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Sol–gel synthesis and structural characterisation of the perovskite type pseudo solid solution $LaNi_{0.5}Cu_{0.5}O_3$

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The composition $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ has been prepared by heat treating a polyacrylamide xerogel in flowing O_2. A perovskite type structure starts to crystallise at 700 °C and is achieved at 1000 °C. TGA data point to the formation of a rather strongly oxidised compound ($\delta \leqslant 0.09$). As the solid state reaction of a mixture of La_2O_3/NiO/CuO powder oxides never yields a perovskite, the part of the sol–gel route in this synthesis proves to be crucial. On the basis of X-ray and neutron diffraction results, the existence of a cupronickelate having a rhombohedral perovskite type structure is proved. Rather unexpectedly, an electron diffraction study of the as-prepared composition at 1000 °C reveals the presence of two sets of perovskite type cupronickelate microcrystals: a copper rich one with a fixed composition 67% Cu and a nickel rich one with a small range of compositions $59 \leqslant \text{Ni}\% \leqslant 67$. The latter microcrystals feature the rhombohedral $LaNiO_3$ perovskite whereas the former one, due to the partial presence of Cu(II), frequently shows an orthorhombic $[2a_p\sqrt{2} \times 2a_p\sqrt{2} \times a_p]$ supercell. Thus, the composition $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$. has to be understood in terms of a nanoscale segregated pseudo solid solution formed of two lanthanum cupronickelates, enriched in copper and nickel, respectively.

1. Introduction

$LaNiO_3$ perovskite has been prepared by Wold *et al.* in 1957.[1] Fifteen years later, Demazeau *et al.* succeeded to synthesise the cuprate analogue $LaCuO_3$ at high oxygen pressure (65 kbar).[2] In both compounds, the transition metal exhibits the formal (III) valence[3,4] and its oxygen co-ordination is a nearly symmetrical octahedron.

In contrast to Ni(III) which is easily obtained at air, only high pressure PO_2 treatments enable stabilisation of Cu(III). At moderate pressure $PO_2 = 0.4$–1 kbar, the oxygen deficiency of $LaCuO_{3-\delta}$ is rather large $0.2 \geqslant \delta \geqslant 0.4$;[5] when PO_2 is close to 1 kbar, a slightly oxygen deficient phase $LaCuO_{2.95}$ is obtained with a tetragonal distortion.[6] The tetragonal form of $LaCuO_{3-\delta}$ is stable up to at least 20 kbar.[7]

Taking into account these data, the simultaneous presence of copper and nickel atoms is expected to facilitate the formation of a strongly oxidised perovskite-type $La(Cu,Ni)O_{3-\delta}$ solid solution. Surprisingly, very few attempts of this method have been reported. To our knowledge, only Bazuev *et al.*[8] have prepared several oxygen deficient compositions $LaCu_{1-x}Ni_xO_{2.5+y}$ ($0.15 \leqslant x \leqslant 0.4$; $y \leqslant 0.29$) in air. None of these phases has the rhombohedral $LaMO_3$ structure.

The present work regards the observation of a synergetic oxidation phenomenon due to the simultaneous presence of nickel and copper in $LaMO_3$ perovskite. We herein report on the sol–gel synthesis and structural characterisation of the as-prepared $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ composition which is understood in terms of the pseudo solid solution of a slightly oxygen deficient copper rich perovskite and an oxidised nickel rich rhombohedral one.

