Experimental report

15/05/2024

Proposal: **5-23-810**

Council: 10/2023

Title: Unveiling the structure and the role of hydrogen content in rare-earth infinite-layer nickelates

Research area: Materials

This proposal is a new proposal

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Samples: $LaNi_{0.9}Al_{0.1}O_2$
$La_{0.85}Sr_{0.15}Ni_{0.9}Al_{0.1}O_3$
$NdNi_{0.9}Al_{0.1}O_3$
$Nd_{0.85}Sr_{0.15}Ni_{0.9}Al_{0.1}O_2$
$LaNi_{0.9}Al_{0.1}O_3$
$La_{0.85}Sr_{0.15}Ni_{0.9}Al_{0.1}O_2$
$NdNi_{0.9}Al_{0.1}O_2$
$Nd_{0.85}Sr_{0.15}Ni_{0.9}Al_{0.1}O_3$

Instrument	Requested days	Allocated days	From	To
D2B	2	2	12/04/2024	15/04/2024
D20	2	0		

Abstract:

Rare-earth nickelates have recently been discovered as a new family of superconductors. With an infinite-layer crystal structure and electronic configuration of Ni^{1+} reminiscent of Cu^{2+} in cuprates, they have become a very active field of research today.

We have prepared several nickelate compositions, both in their oxidised $RNiO_3$ and infinite-layer $RNiO_2$ forms by the citrate-nitrate route, yielding high-purity samples. To date, superconductivity has only been observed in thin films, but not in the bulk material. Some reports suggest that the crystalline quality, including the exact stoichiometry of the oxygen, may be determinant in the occurrence or not of superconductivity. Another recent hypothesis has to do with the effect of hydrogen trapped in the infinite-layer structure, which would be crucial for the presence of superconductivity. In this proposal we intend to investigate both, being necessary the use of neutrons to study both the oxygen stoichiometry and the presence of hydrogen owing to its negative scattering density.

Rare-earth nickelates $RNiO_3$ are electron-correlated materials where the interplay between charge and spin order leads to a rich phase diagram, passing through antiferromagnetic insulators to paramagnetic metals. In 2019, $RNiO_2$ derivatives were found in 2019 to constitute a new family of superconductors, mimicking some of the properties of cuprates, with a quasi-two-dimensional structure, a weak interplane coupling, and a key structural unit equivalent to the CuO_2 plane.

Although our group has been able to synthesize some of the infinite-layer compounds ($RNiO_2$) in powder form (bulk), we have not observed superconducting properties so far.

However, there are several unanswered questions about this phenomenon that we planned to address with this experiment. For example, whether the perfect oxygen stoichiometry can be a reason for the appearance of this superconductivity. And on the other hand, whether it is possible that part of the hydrogen used in the reduction from the O_3 phase to the O_2 phase could be trapped between the layers of the reduced phase.

To shed light into this field, in this experiment, we planned to study several nickelate compositions, both in the oxidized $RNi_{1-y}Al_yO_3$ phase and in the infinite layer $RNi_{1-y}Al_yO_2$ phase (R = La, Nd).

During the experiment, we were able to measure the intended samples from room temperature (RT) down to 3.5 K. A total of four patterns for the $NdNiO_2$ sample collected at different temperatures can be seen in Figure 1a.

Fig 1b shows the refined pattern of $NdNiO_2$ at RT (work in progress). One of the preliminary results suggested by the refinement at RT is the partial presence of apical oxygens in the structure, so the refined composition would be closer to $\sim NdNiO_{2.3}$ than to $NdNiO_{2.0}$. This unexpected presence of a small amount of oxygen at the apical sites could explain the absence of superconductivity in these bulk samples.

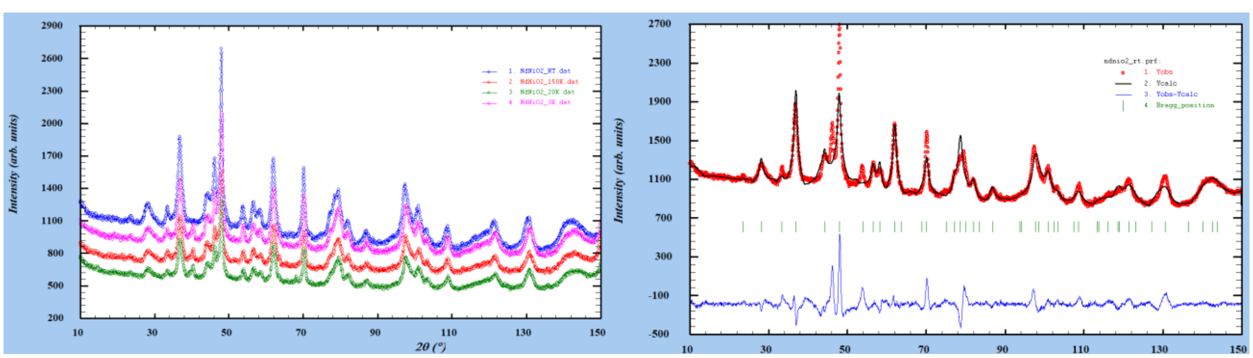

Figure 1: (a) NPD patterns collected at 3.5 K, 20 K, 150 K, and 300 K for the $NdNiO_2$ sample. (b) First refinement of the pattern at RT.

