

High Pressure XAS at the Ti K Edge on Titanate Perovskites

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Abstract. X-ray absorption measurements have been performed on BaTiO₃ and SrTiO₃ at the Ti K edge under pressure. For BaTiO₃, the phase transformation to the cubic phase is observed at 2 GPa. In this structure the Ti atoms remain off centre with respect to the oxygen octahedron up to 10 GPa. Above this pressure the Ti atoms are at the centre of the octahedron. For SrTiO₃, a first transformation is observed above 5 GPa with a modification of the pre-edge features. A second one is observed close to 14 GPa with a complete change of the absorption spectrum.

Keywords: High pressure, titanate perovskites

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INTRODUCTION

ATiO₃ perovskites often exhibit distortions from the ideal cubic structure due to instabilities related to the off centre position of the Ti atom with respect to the oxygen octahedron (BaTiO₃, PbTiO₃) or the tilt of the octahedra (CaTiO₃). SrTiO₃, which is cubic at ambient conditions, is supposed to be undistorted.

Under pressure, phase transformations occur corresponding to the vanishing of the ferroelectricity (BaTiO₃: tetragonal $\Rightarrow$ cubic) or to the onset of the antiferrodistorsive (AFD) distortion (SrTiO₃: cubic $\Rightarrow$ tetragonal). These transitions have been determined by x-ray [1] or neutron diffraction [2], by Raman [3,4] and Brillouin [5] spectroscopies. Some questions about the local order around the Ti atom (local ferroelectric distortion) and the existence of broad Raman modes in the cubic structure (not allowed by the selection rules) remain open.

X-ray absorption spectroscopy at the Ti K edge is well adapted to answer these questions. In particular the pre-edge part of the spectrum has been shown to be very sensitive to the off centre position of the Ti atom in the surrounding oxygen octahedron [6]. Due to the combination of third generation synchrotron light sources and of a specific design of the diamond anvils of the high pressure cell, high pressure XAFS experiments at the Ti K edge (4966 eV) are now possible.

In this paper we present results obtained under pressure on SrTiO₃ up to 23 GPa and BaTiO₃ up to 20 GPa.

EXPERIMENTAL

Experiments have been performed at the LUCIA beamline [7] of the SLS (Swiss Light Source) synchrotron facility (PSI, Villigen, Switzerland) at the Ti K edge (4.966 keV) in a membrane diamond anvil cell [8]. The sample was loaded in the 100 μ m diameter hole of a pre-indented inconel gasket with methanol-ethanol-water (16:3:1) mixture as pressure transmitting medium and a ruby sphere [9] to measure the pressure. The diameter of the diamond culets was 200 μ m. Different experiments performed on single crystals or powdered sample have given the same results. Thanks to the focusing optic of the beamline (two mirrors in the Kirkpatrick-Baez geometry), the x-ray beam spot was smaller than $5 \times 10 \mu\text{m}^2$ (FWHM). The spectra were recorded in the transmission geometry. The main difficulty in performing such an experiment is that the absorption of the x-rays by the diamond anvils may be too high to enable transmission measurements. In order to reduce this absorption we have used thin diamonds (500 μ m thick) mounted on fully perforated diamond anvils [10,11]. Using this geometry, the total transmission of the two anvils is 2×10^{-3} at 5 keV, which is not too low considering the high incident flux (2×10^{11} ph/s/0.1%bw in the x-ray spot). The entire experiments, including pressure steps and pressure measurements, have been performed under vacuum in order to reduce absorption by air.

RESULTS

One of the main characteristic features observed in the absorption spectra of the titanate perovskites is the existence of peaks observed below the Ti K absorption edge. There are four such features, labeled A, B, C₁ and C₂.

SrTiO₃

Figure 1 shows the pre-edge part of the X-ray absorption spectra of SrTiO₃ at the Ti K edge for different pressures. At the transition the peak labeled A remains unchanged while the other features are slightly modified. In particular the intensity of the peak B decreases which means that the Ti atom was not exactly at the centre of the oxygen octahedron in the low pressure phase (cubic). Because SrTiO₃ is not ferroelectric at ambient conditions, the displacement of the Ti atom has to be disordered. The spectrum recovers its initial shape when pressure is released.

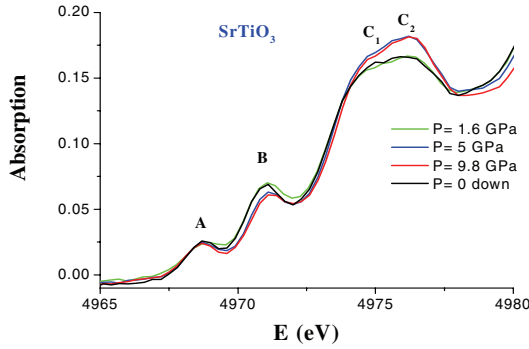


FIGURE 1. Pre-edge part of the absorption spectrum of SrTiO₃ at the Ti K edge for various pressures.

