Experimental report

29/08/2022

Proposal: **5-24-675** **Council:** 4/2021

Title: Role of the crystal structure and oxygen vacancies in the transport properties and electrochemical performance of LaNi0.6Fe0.4-xMxO3-¿

Research area: Materials

This proposal is a new proposal

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Experimental team:

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Samples: LaNi0.6Fe0.3Cu0.1O3-¿
LaNi0.6Fe0.2Cu0.2O3-¿
LaNi0.6Fe0.3Cr0.1O3-¿

Instrument	Requested days	Allocated days	From	To
D2B	3	3	08/10/2021	11/10/2021

Abstract:

We have investigated LaNi0.6Fe0.4-xMxO3-¿ (M= Cu, Cr) oxides as contact materials for the Reversible Solid Oxide Fuel Cells (RSOFCs) stacks. As B-site dopants influence the crystal structure and electrical properties, the goals of this neutron thermodiffraction proposal are: i) To determine the thermal evolution of the crystal structure of LaNi0.6Fe0.3Cu0.1O3-¿, LaNi0.6Fe0.2Cu0.2O3-¿, and LaNi0.6Fe0.3Cr0.1O3-¿ samples at the working conditions of a RSOFC. We will pay special attention to the oxygen vacancies concentration, the orthorhombic ¿ rhombohedral structural transition and the possible cation and anion structural ordering; ii) To correlate the effect of the crystal structure on the transport and electrochemical properties of the selected materials.
For these tasks we ask for 3 days at D2B diffractometer.

Role of the crystal structure and oxygen vacancies in the transport properties and electrochemical performance of $LaNi_{0.6}Fe_{0.4-x}M_xO_{3-\delta}$

Room temperature NPD patterns for $LaNi_{0.6}Fe_{0.2}Cu_{0.2}O_{3-\delta}$ and $LaNi_{0.6}Fe_{0.3}Cr_{0.1}O_{3-\delta}$ samples are shown in Figure 1. These two compounds' structures were refined in the rhombohedral *R-3c* (#167) space group, which is formed by the perovskite's anti-phase three tilt scheme $a^-a^-a^-$ of the perovskite [1]. Figure 2 shows a representation of the rhombohedral perovskite's crystal structure. The large size of La^{3+} for the A site causes the slightly deformed rhombohedral structure, similar to $LaNiO_{3-\delta}$, therefore the perovskite is generated by a displacement of O^{2-} from their model position in the cubic perovskite [2,3]. The ideal ideal AO_{12} cuboctahedron in ABO_3, which has 12 equal A-O distances, is thus changed into a polyhedron with 3 A-O short-bonds, 6 medium-bonds, and 3 long-bonds. In the case of the BO_6 octahedra, B-O distances are the same. However, the O-B-O angles for the BO6 octahedron are slightly off from 90o, but the B-O distances are the same. The 8 short A-B lengths are changed to two shorter and six longer, while the A-A and B-B distances remain equal.

La atoms occupy the *6a* (0, 0, 1/4) Wyckoff sites in the prepared compositions, while Ni, Fe, and Cu/Cr are randomly dispersed at the *6b* (0, 0, 0) site and O is situated at the *18e* (x, 0, 1/4) Wyckoff location. The crystallographic formulae of $LaNi_{0.59(2)}Fe_{0.20(3)}Cu_{0.20(3)}O_{2.87(1)}$ and $LaNi_{0.63(2)}Fe_{0.27(2)}Cr_{0.10(1)}O_{2.96(1)}$ (at room temperature) were obtained by refining the atomic site occupancies.. Table 1 and Table 2 summarize the unit-cell parameters, atomic positions, isotropic displacement parameters for metal and O atoms, agreement factors and main interatomic distances, after the Rietveld refinement of the crystal structure at room temperature, 400, 700 and 900 ºC (figure 3 and figure 4). The neutron powder diffractograms show no extra reflections, indicating that there is no evidence of a superstructure resulting from a potential ordering of the oxygen vacancies or metal cations. The amount of oxygen vacancies increases somewhat for both phases when the samples are heated, resulting in compositions of $LaNi_{0.59}Fe_{0.20}Cu_{0.20}O_{2.71(1)}$ and $LaNi_{0.63}Fe_{0.27}Cr_{0.10}O_{2.90(1)}$ at 900 ºC.

