Experimental report

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Proposal: 5-22-810 **Council:** 10/2022

Title: Oxygen defects and diffusion pathways in n=2,3 Ruddlesden-Popper phases for solid oxide water electrolysis application

Research area: Materials

This proposal is a new proposal

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Samples: La3Ni2O7
Pr4Ni3O10

Instrument	Requested days	Allocated days	From	To
D2B	3	3	02/06/2023	05/06/2023

Abstract:

The perovskite-derived Ruddlesden-Popper (RP) series Lnn+1NinO3n+1±¿ (Ln = La, Nd, Pr), are considered as oxygen electrode materials of substantial interest for solid oxide fuel and electrolysis cell application. The oxygen transport properties and performances of the materials are highly dependent on the oxygen stoichiometry, the degree of octahedral tilting and the anionic interstitial site occupancy. Although these structure-properties relationships have been established in details for perovskite and n=1 RP phases, they remain to be unraveled for higher n members of the RP series. We wish to tackle this problematic through a high-resolution powder neutron diffraction study at room temperature and at temperatures close to the operating conditions of devices, where oxygen starts to diffuse, on n=2 La3Ni2O7±¿, and n=3 Pr4Ni3O10±¿. Rietveld refinements will allow to get accurate information on the position, occupancy and displacement parameters of the multiple oxygen sites at high T. Visualization of diffusion pathways will be attempted by the reconstruction of the nuclear density using the Maximum Entropy Method (MEM), an analysis that has yet never been done on n=2,3 RP members.

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Oxygen defects and diffusion pathways in n = 2,3 Ruddlesden-Popper phases for solid oxide water electrolysis application

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Introduction

The development of solid oxide electrolysis cells (SOECs) for the production of carbon-free hydrogen is a priority research area in France. Rare-earth nickelates of the Ruddlesden-Popper (RP) homologous series ($Ln_{n+1}Ni_nO_{3n+1\pm\delta}$, Ln = La, Pr) are promising oxygen electrode materials for SOECs due to their mixed electronic and oxygen ionic conductivity. However, the oxygen defect chemistry and conductivity mechanism in high n RP nickelate phases remain unclear. This study aims to investigate the oxygen anion defects and diffusion pathways in n = 2 and n = 3 RP phases using neutron powder diffraction (NPD) at room temperature and high temperatures.

Sample Preparation

Three RP nickelate samples were prepared using the citrate nitrate route: n = 2 $La_3Ni_2O_{7\pm\delta}$, n = 3 $La_4Ni_3O_{10\pm\delta}$ and $Pr_4Ni_3O_{10\pm\delta}$. Compounds are calcined under air for La containing phases, or O_2 gas flow for $Pr_4Ni_3O_{10\pm\delta}$ at 1100 °C and 1050 °C, respectively, for 3 × 24 h (with intermediate grindings). Sample purity was checked with laboratory X-ray diffraction prior to the experiment at ILL. Only small amounts of NiO and Pr_6O_{11} were found in the $Pr_4Ni_3O_{10\pm\delta}$ sample.

Experimental Setup

Neutron powder diffraction data were collected at room temperature, 600 °C and 900 °C for all samples (plus an additional temperature, 400°C, for $Pr_4Ni_3O_{10\pm\delta}$) on the D2B high resolution diffractometer using a standard vanadium furnace. Samples were loaded in quartz tube of 1 cm diameter open to the air, with powder height of ~ 4.5 cm for $La_3Ni_2O_{7\pm\delta}$ and $La_4Ni_3O_{10\pm\delta}$ and ~5 cm for $Pr_4Ni_3O_{10\pm\delta}$. Bragg reflections were measured in the two-theta range of [4 ° – 160 °], with step size 0.050019 ° and wavelength 1.594 Å. Scans were repeated 8 times, leading to an acquisition time of 4 hours for each pattern. Heating was performed with a ramp rate of 5 $K \cdot min^{-1}$ and a 15 min equilibration time at each targeted temperature. Background measurements were conducted on an empty quartz tube at each temperature for background subtraction, and room temperature acquisition on the NAC reference sample was performed to create an instrument resolution file for accurate refinements.

Results

The analysis was first conducted on the $Pr_4Ni_3O_{10}$ and $La_3Ni_2O_7$ samples. Refinements were performed using the FullProf suite. Analysis started with Le Bail refinement for peak shape modelling and the space group determination and/or validation. Structural models were then refined by the Rietveld method. Peak shapes were modelled using the Thompson-Cox-Hastings function with spherical harmonic expansion for anisotropic size broadening. Moreover, the relaxing of peak broadening for a few individual reflections for which general models did not lead to satisfactory refinement was used.