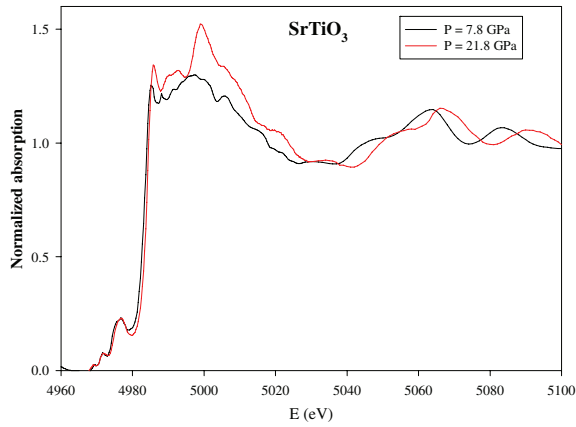


FIGURE 2. XANES of SrTiO₃ at the Ti K edge at 7.8 GPa (tetragonal phase) and 21.8 GPa (new high pressure phase)

When pressure is increased above 14 GPa a complete change of the spectrum is observed. The modification of the XANES is shown in Figure 2.

In the new phase, the pre-edge feature A is shifted to low energy while the feature C₁ is shifted to higher energy. Such variation can be reproduced by calculations when a strong distortion of the oxygen octahedron is included⁶. This transition is also reversible when pressure is released.

BaTiO₃

Figure 3 shows the evolution with pressure of the pre-edge of BaTiO₃. At room pressure the feature B is more intense than in the case of SrTiO₃. This enhancement of this peak is due to the off-centre position of the Ti atom with respect to the oxygen octahedron (BaTiO₃ is ferroelectric at ambient conditions).

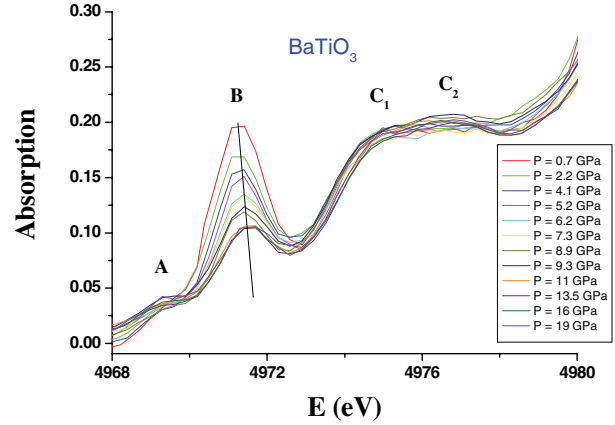


FIGURE 3. Pre-edge part of the absorption spectrum of BaTiO₃ at the Ti K edge as a function of pressure.

When pressure increases, the intensity of the pre-edge feature B decreases up to 10 GPa and remains constant above this pressure (Figure 4).

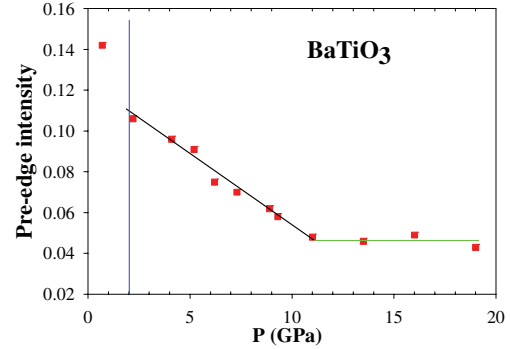


FIGURE 4. Variation of the feature B intensity with pressure. The vertical line indicates the tetragonal to cubic phase transition. The other lines are only guide for the eyes.

At the transition, a clear discontinuity in the intensity of the feature B occurs, but the peak remains intense which indicates that the Ti atom is still out of centre with respect to the oxygen octahedron. In the high pressure cubic phase, local rhombohedral distortion remains, as it is the case for the high temperature cubic phase [12,13]. This distortion decreases when pressure is increased up to 10 GPa and disappears above this pressure, where the intensity of the feature B does not change anymore. As in the case for SrTiO_3 , a small shift to higher energy of feature B is observed.

DISCUSSION

One of the remaining questions about titanate perovskites was the origin of broad Raman peaks in the cubic phase, where they are not allowed by the selection rules. A possible explanation for the existence of a Raman activity is an off-centre position of the Ti atom in the structure which would modify the selection rules. Another possible explanation is a strong anharmonicity of the vibrations which could induce second order Raman activity. This would also explain why the Raman bands are so broad.

The Raman activity is observed for BaTiO_3 up to 30 GPa (at least) and for SrTiO_3 up to 14 GPa, whatever the structure, cubic or tetragonal. We have shown in the preceding section that the Ti atom was off-centre in the cubic phase of SrTiO_3 but not in the tetragonal one and that for BaTiO_3 the Ti atom was at the centre of the oxygen octahedron above 10 GPa, where Raman activity is still observed. Therefore there is no correlation between the position of the Ti atom and the Raman activity. Therefore the first explanation for the Raman activity can be rejected. On the other hand our results are not in contradiction with the second hypothesis.

CONCLUSION

We have shown that SrTiO_3 at ambient conditions was locally slightly distorted with the Ti atoms displaced from the centre of the oxygen octahedron. This displacement vanishes above 5 GPa when SrTiO_3 undergoes a phase transition to the tetragonal phase.

BaTiO_3 , ferroelectric at ambient conditions, keeps its local distortion in the cubic high pressure phase. The local displacement of the Ti atom is reduced at the transition and vanishes at 10 GPa. Above this pressure, the Ti atom is the centre of the oxygen octahedron.

Finally we have demonstrated that the origin of the Raman activity for both titanate perovskites was not related to the off-centre position of the Ti atom.

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