2. Experimental

2.1. Sample preparation

The first step of the synthesis involves forming a precursor which has a high degree of chemical homogeneity and a high reactivity. This can be reached by the organic gel procedure already described elsewhere by one of us P.O.[9] To obtain 10 g of $LaNi_{0.5}Cu_{0.5}O_3$, the following procedure was chosen: 1.351 g of Ni metal and 1.463 g of Cu metal are dissolved separately in 10 ml HNO_3 and 100 ml of hot H_2O (30 °C). The pH is then adjusted to 3 with NH_4OH additions, this permits the efficient chelation of Ni^{2+} and Cu^{2+} by addition of 7.397 g of H_4(EDTA). After a few minutes, the colour turns to deep blue, due to the complexation of Ni^{2+} and Cu^{2+} by EDTA. After drying, 7.5 g of La_2O_3 are dissolved in 10 ml HNO_3 and 100 ml of hot (30 °C) H_2O and the pH of the solution is increased to 5. The three solutions are mixed together and the pH adjusted again to a value within the range 4–6. To this solution are added 20 g of acrylamide and 2 g of *N*,*N*′-methylenebisacrylamide and a few mg of AIBN that initiates the polymerisation. Heating up to 80 °C results in the formation of a hard blue gel within a few minutes.

This gel is then dehydrated in a domestic microwave oven. The heating of the whole mass of the product is controlled *i.e.* the temperature is constrained to be below 180 °C. This treatment yields a solid brown plastic which is crushed into a powder and put into a ventilated oven under flowing N_2 in order to avoid excessive exothermic carbon combustion. The temperature is slowly raised (100 K h^{-1}) to 700 °C and then maintained 10 h at this temperature. In the final step, the furnace is cooled to room temperature in flowing oxygen. The resulting precursor is a black powder with a low apparent density (0.3–0.5 g cm^{-3}).

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The progressive crystallisation of the product is obtained by repeated heating of the precursor in flowing oxygen, with intermediate grinding (the typical dwell time is 10 h and the heating and cooling rate 300 °C h^{-1}). The crystallisation is followed by X-ray diffraction.

The TGA analysis of the as-prepared composition was made from the reduction under flowing hydrogen at 250 °C, followed by an annealing at 450 °C in order to achieve the total reduction into La_2O_3 and Ni and Cu metals.

2.2. Structural characterisation

X-Ray powder diffraction (XRPD) data (Philips PW3020 goniometer, Cu-Kα) were obtained from diffractograms recorded in the angular 2θ range 5–120°. Neutron powder diffraction (NPD) data were collected at room temperature on the high resolution D2B diffractometer (ILL Grenoble) by using the monochromatic wavelength $\lambda = 0.1594$ nm. The volume of our sample (~ 1.3 cm^3 for 3 g of powder) allowed us to obtain a satisfactory noise ratio (noise/signal $<3\%$) for the diffractogram recorded in the 2θ range 10–160° during 10 h. The Rietveld profile analysis (for XRPD and NPD) was performed with the Fullprof program.[10]

Samples for electron microscopy were prepared by grinding powders in ethanol. The small particles in suspension were deposited onto a holey carbon film. The electron diffraction was carried out with a JEOL 200 CX electron microscope. Energy dispersive spectroscopy (EDS) analyses were performed on one hundred crystallites. The reciprocal space for several of them was reconstructed by tilting around the crystallographic axes.

3. Results and discussion

3.1. Synthesis and thermal behaviour

Several samples have been prepared by using the above described procedure. They were heat treated at increasing temperatures in O_2. At 950 °C, in most cases, the XRPD pattern is that of a perovskite with no trace of La_2O_3, NiO nor CuO, suggesting that the reaction of formation of a perovskite phase has developed (Fig. 1). This XRPD pattern remains unchanged after a subsequent annealing (10 days) of the powder at 1000 °C in O_2. The as-prepared composition begins to decompose at 1150 °C into a mixture of La_2NiO_4 and La_2CuO_4 plus NiO and CuO. This is a higher temperature than for $LaNiO_3$ and $LaCuO_3$. In some cases, the samples already show La_2NiO_4 and/or La_2CuO_4 reflections after treatment at 750 °C. This probably comes from an uncontrolled auto-ignition that sometimes occurs during the microwave dehydration step.

