ESRF	**Experiment title: Study of the crystal structure of non-superconducting doped polycrystalline ($Nd_{1-x}Ca_x$)NiO2 nickelates in the 4K-300K range**	**Experiment number**: HC-4997
Beamline: ID22	**Date of experiment**: from: 28/10/2022 to: 31/10/2022	**Date of report**: 14/09/2023
Shifts: 9	**Local contact(s)**: Catherine Dejoie	*Received at ESRF:*

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Report:

The aim of our experiment was to measure, by powder x-ray diffraction (XRD), the evolution of the crystal structure in the solid solution $Nd_{1-x}Ca_xNiO_2$ (with x = 0 to 0.3) as a function of the temperature in the 4K – 300 K range, for different Ca content, to evidence possible structural transitions. We wanted to quantify the Ni vacancies amount and the real oxygen and calcium contents thanks to structural refinements.

A similar experiment was realized at beamline CRISTAL of SOLEIL few weeks before the one at id22/ESRF on different compositions. We obtained good data to refine the lattice parameters as function of the temperature. Unfortunately, there was a non-negligible amount of impurities in the powders, making the refinement of the occupancies more complicated. So, for the ESRF experiment we chose a composition (x = 0.2) with a better purity. Furthermore, to get supplementary information about the crystal structure, we acquired 3 XRD patterns with a long exposition time and a high Q-range to be able to perform later a PDF analysis at 4 K, 100 K and room temperature.

We have also measured the XRD pattern of another $NdNiO_{2+y}$ nickelate with an unusual lattice for which we have previously established a first structural model by TEM analysis at 300 K. Physical properties characterizations were done down 2 K, but the precise crystal structure was missing in the 2K-300K temperature range, so we decided to measure it at the ID22 beamline.

We are collaborating with a research group from ICMCB (France, Bordeaux) on the nickelates compounds. A powder diffraction experiment under high-pressure at the ESRF-ID15b was realized in February 2022 on several solid-solution $Ln_{1-x}A_xNiO_2$ from ICMCB group, and from our group, with x = 0.2 and Ln,A = Nd,Ca or Pr,Sr. So, we have also measured some of these samples at low temperature during the id22 experiment.

Powder diffraction patterns at room temperature for the full solid solution $Nd_{1-x}Ca_xNiO_2$ synthesized have been acquired. This will allow us to get more precise lattice parameters and chemical compositions for each composition than the ones obtained from conventional laboratory XRD.

As shown in Figure 1, the (200) and (002) Bragg peaks are shifting towards lower 2θ angle when the temperature is increasing, which is expected due to thermal dilatation of lattice. No significant change of relative intensities or new reflections originated from a structural transition, have been observed in the full temperature range.
The comparison of the theoretical pattern obtained from a structural model, using the Rietveld method, with the experimental data is displayed in Figure 2 for $x_{nominal}(Ca)=0.20$. The agreement is good, but the intensity of some calculated peaks remain wrong. The refined composition is found to be $Nd_{0.78}Ca_{0.22}Ni_{0.94}O_2$ which shows an overestimation of the Ca content, whereas the found 6% of Ni vacancies was expected. Different models have still to be tested to improve the refinement.

