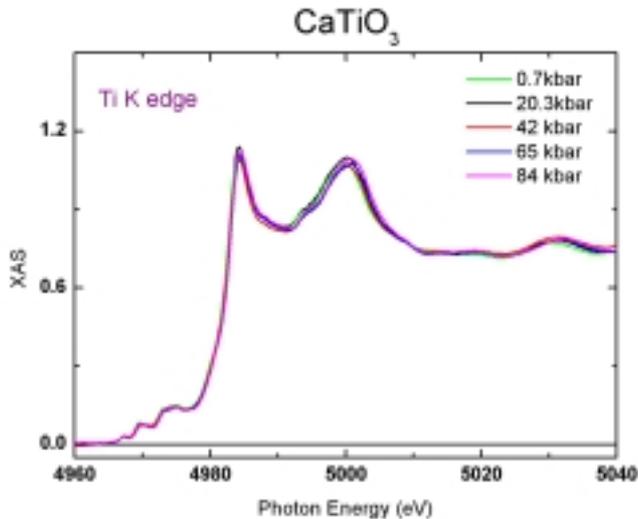
Report: XANES and EXAFS spectroscopies are now a powerful technique routinely employed to probe the local structure of the absorbing atom under very high pressure but mainly for elements with rather high atomic number ($Z > 26$) at incident X-ray energies ≥ 7 keV. Taking into account of the wide 2 – 16 keV energy range provided by the ID12 beamline, we have investigated the effect of pressure on the local structure at the Ti – K edge (4.9 keV) in titanium oxides. In the initial project we planned to collect XANES and EXAFS data on two samples BaTiO₃ and CaTiO₃ but we finally skipped the former to replace it by a more interesting one and even more challenging regarding the strong absorption of X-rays by Pb: PbTiO₃ and its Zr-substituted PbZr_{0.3}Ti_{0.7}O₃ phase. That decision was fixed considering the great interest of such samples belonging to the relaxor ferroelectrics family widely investigated because of their outstanding electromechanical properties of which the understanding remains a challenging problem.

Pure powder samples have been previously synthesized and fully characterized in term of purity and structure by XRD experiments. In order to reduce the absorption of the diamonds, specific diamond anvil cells with perforated diamonds have been used. Such specificity developed at PMC Paris leads to reduce the total thickness of the diamond anvils to 1 mm. Silicon oil was used as pressure transmitting medium for all the experiments.

High quality XANES spectra were recorded in transmission geometry by using an unique photodiode. The incoming X-rays delivered by the HU38 undulator (in linear mode) have been focused vertically using the V2FM down to 20 μm FWHM and collimated to ~ 100 μm horizontally using the beamline slits.