$La_3Ni_2O_{7\pm\delta}$

We confirmed that $La_3Ni_2O_{7\pm\delta}$ crystallizes in an orthorhombic crystal system at room temperature, and undergoes as phase transition to a tetragonal symmetry from 600 °C. Contradictory results were found in the literature regarding the RT space group of $La_3Ni_2O_{7\pm\delta}$. Refinement using different space groups (*Cmmm*, *Cmcm*, *Amam*, and *Amma*) were tested.

The lattice centering is found to be *A* (not *F*, as initially expected, and certainly not *C* or *B*), considering the number of calculated peaks (almost identical between lattice centering *A*, *B*, and *C*, but not at the

same 2θ positions). The agreement factors, as well as the presence of poorly fitted peaks due to incorrect lattice extinction, further confirm the *A*-type lattice. To determine the space group, all non-isomorphic subgroups of *Fmmm* with a long *c*-axis centered on *A* were considered (a total of 8). Their structures were generated using Jana, and the results showed one Ni equivalent in *Amam* and two Ni equivalents in *Amma*. The latter yielded a better Le Bail fit ($\chi^2 = 0.35$, $R_p = 7.03$ %) than *Amam*, and therefore, this space group was validated, with lattice parameters: $a = 5.39628$ Å, $b = 5.45084$ Å, $c = 20.52012$ Å. Interestingly, this space group was never reported for $La_3Ni_2O_7$. The next step in the analysis will be Rietveld refinements to determine the correct structure.

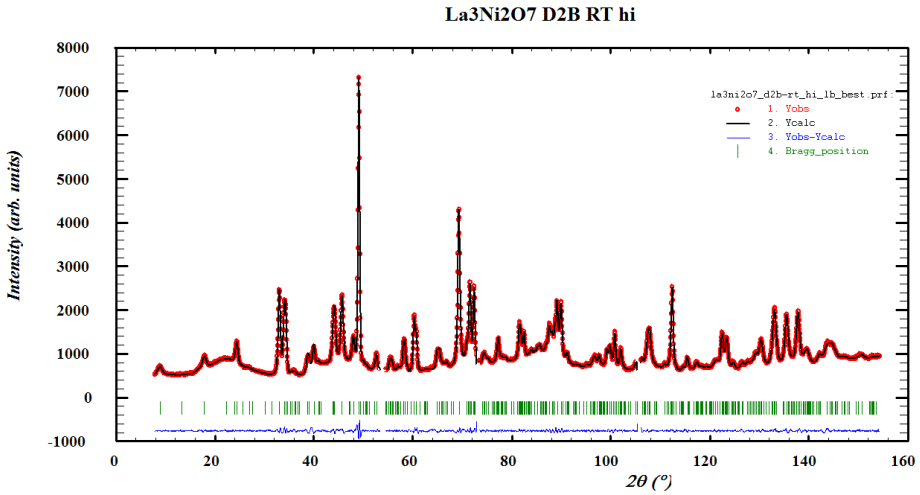

Figure 1. Le Bail fit for $La_3Ni_2O_7$ at room temperature.

$Pr_4Ni_3O_{10}$

Different space group are reported in the literature concerning the $Pr_4Ni_3O_{10}$ phase, in both the orthorhombic (*Fmmm*, *Bmab*) and monoclinic ($P2_1/a$) crystal systems, with no phase transition up to 1000 °C. Here, with the Le Bail refinement against the neutron diffraction data performed in this study, coupled with refinement against synchrotron X-ray diffraction (SXRD) data acquired at ESRF (ID22), we validated the $P2_1/a$ space group as well as the absence of phase transition up to 900 °C. The room temperature lattice parameters are: $a = 5.37157(10)$ Å, $b = 5.46284(10)$ Å, $c = 27.60669(69)$ Å, $\beta = 90.27975(192)$ °. Rietveld refinement analysis was conducted for the data acquired at 900 °C. The structural model published by Tsai et al. (*Journal of Solid State Chemistry* 289, 2020) was used. Lattice parameters at 900 °C are: $a = 5.44242(6)$ Å, $b = 5.49241(6)$ Å, $c = 27.99453(53)$ Å, $\beta = 90.15784(178)$ °.