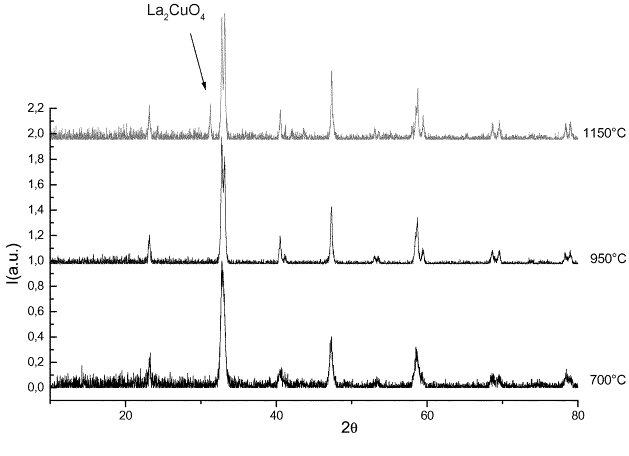

Fig. 1 XRPD pattern of $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ after crystallisation at different temperatures in an oxygen flow.

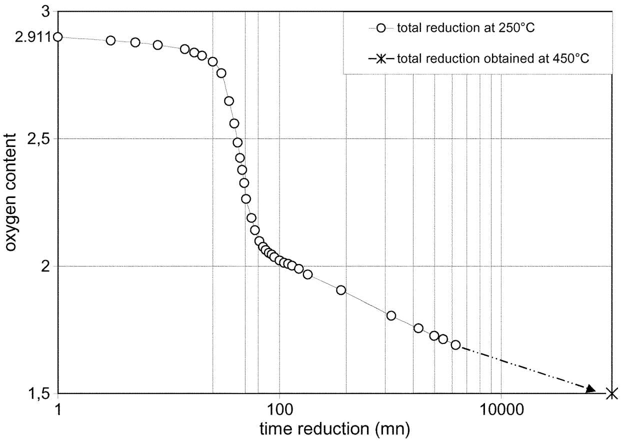

Fig. 2 TGA analysis of $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ under hydrogen flow.

TGA results (Fig. 2) point to a mean oxygen content of the composition $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ close to 2.91(2) ($\delta \leqslant 0.09$). This is the most striking difference with the results of the synthesis based on usual solid state reactions,[8] which point to the systematic formation of largely oxygen deficient phases $\delta \geqslant 0.21$. From this, it is clear that the formation of a strongly oxidised composition requires the use of the organic gelification as a precursor step. Nevertheless, it cannot be stated that the (III) oxidation state of both Cu and Ni has been reached. As a matter of fact, when heated at 900 °C under 150 bar of O_2, some slight modification of the relative intensities of the diffraction peaks (Fig. 3) point to a likely further evolution of the oxidation state of Cu.

3.2. A rhombohedral perovskite type phase by diffraction (XRPD, NPD)

Indexing the XRPD data was made in an hexagonal cell. The refined values of the cell parameters $a = 0.54751(1)$ nm and $c = 1.31696(3)$ nm are intermediate between those reported for $LaNiO_3$[10] and $LaCuO_3$[12] (Table 1).

To solve the structure we used the structural model of the rhombohedral $LaMO_3$ perovskites, space group $R\bar{3}c$.[11] Atomic positions, oxygen site occupancy, Ni/Cu balance and thermal parameters for La, Ni, Cu and O were refined in the Rietveld calculation procedure. The results are given in Table 1 together with those reported for $LaNiO_3$[11] and $LaCuO_3$[12] and the experimental and calculated XRPD and NPD patterns are compared in Fig. 4. However some very weak reflections are not taken into account by this model. As ensured by the value of the R_B reliability factor 4.6, the validity of the rhombohedral model is not doubtful. Still, on the basis of the presence of very weak extra peaks, especially in the NPD data,