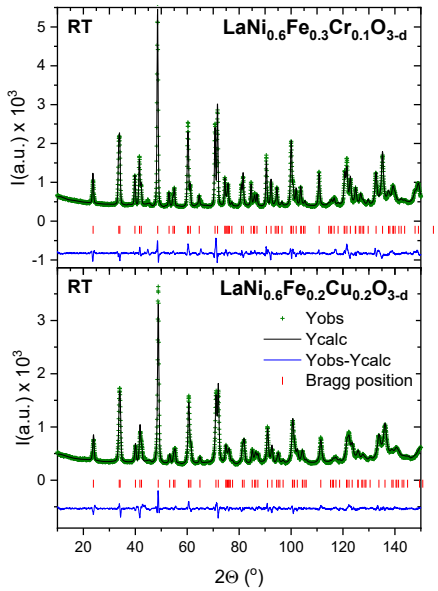

Figure 1. *Observed (green crosses), calculated (black, full line), and difference (blue line) neutron powder diffraction profile for* $LaNi_{0.6}Fe_{0.2}Cu_{0.2}O_{3-\delta}$ *and* $LaNi_{0.6}Fe_{0.3}Cr_{0.1}O_{3-\delta}$ *perovskites. The vertical red bars correspond to the allowed Bragg reflections.*

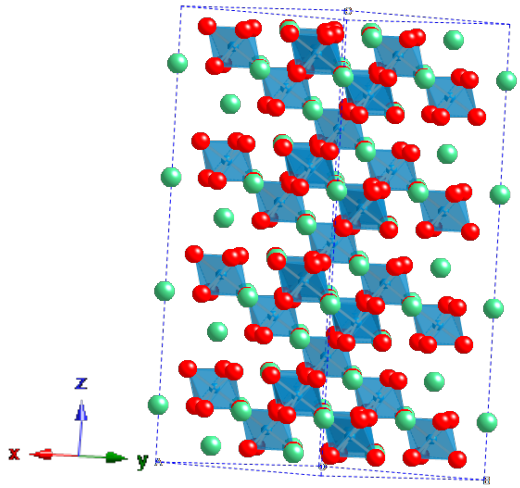

Figure 2. *View of the crystal structure, emphasizing* BO_6 *octahedra (blue). Green spheres indicate La atoms while red spheres show O atoms.*

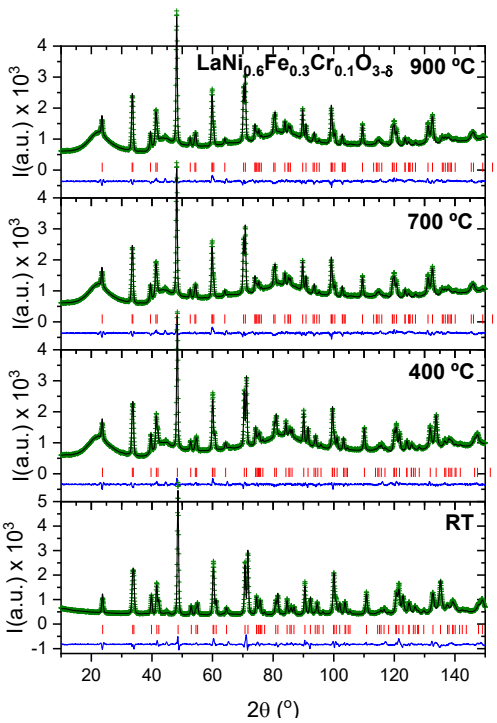

Figure 3. . Neutron powder thermodiffraction profiles in air for $LaNi_{0.6}Fe_{0.3}Cr_{0.1}O_{3-d}$

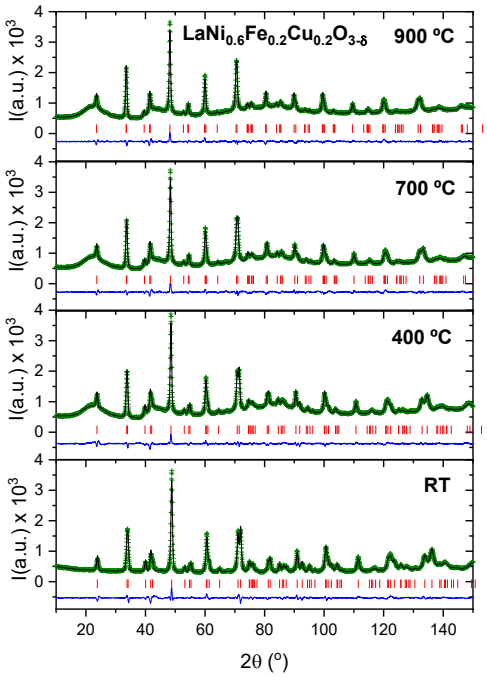

Figure 4. Neutron powder thermodiffraction profiles in air for $LaNi_{0.6}Fe_{0.2}Cu_{0.2}O_{3-\delta}$.

