Stabilisation of bulk infinite-layer nickelates and new structural insights by means of high-resolution powder X-ray and neutron diffraction

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Recently, a new class of high-temperature superconductors, $RNiO_2$ (R, rare-earth elements) with infinite-layer structure, has been identified [1]. They possess the same structural framework as the renowned high-T_c cuprates but with nickel replacing copper as the central element. Although the first measurements found the transition temperature to be below 15 K, recent reports also show that applied pressure can significantly increase this T_c. Although in the last two years some other Ni-containing compositions, $R_3Ni_2O_7$, have been discovered to be superconductors under applied pressure, superconductivity in bulk $RNiO_2$ still evades experimental observation. Several hypotheses have been proposed to explain the absence of superconductivity in some samples, such as strain (whether chemical or physical), the exact stoichiometry of oxygen, or the presence of hydrogen ions between the layers, which would hinder interlayer transport.

We have successfully synthesized infinite-layer samples of $RNi_{0.9}Al_{0.1}O_{2+\delta}$ (R = Nd, Pr) in the bulk polycrystalline form through topotactic reduction of the $RNi_{0.9}Al_{0.1}O_3$ orthorhombic perovskite [2,3]. The incorporation of aluminium at the octahedral sites promotes the stabilization of the infinite-layer and X-ray absorption spectroscopy (XAS) measurements confirm the Ni^{1+} oxidation state. Using neutron powder diffraction, we also find hydride ions within the infinite-layer lattice in Pr samples, but not in the Nd ones. Magnetic measurements could not provide evidence of superconductivity, being the susceptibility masked by the presence of tiny amounts of Ni metal. The results of synchrotron X-ray diffraction and powder neutron diffraction agree on the small excess of oxygen observed in the case of the infinite-layer phase, deviating slightly from the perfect O2 stoichiometry. Synchrotron X-ray diffraction data collected at ID22 proves to be a useful technique to study deviations in oxygen occupancy even in the absence of neutron diffraction data.

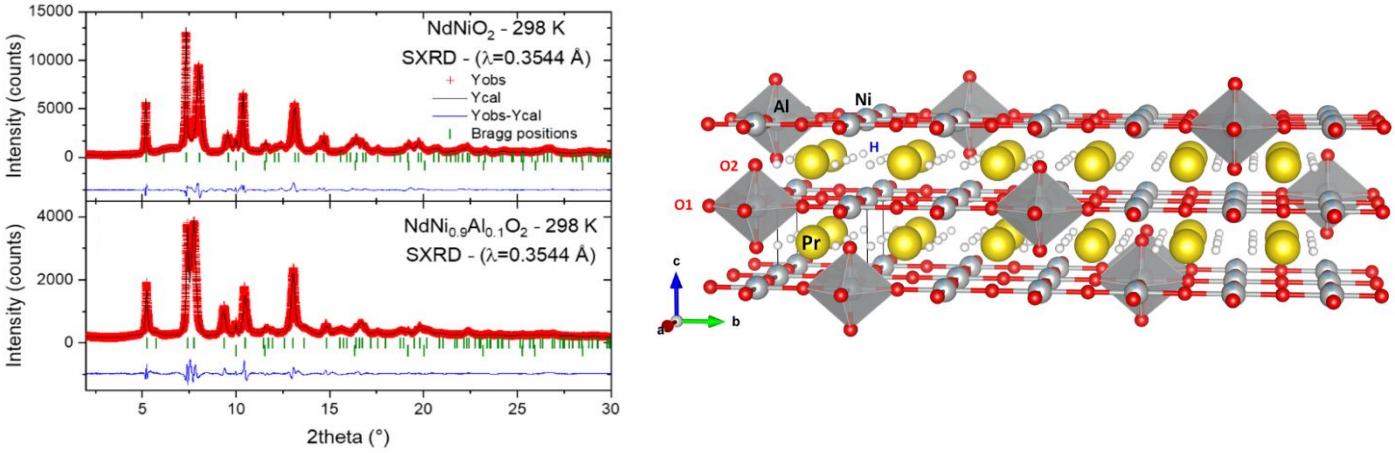


Figure 1. *Left: SXRD patterns of the $NdNi_{1-x}Al_xO_2$ infinite-layer phase without aluminium (up, refined stoichiometry $NdNiO_{2.34}$) and with aluminiun substitution (down, refined stoichiometry $NdNi_{0.9}Al_{0.1}O_{2.29}$). Right: Drawing of the refined crystalline structure (space group P4/mmm) of the $PrNi_{0.9}Al_{0.1}O_{2.1}H_{0.16}$ composition.*

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