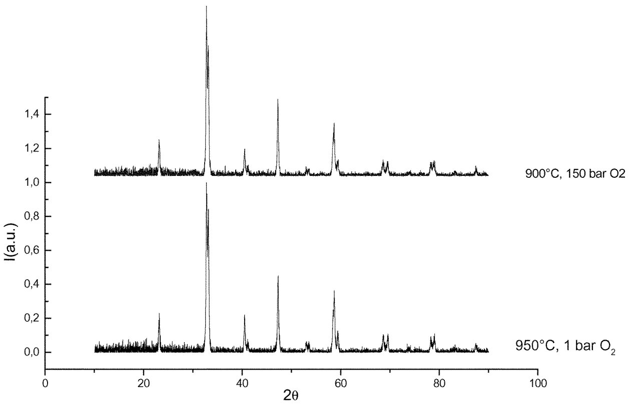

Fig. 3 XRPD pattern of $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ after annealing in oxygen.

Table 1 Atomic parameters of the structure of the $LaMO_3$ perovskites (M = Ni, Cu)

	$LaNiO_3$[a]	$LaNi_{0.5}Cu_{0.5}O_{3-\delta}$[b]	$LaCuO_3$[c]
a_H	0.54573(1)	0.54751(1)	0.550195(1)
c_H	1.31462(3)	1.31696(4)	1.32124(4)
B_{La}[d]	0.36(2)	0.57(4)	Anisotropic motion
B_M M = Ni, Cu[d]	0.21(2)	0.52(5)	Anisotropic motion
Ni/Cu	1/0	0.53(2)/0.47(2)	0/1
x_O	0.5456(2)	0.5466(4)	0.5487(4)
B_O[d]	0.55(2)	1.10(5)	Anisotropic motion
O occ.	3	2.96(3)	3
Reliability	R_B 4.5	R_B 4.61	[c]R_{WP} 5.3

[a]Ref. 10. [b]This work: results of coupled XRD and NPD calculations. [c]Ref. 12; only R_{wp} is available. [d]$nm^2 \times 10^{-2}$.

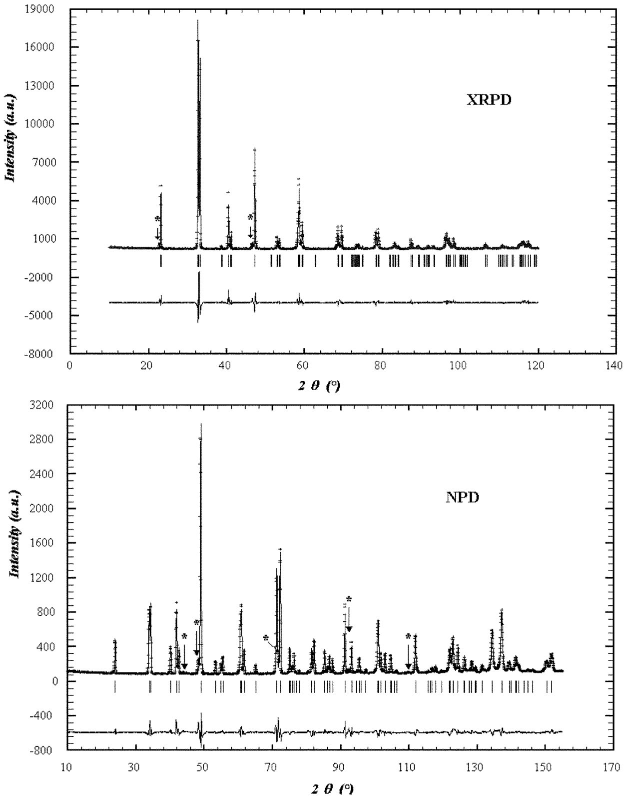

Fig. 4 Experimental (dots), calculated and difference (solid lines) XRPD and NPD patterns for $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$. Vertical bars indicate the Bragg angle positions. * denotes some very weak reflections not taken into account in the model.

