# Experimental report

16/10/2022

**Proposal:** CRG-2934

**Council:** 4/2021

**Title:** In situ structural study of the reduction/oxidation of La2CoO4+d

**Research area:** Physics

**This proposal is a new proposal**


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**Samples:** Pr2NiO4
LCO

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D1B | 2 | 2 | 29/09/2021 | 01/10/2021 |


**Abstract:**

The abstract is in the scientific case pdf file.

# In situ structural study of the reduction/oxidation of $La_2CoO_{4+d}$

## Introduction

$La_2CoO_{4+\delta}$ compound shows a quite complex phase diagram as a function of the oxygen content $\delta$ and temperature. Early works on this system have shown several structural phase transitions between orthorhombic and tetragonal states as a function of $\delta$ and T.

However, a detailed structural study is not so far reported and, there is no evidence of any study of the thermal evolution of $La_2CoO_{4+\delta}$ performed *in situ* by neutron diffraction in reducing/oxidizing atmosphere. This is fundamental interest when tuning mechanical stability, chemical reactivity and catalytic solid/gas reactions, particularly with regard to oxygen diffusion and transport properties, but above all when it comes to identifying a possible oxygen ordering. Thus, one of the aims of our work is a detailed exploration of the structural phase diagram of $La_2CoO_{4+\delta}$ as a function of T and $\delta$. To this end starting from the stoichiometric compound $La_2CoO_{4.00}$, we investigated the phase diagram during the oxygen uptake reaction in air heating up to 763K by *in situ* neutron powder diffraction, which is more sensitive than X-rays to low-Z elements such a oxygen. In addition, neutron diffraction provides bulk information, while the penetration depth is limited to several micrometres. We were also especially interested in exploring possible oxygen ordering during oxygen intercalation. This would obviously enhance the comprehension of the oxygen diffusion mechanism by providing the knowledge of the precise oxygen positions and displacements.

## Experimental

*In situ* neutron powder diffraction (NPD) studies were performed on the D1B. In order to access diffraction data up to high momentum transfers allowing to refine precisely the O occupations, i.e. scattering density of the O-site, a wavelength of 1.287 Å was used. Due to the impossibility to use N2/H2 (95% - 5%) gas, we decides to follow the oxidation reaction and not the reduction. Thus, NPD experiments were carried during the oxidation reaction of the starting stoichiometric $La_2CoO_{4.00}$ compound in air to reach the oxygen rich phase $La_2CoO_{4.25}$. Approximately 2 grams of powder have been placed inside an open quartz tube, corresponding to a pressure of oxygen $P(O_2) \approx 0.21$ bar. The tube was installed n the furnace inside a vacuum chamber. Each diffractogram was acquired in 5 minutes, while the temperature went up from room temperature to 763K with a rate ok 0.2 K/min. To have a better statistic and to refine the data with good accuracy, the diffractograms were then added in a small temperature interval, where they were almost identical. A good compromise has been found by adding 13 diffraction patterns, corresponding to approximately 12K. All the diffractograms were analysed by Rietveld refinements using the Fullprof suite.

NPD patterns of $La_2CoO_{4+d}$ measured *in situ* during its complete oxidation are shown in figure 1, as a function of the temperature. We can clearly distinguish four distinct phases as indicated in the figure:

1) The orthorhombic starting phase (LTO) with *Bmab* symmetry (up to 420K);
2) A tetragonal intermediate phase (LTT) with *F4/mmm* symmetry (from 320K to 490K);
3) An orthorhombic phase ($LTO_1$) with *Fmmm* symmetry (from 490K to 632K);
4) And finally, the $LTO_2$ phase with *Fmmm* symmetry.

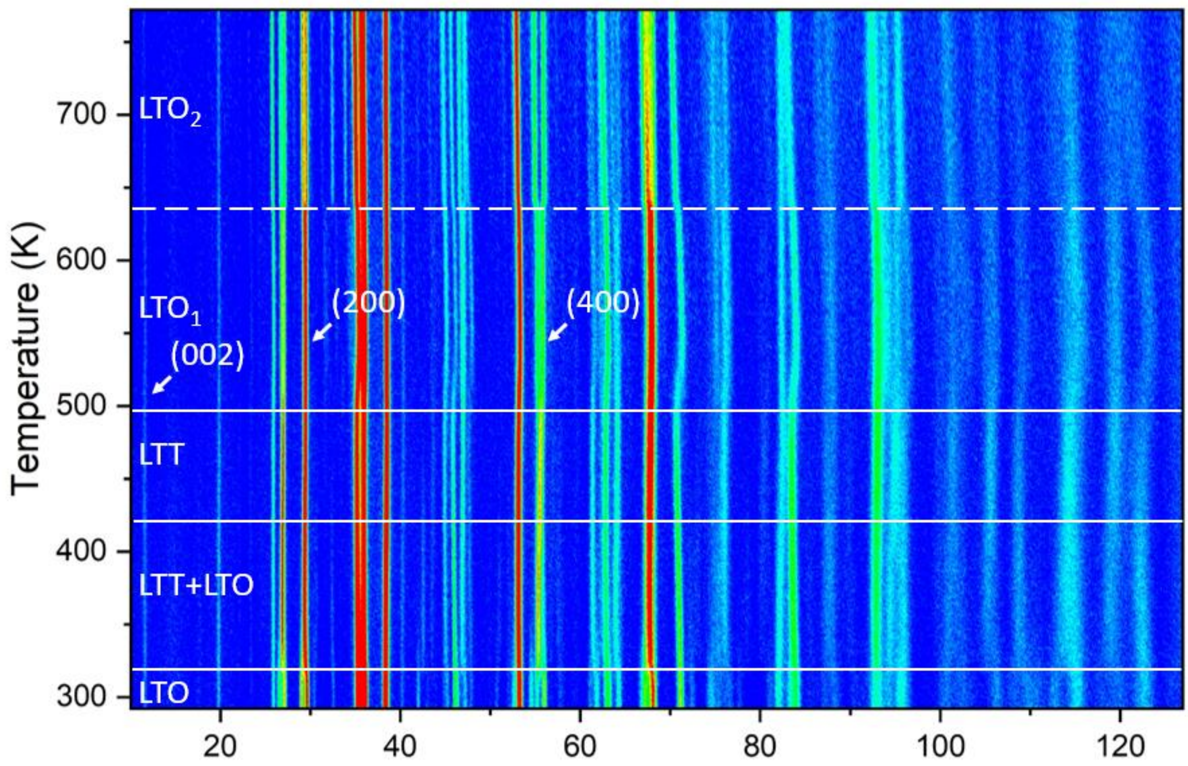


***Figure 1:*** *In situ NPD patterns of $La_2CoO_{4.00}$ as a function, as obtained on D1B (λ = 1.287 Å). Experiments have been performed in air.*

It is worth to underlying that after 420K and up to 490 K, there is  only the LTT phase. This is the first time that a pure tetragonal phase is observed and reported. The structure has beee solved with the space group *F4/mmm*.