We were also able to measure during the scheduled time the composition of $NdNi_{0.9}Al_{0.1}O_2$ (with Al substitution to help keep the infinite layers together). Figure 2 shows the NPD patterns collected at different temperatures.

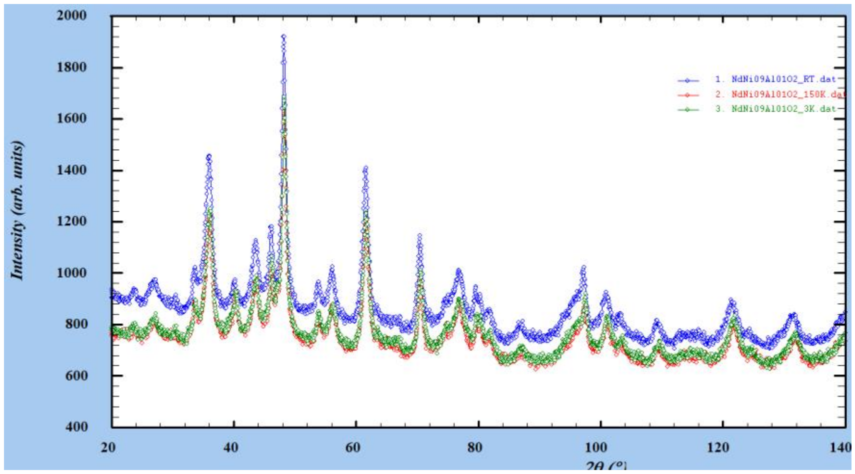

Figure 2: NPD patterns collected at 3.5 K, 150 K, and 300 K for the $NdNi_{0.9}Al_{0.1}O_2$ sample.

Lastly, another main objective of the present experiment was to demonstrate the presence of hydrogen between the layers in the $RNiO_2$ phase. With this in mind, we were able to measure the compositions of $La_{1-x}Sr_xNi_{0.9}Al_{0.1}O_3$ and $La_{1-x}Sr_xNi_{0.9}Al_{0.1}O_2$ (x = 0, 0.15) (those with the best crystallinity) at RT to check this hypothesis.

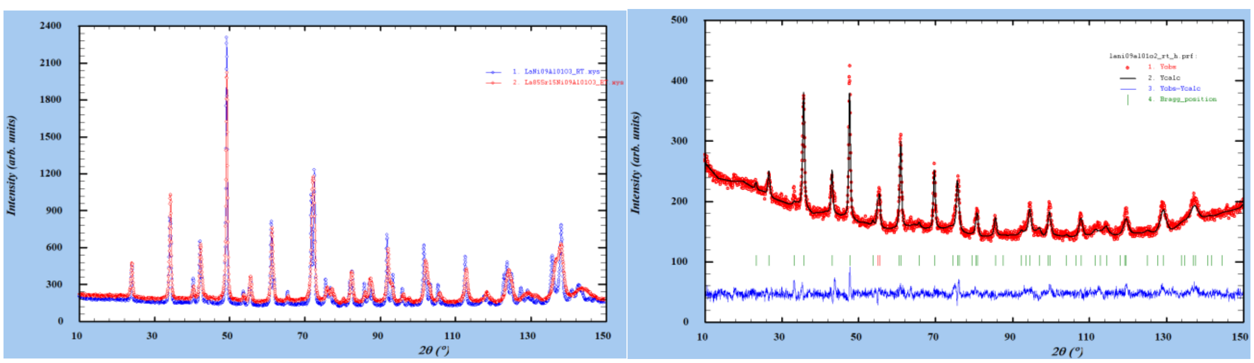

Figure 3: (a) NPD patterns collected at RT for the $LaNi_{0.9}Al_{0.1}O_3$ and $La_{0.85}Sr_{0.15}Ni_{0.9}Al_{0.1}O_3$ samples. (b) Refined pattern of the $LaNi_{0.9}Al_{0.1}O_2$ composition.

The NPD patterns for these two compositions can be seen in Figure 3a. Figure 3b, on the other hand, shows the refinement of the $LaNi_{0.9}Al_{0.1}O_2$ composition at RT.

The refinement of this composition has given us very important information, since we have been able to detect the presence of hydrogen (5%) between the layers (see Fig. 4), thus confirming the hypothesis suggested by the community. This information is very important for research on superconducting nickelates, so we can consider it as a main result of the experiment.

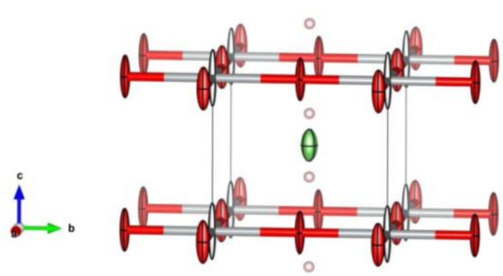

Figure 4: Crystalline structure obtained by the Rietveld refinement of the NPD data. The hydrogen (negative scattering density) is represented as tiny pink spheres.