Table 2 Metal–oxygen distances (nm) and M–O–M (°) angles (M = Ni, Cu)

		$LaNiO_3$[a]	$LaNi_{0.5}Cu_{0.5}O_{3-\delta}$	$LaCuO_3$
La–O	× 3	0.2480(2)	0.2482(2)	0.2483(3)
La–O	× 6	0.2710(1)	0.2717(1)	0.2728(1)
La–O	× 3	0.2978(2)	0.2993(2)	0.3019(3)
Ni(Cu)–O	× 6	0.1935(1)	0.1941(1)	0.1951(1)
M–O–M°		165.2(1)	164.9(1)	164.2(2)

[a]Ref. 10.

the "structural purity" of the composition $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ may be questionable.

In any case, these results well compare with those of $LaNiO_3$ and $LaCuO_3$. As expected, the calculated oxygen composition 2.96(3) is rather close to three and the Ni/Cu balance, within the standard deviation, can be considered as equal to one. The values of the M–O distances and M–O–M angles, namely 0.1941 nm and 164.9°, remarkably rank within the narrow range of values corresponding to both nickelate and cuprate (Table 2). Consequently, both XRPD and NPD results point to the existence of an homogeneous solid solution of $LaNiO_3$ and $LaCuO_3$ corresponding to the composition $LaNi_{0.5}Cu_{0.5}O_{2.96}$.

3.3. EDS analyses: a pseudo solid solution of two cupronickelate

EDS analyses undertaken to check the Cu/Ni balance in microcrystals give evidence for a rather unexpected phenomenon. Instead of finding an equal amount of Cu and Ni, as expected from powder diffraction results, two well defined sets of compositions of microcrystals are revealed. The first set regards copper rich microcrystals whose composition can be considered as fixed: Cu/Ni = 0.67/0.33. The second set of microcrystals is nickel rich with a small homogeneity range: $0.67 \geqslant Ni \geqslant 0.59$ balanced by $0.33 \leqslant Cu \leqslant 0.41$, with a mean value close to Cu = 0.37 and Ni = 0.63. A subsequent annealing at 1000 °C for 10 days under flowing oxygen does not modify this result stressing that it corresponds to a stable thermodynamic state.

The symmetry of the nickel rich microcrystals is typical of rhombohedral $LaNiO_3$, as illustrated by the two ED patterns of Fig. 5a and 5b. Owing to the absence of extra reflections, diffuse streaks and any sign of long range and short range ordering as well, one can think of a random distribution of Cu and Ni atoms in a ReO_3 type network. Concerning the copper rich composition $LaNi_{0.33}Cu_{0.67}O_{3-\delta}$, the ED results give evidence for frequent faint extra reflections, pointing to the existence of superstructures of the perovskite cell. A systematic study was not performed, but the more likely cell is the $[2a_p\sqrt{2} \times 2a_p\sqrt{2} \times a_p]$ orthorhombic one. In this respect, the existence of some very weak extra peaks in the NPD and in the XRPD pattern mentioned above, is well accounted for when a rhombohedral phase plus an orthorhombic one is considered in Rietveld calculations (Fig. 6). Rough values of the parameters of the orthorhombic cell can be proposed: a = 10.90 Å; b = 10.88 Å; c = 3.9 Å. Interestingly, the existence of this superstructure meets a similar result reported by Bazuev *et al.*[8] for the composition $LaNi_{0.25}Cu_{0.75}O_{2.63}$.

As a logical consequence, the oxygen deficiency is assumed to concern only the cuprate, because a distortion from the rhombohedral structure can be safely disregarded in the nickel rich microcrystals stressing an oxygen stoichiometry equal to 3. A tentative calculation of the oxygen content of the cuprate, on the basis of the mean value found in the as-prepared starting sample, gives for the cuprate $LaNi_{0.33}Cu_{0.67}O_{3-\delta}$ a value close to 2.86 (δ = 0.14) which value means that approximately 58% of the Cu atoms show the oxidised (III) state.