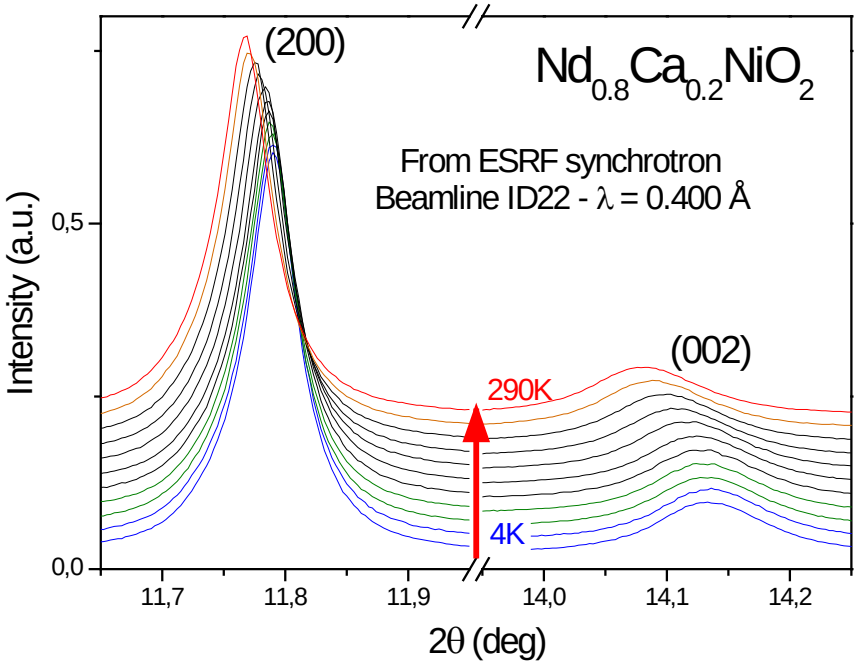

Figure 1: Powder diffraction patterns of the $Nd_{0.8}Ca_{0.2}NiO_2$ phase as function of the temperature (4K to 290K), with enlarged view on the (200) and (002) Bragg peaks.

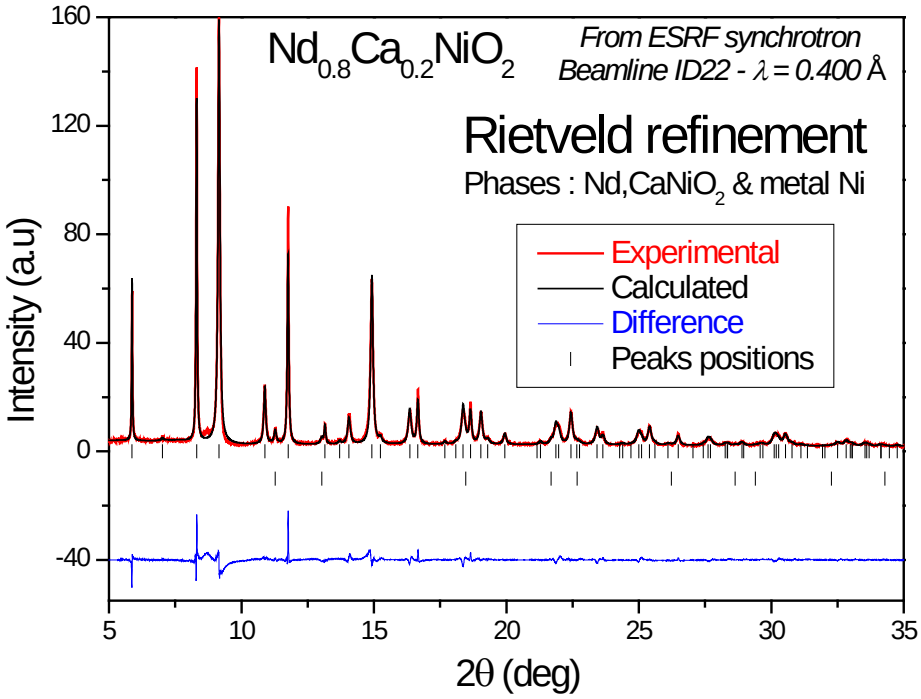

Figure 2: Calculated pattern from the refined structural model (black curve) compared with the powder diffraction pattern for $Nd_{0.8}Ca_{0.2}NiO_2$ (red curve) acquired outside the cryostat. The difference between the two is the blue curve, the upper ticks are the Bragg peaks positions of the phase $Nd_{0.8}Ca_{0.2}NiO_2$, and the lower sticks those of the metal Ni impurity.

Once a better structural model will be found to fit the data by the Rietveld refinement, we will use these results to write an article on the solid solution $Nd_{1-x}Ca_xNiO_2$ with x = 0 to 0.5. And then, we will finish the analysis the $NdNiO_{2+y}$ data to write a second article.