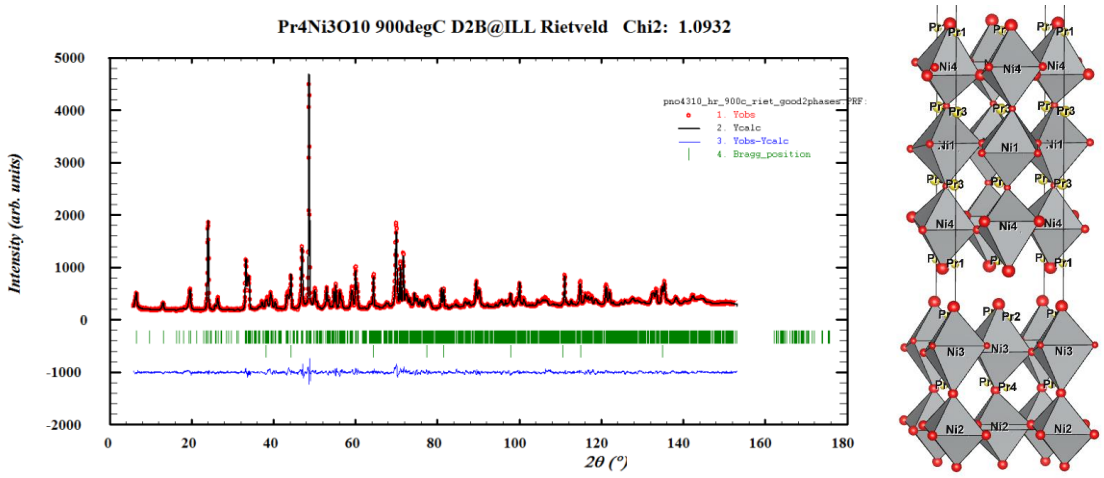

Figure 2. Rietveld refinement for $Pr_4Ni_3O_{10}$ at 900 °C and crystal structure ($P2_1/a$ space group).

Table 1. Crystal structure of $Pr_4Ni_3O_{10}$ at 900°C.

Name	x sx	y sy	z sz	B sB	occ. socc.
Pr1	0.01437(389)	0.02562(310)	0.30152(61)	0.799(284)	1.000
Pr2	0.50947(492)	-0.00214(555)	0.79335(62)	1.946(453)	1.000
Pr3	-0.01234(358)	0.00067(461)	0.42611(62)	1.374(366)	1.000
Pr4	0.50774(651)	0.00371(637)	0.93135(92)	3.115(435)	1.000
Ni1	0.00000	0.50000	0.50000	1.299(228)	0.500
Ni2	0.00000	0.00000	0.00000	0.551(186)	0.500
Ni3	-0.01088(164)	0.00447(182)	0.13757(28)	0.405(90)	1.000
Ni4	0.48711(240)	0.01583(229)	0.64091(38)	2.136(165)	1.000
O1	0.29710(282)	0.29716(277)	0.49733(68)	0.972(252)	0.869(17)
O2	0.25654(416)	0.25514(411)	0.98990(64)	1.866(304)	1.000
O3	-0.00631(552)	0.03408(403)	0.06888(82)	3.189(400)	1.000
O4	0.51240(410)	0.06379(309)	0.56831(85)	2.432(347)	1.000
O5	0.24272(390)	0.25947(391)	0.14764(72)	2.101(414)	1.009(37)
O6	0.75450(388)	0.23605(383)	0.65045(74)	2.249(395)	1.000
O7	-0.01057(647)	-0.04376(548)	0.21594(115)	4.406(588)	1.000
O8	0.48522(548)	-0.04552(447)	0.71710(105)	3.428(479)	1.000
O9	0.76872(384)	0.27473(424)	0.86531(84)	2.288(405)	1.000
O10	0.24190(391)	0.22631(433)	0.36612(90)	1.409(448)	0.820(37)
Oi1	0.25000	0.25000	0.75601(625)	1.702(0)	0.103(0)
Oi2	0.25000	0.75000	0.73716(446)	1.203(0)	0.122(0)

This analysis revealed that:

- The use of anisotropic displacement parameters for any of the atoms could not be used, as their refinement leads to negative values. The displacement parameters were then kept as isotropic at this stage, while this strongly affect the quality of the fit. Large displacement parameters were found for O7 and O8 sites.
- Anion vacancies were found on the O5, O10, and O1 sites, with the other apical and equatorial sites showing no signs of vacancies.
- A preliminary Maximum Entropy Method (MEM) analysis using Dysnomia program reveals residual electron density in positions close to the classical interstitial site within the rocksalt layer (distorted tetrahedron). By introducing an occupation of the site by an oxygen atom at this position, we observe a significant improvement in the fit.

Future Work

Further analysis will be conducted on this study, with the aim of publishing an article in the coming year. The remaining work will focus on several key objectives. Firstly, a Le Bail refinement will be performed against the diffraction data of $La_4Ni_3O_{10}$ to determine the space group and peak profile. This will be followed by a Rietveld refinement using the RIETAN program, which will incorporate special peak profiles (split-Pseudo Voigt) and a composite background to improve the fit on the three samples. The goal of these refinements is to accurately determine the amount and position of oxygen vacancies, as well as the presence or absence of oxygen interstitials at each temperature and obtain the best fit possible for further MEM analysis. The latter method will be conducted, using all diffraction lines to reconstruct nuclear density maps and obtain more detailed information on atomic displacement factors and anion defects, and potentially visualize oxygen diffusion pathways. Finally, a combined refinement of synchrotron X-ray diffraction (SXRD) and neutron diffraction data will be performed and other experiments (oxygen stoichiometry determination with TGA and transport property measurements) will be done to provide a comprehensive understanding of the material's structure and properties.