



	Experiment title: High pressure, doping and temperature dependence of the structure of crystal of Nd_{1-x}Sr_xNiO₂	Experiment number: HC-4652
Beamline: ID15B	Date of experiment: from: 12/02/2022 to: 14/02/2022	Date of report: 23/09/2022
Shifts: 12	Local contact(s): Gaston Garbarino (email:gaston.garbarino@esrf.fr)	<i>Received at ESRF:</i>
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The existence of a superconducting phase in infinite-layer Nickelates has been predicted twenty years ago in LaNiO₂ [1] but has remained elusive until the discovery in 2019 of a superconducting state in thin films of Sr-doped NdNiO₂ (Nd_{0.8}Sr_{0.2}NiO₂)[2] deposited on a STO substrate. The crystal structure of these infinite-layer nickelates (SG:P4/mmm, tetragonal cell) consists in a stacking of NiO₂ layers separated by rare-earth spacer layer, stabilizing the unusual Ni¹⁺ oxidation state, corresponding to 3d⁹ electronic configuration, similarly to the cuprates. Many open questions remain regarding the origin of the superconducting state in infinite layer Nickelates and their similarities with the cuprates: What is the role played by the STO substrate (STO phonon contribution, extra-oxygen located at the interface)?

Recently, resistivity measurements under pressure have demonstrated a strong increase of T_c, from 9-15K[3] at atmospheric pressure, to 31 K at 12 GPa [4]. Understanding the origin of this boost in T_c will shed light on the mechanism responsible for the occurrence of a superconducting state. Measuring the evolution of the crystal structure of *thin films* of Nd_{0.8}Sr_{0.2}NiO₂ deposited on a STO substrate as a function of applied pressure is very challenging and has not been reported yet. This renders the understanding of the origin of the boost in T_c as pressure is applied very difficult, first of all because no experimentally determined evolution of the lattice parameters and crystal structure under pressure are available as an input for band structure calculation. The aim of proposal HC-4652 whose results are reported herein was to overcome the limitations due to the thin film configuration by performing powder X-ray diffraction on *high quality bulk (powder) samples* of infinite-layer Nickelate and to study the evolution of the crystal structure under applied pressure. We have measured different compositions where i) the rare earth (Nd vs La and Pr), ii) the doping level (x = 0.05, 0.07, 0.2) iii) the dopant

atoms (Sr vs Ca) were varied. As a bonus, and thanks to the high efficiency of the beamline ID15B, we have also been able to collect preliminary data on “super-oxygenated” $\text{LaNiO}_{2.5}$ during the last hours.

A total of 5 diamond anvil cells (DAC) were loaded with Helium acting as pressure transmitting medium, a membrane offering the opportunity to tune the pressure in-situ during the experiment. We managed to measure 5 diamond anvil cells (DAC) during the 12 shifts, with the following compositions: DAC1 – (LaNiO_2 & NdNiO_2); DAC2 – ($\text{Nd}_{0.93}\text{Sr}_{0.07}\text{NiO}_2$); DAC3 – (NdNiO_{2+x} & $\text{Nd}_{0.95}\text{Sr}_{0.05}\text{NiO}_{2+x}$); DAC4 – ($\text{Nd}_{0.8}\text{Ca}_{0.2}\text{NiO}_2$ & $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{NiO}_2$); DAC5 – ($\text{LaNiO}_{2.5}$). The pressure was measured before and after each pressure change. All cells were measured at room temperature and were loaded with powder samples of $\text{RE}_{1-x}\text{Sr}_x\text{NiO}_2$. The measurements were performed up to ~ 20 GPa for each cell, which was the targeted maximum pressure of the experiment.

A representative example of the preliminary analysis of the data (Rietveld refinement using Jana2006 and Fullprof) that we have obtained for LaNiO_2 and NdNiO_2 are summarized below (similar results have been obtained for the other compositions).