4. Concluding remarks

The composition $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ is a pseudo solid solution composed of two sets of cupronickelates on a nanoscale

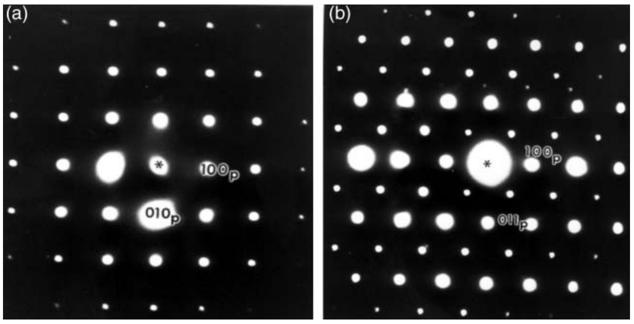

Fig. 5 $[001]_p$ (a) and $[011]_p$ (b) ED patterns. The suffix p refers to the cubic perovskite subcell.

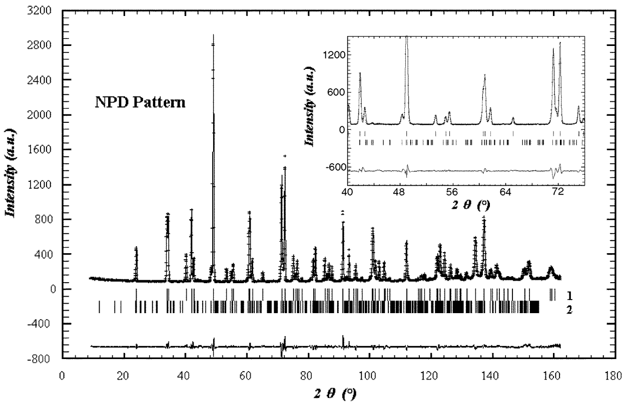

Fig. 6 Experimental (dots), calculated and difference (solid lines) NPD patterns of two phases (rhombohedral and orthorhombic). Rietveld calculation of $LaNi_{0.5}Cu_{0.5}O_{3-\delta}$ (see text).

($<$100 nm), enriched in nickel and copper respectively: the fully oxidised solid solution $LaNi_{1-x}Cu_xO_3$ ($0.33 \leqslant x \leqslant 0.41$) and the oxygen deficient phase $LaCu_{0.67}Ni_{0.33}O_{2.86}$. This material has metallic properties down to liquid helium temperatures as expected from both $LaNiO_3$ and $LaCuO_3$ transport properties.

The very likely explanation of such a result is found in the extreme difficulty to oxidise Cu(II) atoms into Cu(III). Above all, it was checked that the preparation of the pure cuprate $LaCuO_3$ is not possible by the sol–gel method. Interestingly, the simultaneous presence of nickel and copper atoms during the sol–gel synthesis allows some synergetic oxidation of Cu(II) into Cu(III) to take place. Supplementary attempts to prepare other $LaNi_{1-x}Cu_xO_{3-\delta}$ compositions prove that the oxidation of a significant amount of copper atoms occurs when the content of nickel is not smaller than 40%, *i.e.* the composition $LaNi_{0.4}Cu_{0.6}O_{3-\delta}$, which confirms the existence of the pseudo solid solution herein described. The composition of the copper rich cupronickelate $LaCu_{0.67}Ni_{0.33}O_{2.86}$ found in the pseudo solid solution, seems to be fixed by an amount of Cu(III) which cannot be overcome during the sol–gel synthesis. As a matter of fact, the amount of Cu(III) which exists in La $Ni_{0.33}Cu_{0.67}O_{2.86}$ (0.42) is similar to that found in the copper rich limit $LaNi_{0.59}Cu_{0.41}O_3$ of the fully oxidised solid solution (0.41). Finally, it has to be emphasised that the presence of Cu(II) atoms cannot be prevented if the amount of copper exceeds $x = 0.41$. Moreover, it triggers very quickly the formation of an eight times larger ordered supercell, at the expense of the rhombohedral type solid solution which does not tolerate the presence of oxygen vacancies. The simultaneous presence of both Cu(II); Cu(III) and Ni(III) might be an interesting medium for electrocatalysis.

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