Table 1. Refined structural parameters obtained from NPD for $LaNi_{0.6}Fe_{0.2}Cu_{0.2}O_{3-\delta}$ from room temperature to 900 ºC. Space group: *R-3c*

T (ºC)	RT	400	700	900
a (Å)	5.4850 (2)	5.5030 (2)	5.5185 (3)	5.5296 (2)
b (Å)	5.4850 (2)	5.5030 (2)	5.5185 (3)	5.5296 (2)
c (Å)	13.2243 (6)	13.3176 (7)	13.4005 (8)	13.4654 (8)
La				
x	0	0	0	0
y	0	0	0	0
z	0.25	0.25	0.25	0.25
Occ.	1	1	1	1
B_{iso} (**Å²**)	0.29(2)	0.95(3)	1.39(4)	2.11(2)
Ni/Fe/Cu				
x	0	0	0	0
y	0	0	0	0
z	0	0	0	0
Occ.	0.59(2)/0.20(3)/0.20(3)	0.59/0.20/0.20	0.59/0.20/0.20	0.59/0.20/0.20
B_{iso} (**Å²**)	0.10(1)	0.21(3)	0.56(3)	0.95(2)
O1				
x	0.5485(2)	0.5449(2)	0.5437(2)	0.5389 (3)
y	0	0	0	0
z	0.25	0.25	0.25	0.25
Occ.	0.96(1)	0.94(1)	0.92(1)	0.90(1)
B_{iso} (**Å²**)	0.43(1)	0.92(4)	1.48(3)	2.24(2)
R- factors				
R_p	2.98	1.97	1.80	1.80
R_{wp}	4.09	2.72	2.44	2.50
R_{exp}	1.83	1.45	1.44	1.43
R_{Bragg}	2.1	2.9	2.80	2.60

Table 2. Refined structural parameters obtained from NPD for $LaNi_{0.6}Fe_{0.3}Cr_{0.1}O_{3-\delta}$ from room temperature to 900 ºC. Space group: *R-3c*

T (ºC)	RT	400	700	900
a (Å)	5.5085 (1)	5.5260 (1)	5.5410 (1)	5.5527 (2)
b (Å)	5.5085 (1)	5.5260 (1)	5.5410 (1)	5.5527 (2)
c (Å)	13.2620 (4)	13.3504 (3)	13.4281 (4)	13.4862 (5)
La				
x	0	0	0	0
y	0	0	0	0
z	0.25	0.25	0.25	0.25
Occ.	1	1	1	1
B_{iso} (**Å²**)	0.33(2)	0.59(1)	0.75(2)	0.97(2)
Ni/Fe/Cr				
x	0	0	0	0
y	0	0	0	0
z	0	0	0	0
Occ.	0.63(2)/0.27(2)/0.10(1)	0.63/0.27/0.10	0.63/0.27/0.10	0.63/0.27/0.10
B_{iso}	0.06(2)	0.17(1)	0.22(1)	0.26(2)
O1				
x	0.5542(1)	0.5518(1)	0.5500(1)	0.5483(2)
y	0	0	0	0
z	0.25	0.25	0.25	0.25
Occ.	0.99(1)	0.98(1)	0.97(1)	0.96(1)
B_{iso} (**Å²**)	0.56(2)	0.77(1)	0.81(3)	0.97(2)
R- factors				
R_p	3.98	1.76	1.98	2.13
R_{wp}	5.41	2.40	2.64	2.82
R_{exp}	1.78	1.57	1.41	1.41
R_{Bragg}	4.3	3.60	4.70	4.10

References:

[1[R.H. Mitchell, Perovskites: modern and ancient, Almaz Press Thunder Bay2002.

[2] O. Myakush, V. Berezovets, A. Senyshyn, L. Vasylechko, Preparation and crystal structure of new perovskite-type cobaltites $R_{1-x}R'_xCoO_3$, Chemistry of metals and alloys (3) (2010) 184-190.

[3] M. Retuerto, A.G. Pereira, F.J. Pérez-Alonso, M.A. Peña, J.L.G. Fierro, J.A. Alonso, M.T. Fernández-Díaz, L. Pascual, S. Rojas, Structural effects of $LaNiO_3$ as electrocatalyst for the oxygen reduction reaction, Applied Catalysis B: Environmental 203 (2017) 363-371.