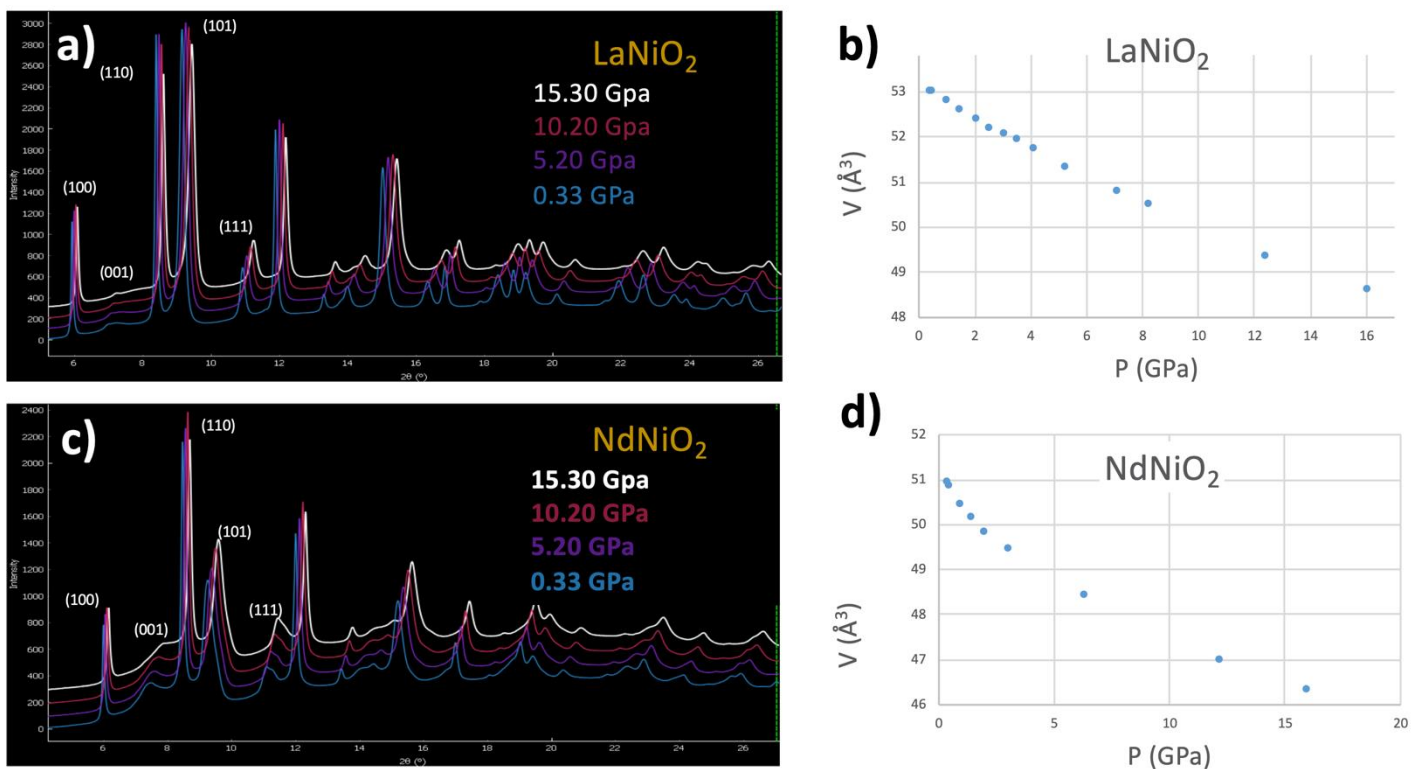


Figure 1: Evolution of the X-ray diffractograms of LaNiO_2 (a) and NdNiO_2 (c) as a function of applied pressure. Rietveld refinement of LaNiO_2 (b) and NdNiO_2 (d) allows the volume of the cell to be extracted.

Figure 1 displays the diffractograms of LaNiO_2 (a) and NdNiO_2 (c) as a function of applied pressure. The high quality of the data enables the detection of a peak broadening for reflection with integer l values (associated to a strong decrease of intensities) for NdNiO_2 . We interpret this peak broadening with additional shoulders (thanks to electronic microscopy and simulation by Faults program) as being due to stacking faults along the c -axis. This broadening tends to diminish as pressure is increased whereas related intensities slightly raises (shoulders are also attenuated). This result is quite original : the strong tendency of neodymium to generate stacking faults

in bulk infinite layers can be reduced by physical pressure and is probably due to steric effects. The continuous shift of the peaks towards larger angles indicates a contraction of the unit cell, with no noticeable phase transition. Rietveld refinements allow the lattice parameters to be extracted as exemplified by figure 1-c and 1-d which shows the evolution of the volume of the unit cell. These results will allow to establish the equation of states describing the compressibility of the system. In a first approximation, it's worth to note that the compressibility of the RNiO₂ is independent of the rare earth R, the nature of the dopant and of the level of doping. Our results will also be valuable as an input for DFT calculations, towards a better understanding of the enhancement of T_c under pressure. These results will also be used as a benchmark for the evolution of the lattice parameters predicted by DFT.

To close this report, let us briefly mention the preliminary data on “super-oxygenated” LaNiO_{2.5} that we were able to collect up to 20 GPa during the last hours of the beamtime. The crystal structure of LaNiO_{2.5} has been reported and consists in a succession of Ni in square planar and octahedral coordination, with a monoclinic space group (P2₁/n). The evolution of the X-ray diffractograms as pressure is increased is presented in the left panel of figure 2, while the evolution of the β angle is presented in the right panel. These measurements strongly suggest the nearness to a structural phase transition, from monoclinic to an as yet unreported orthorhombic phase. In order to firmly establish this phase transition, measurements up to higher pressure will be required, and measurements on single crystals are highly desirable, in order to establish the space group of this new phase. Extending these measurements to NdNiO_{2.5} will also be extremely valuable, to check for the ubiquity of this phase transition (the crystal structure of NdNiO_{2.5} has never been reported, even at ambient pressure). We will therefore submit a proposal for single crystal X-ray diffraction under pressure (on ID15B or ID27) to complete this study on LaNiO_{2.5} and NdNiO_{2.5}.

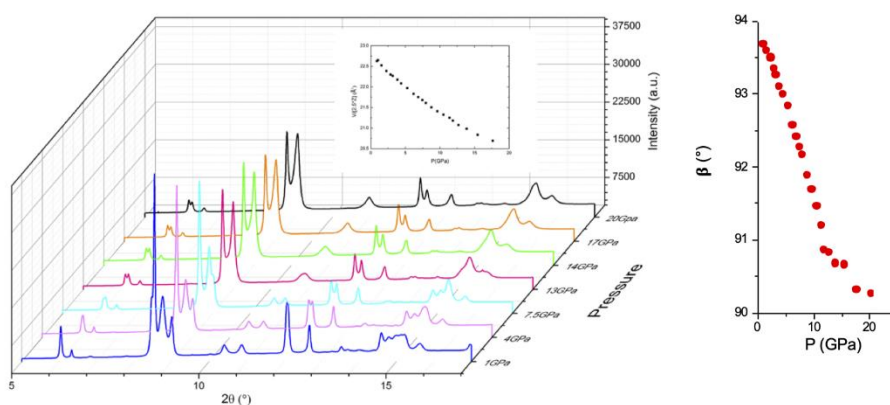


Figure 2 : (left): ID15B X-Ray Diffractograms of LaNiO_{2.5} under applied pressure and evolution of V/ZX value vs pressure. (right): Evolution of the β angle as a function of pressure, showing the close proximity to a phase transition with $\beta = 90^\circ$.

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