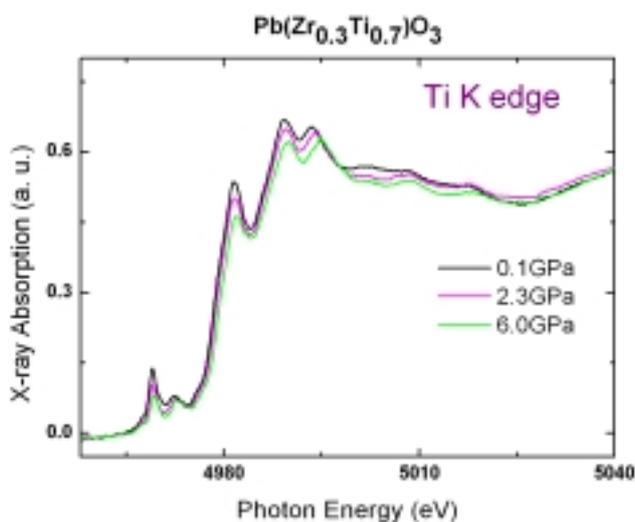
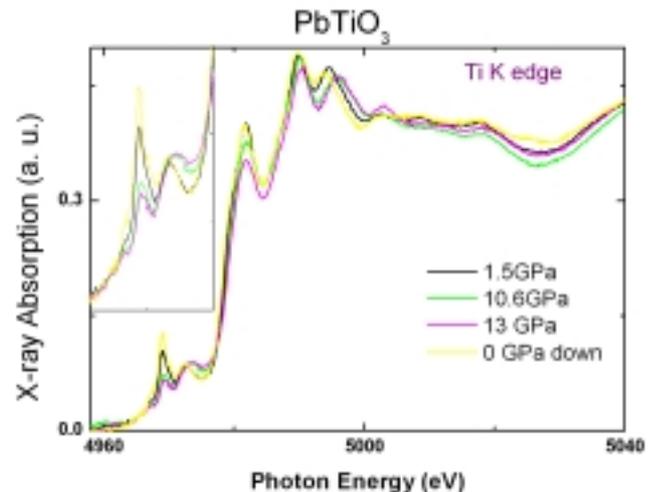
Considering the air absorption as negligible at the Ti–K edge in our setup configuration (~ 2 cm air thickness before and after the cell, perforated diamond and adjusted sample thickness), all the experiments have been performed in air. All contributions of diffraction peaks from the diamonds have been simply avoided by slightly rotating the cell preliminarily mounted on a motorized rotation circle around z axis. Moreover, due to the strong absorption by Pb atoms in the sample (transmission of 10^{-14} through 50 μm of PbTiO₃), the powdered samples have been diluted in BN powder. The relative concentration of sample and BN has been optimized during the allocated beamtime. Nevertheless, despite the low transmission through the setup (diamonds + sample), high quality XANES spectra (see Fig1-2-3) have been successfully recorded at several pressure for all samples thanks both to the high stability and the high quality detection scheme available at the ID12 beamline.

In a first step, the goal of this project was to study the evolution of the pre-edge part of the absorption spectra in order to evidence phase transformations through the local order examination and observation of the Ti-Ti and Ti-O bonds distortion previously described¹.



In PbTiO₃, absorption spectra measured from 1.5 to 15 GPa clearly evidence a phase transition towards a local lower symmetry which seems to occur between 10.6 and 13 GPa with gradual change in the shape of the two pre-edges with applied pressure. In order to precisely describe the phase transition, several pressure points have been recorded (1.5 – 5 – 8 – 10.6 – 13 – 15 GPa) and only four characteristic experimental spectra are shown in figure 2 for clarity. The pre-edges considerations are associated with a shift to higher energy in the XANES region and confirm the pressure induced phase transition which can be correlated with the X-ray diffraction measurements evidencing the tetragonal to cubic phase transition around 12 GPa³.

In the case of CaTiO₃, spectra were recorded in the pressure range 0-8.5 GPa and revealed no change in the local order symmetry when increasing the pressure. XANES were recorded at 0.07 – 2 – 4.2 – 6.5 and 8.4 GPa and typical curves are displayed in figure 1. This first result is directly in relation with the absence of phase transition under pressure detected by X-ray diffraction measurement that have been carried out to 9.7 GPa².



The XANES spectra of the substituted PbZr_{0.3}Ti_{0.7}O₃ phase (Fig.3) performed at 0.1 – 1.5 – 2.3 – 3.9 and 6 GPa indicate that its behaviour is similar to that of PbTiO₃ in that they show gradual decreasing of the pre-edges with a shift to higher energy, a shift that is associated with the phase transition which seems to occur at lower applied pressure (approximately between 4 and 6 GPa).

The absence of any detectable change in the Ti –K XANES of CaTiO₃ when increasing pressure is a strong confirmation that no phase transition occurs in this compound (even at the local level). These results will serve as reference (for both experiments and simulations) for the interpretation of the change observed in the other studied compounds.

For the two other systems, extremely clear variations have been observed in the XANES spectra at the Ti K edge when pressure is applied. Quantitative interpretation of the experimental results is underway using modern simulation.

But an important conclusion can already be drawn is that XANES spectra indicate that local distortion occurs well below the pressure transition evidenced by X-ray diffraction (characteristic of global change of symmetry). This result will certainly shed new light of the type of phase transition occurring under high pressure in these materials.

[1] Ravel et al, Physica B 208-209 (1995)

[2] Ross et al., American Mineralogist, vol 84 (1999).

[3] Sani et al, J. Phys., Condens. Matter 14, 10601 (2002)