Effect of Sr content on the crystal structure and electrical properties of the system $La_{2-x}Sr_xNiO_{4+\delta}$ $(0 \le x \le 1)$ †

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Materials formulated as $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$) have been prepared and investigated by high-resolution neutron powder diffraction in order to correlate the structural variation induced by the incorporation of Sr into the crystal lattice with the electronic and thermal properties of each material. The evolution of the electrical conductivity and thermal expansion coefficients with temperature have been determined in order to study the potential use of these compounds as cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFC). These oxides show a good thermal expansion coefficient (TEC = $11-13 \times 10^{-6} \text{ K}^{-1}$), and high electronic conductivity up to 273 S cm⁻¹. It is noticeable that a great enhancement of the electrical conductivity with the Sr content is concomitant with the shortening of the Ni-O1 bond length.

Introduction

Solid oxide fuel cells (SOFCs) are promising green energy sources because of their high energy conversion efficiency with very low emission of air pollutants.^{1,2} For a viable commercialisation of the SOFC technology, one of the most important challenges is the reduction of the temperature operation below 800 °C. This requires new materials, especially cathode materials with increased electrocatalytic activity, and characterized by an enhanced oxygen transport in addition to the required electronic conductivity.

Recently, K_2NiF_4 type oxides have attracted considerable attention as alternative cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC) due to their interesting transport properties. They present high catalytic activity for oxygen reduction, good ionic and electronic conductivity over a wide temperature range and an adequate thermal expansion coefficient that match with those of the other cell components.^{3,4} The crystal lattice of K₂NiF₄ structures can be described as a stacking of perovskite layers, ABO₃, alternating with AO rock salt layers. The ionic conductivity of these materials is mainly associated to the excess oxygen (δ) accommodated in interstitial form in their AO layers.⁵ La₂NiO_{4+ δ} is a widely studied compound⁶⁻¹⁰ with very appealing transport properties.11 However, it lacks adequate electronic conductivity, which can be improved by doping the A position with alkaline-earth ions. In this regard, calcium and strontium are suitable elements with comparable cationic sizes to that of lanthanum. Since Ca-doping was shown to have little influence on the electrical conductivity of substituted

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La2NiO4 phases,12 the chemical replacement of La by Sr in the series $La_{2-x}Sr_xNiO_{4+\delta}$ was thus studied to monitor structural and transport effects.

During recent years great efforts have been devoted to understand the different electrical behaviour of $La_{2-x}Sr_xNiO_{4+\delta}$ from the that of the isostructural high-temperature superconducting copper oxides $La_{2-x}Sr_{x}CuO_{4+\delta}$.¹³⁻¹⁵ However, there have been much fewer studies conducted to determine the viability of these materials as mixed ionic electronic conductor (MIEC) cathodes for IT-SOFC. The aim of this work is to investigate the evolution of the structure of the system $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$) as a function of the strontium content and its influence on the electric conductivity and thermal expansion; our conclusions are helpful for selecting the most suitable composition as a cathode material for IT-SOFCs.

2 Experimental

 $La_{2-x}Sr_{x}NiO_{4+\delta}$ (x = 0, 0.10, 0.25, 0.50, 0.75, 1) oxides were synthesized via a nitrate-citrate route. Stoichiometric amounts of analytical grade La2O3, Ni(NO3)2·6H2O (99%) and Sr(NO3)2 were dissolved in nitric acid. Citric acid was added in a large excess (3.3 mol per mol of $La_{2-x}Sr_xNiO_{4+\delta}$) with continuous stirring. The obtained solution was dehydrated and slowly heated until self-combustion of the precipitate. The obtained precursors were calcined at 600 °C for 30 min and finally fired in air between 950 and 1200 °C for 8 h.

In order to assess phase purity, X-ray diffraction (XRD) analyses were performed in a Philips "X Pert-MPD" diffractometer using Cu-Ka radiation, $\lambda = 1.5406$ Å. The diffraction patterns were recorded in the 2θ range 20–80° in steps of 0.04°. The oxygen content of the samples was determined by iodometric titration against a standardized potassium thiosulfate solution. Neutron powder diffraction (NPD) data were collected at room temperature for all the compounds using the high-resolution diffractometer HRPT¹⁶ at the SINQ spallation source at the Paul Scherrer Institut (Villigen, Switzerland). The high intensity mode ($\Delta d/d \ge 2 \times 10^{-3}$) was selected, with a neutron wavelength $\lambda = 1.494$ Å within the angular 2θ range 5–165°. 3 g of each sample were contained in a

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vanadium can. The collection time was 2 h per pattern. Diffraction data were analysed by the Rietveld method, using the FULLPROF program,¹⁷ with the use of its internal tables for scattering lengths. The line shape of the diffraction peaks was generated by a pseudo-Voigt function and the background refined to a fifth-degree polynomial. In the final run the following parameters were refined: background coefficients, zero point, half width, pseudo-Voigt and asymmetry parameters for the peak shape, scale factor and unit-cell parameters. Positional and occupancy factors for oxygen atoms and isotropic thermal factors were also refined for NPD data. The coherent scattering lengths for La, Sr, Ni and O were 8.240, 7.020, 1.030 and 5.803 fm, respectively.

Dense compounds are required for the measurements of thermal expansion coefficient and electrical conductivity. The prepared powders were pressed into pellets (10 mm in diameter and 1.4 mm think) using poly(ethylene glycol) as a binder and 3 tons of uniaxial pressure during 5 min. The sintering behaviour of green compacts and thermal expansion of dense ceramics were studied using a Linseis L75/1550C dilatometer with a heating rate of 5 °C min⁻¹.

The electrical conductivity of the system was measured in air by the DC four-probe method. The measurements were carried out in the temperature range 350–950 °C. The dense ceramics were placed onto an alumina support and four platinum wires contacts were pressed onto the sample using a spring loaded alumina tube. A constant current load of 500 mA was applied by a potentiostat/galvanostat (EG & G Model 263) and the potential drop recorded by a Fluke 179 True RMS Multimeter.

3 Results and discussion

The compounds $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0, 0.10, 0.25, 0.50, 0.75, 1) were successfully obtained as black, well crystallized powders. As shown in Fig. 1, XRD data showed no evidence of impurities or starting materials in the prepared powders. However more exhaustive analysis of the structure by neutron powder diffraction revealed the existence of small NiO impurity peaks. Due to the relatively strong scattering of Ni atoms, the small amount of NiO detected is quite prominent in the neutron powder diffraction pattern. The maximum weight fraction value reached was of around 18% in LaSrNiO_{4+δ} and 8% in La_{1.25}Sr_{0.75}NiO_{4+δ}. For Sr contents lower than 0.75 the NiO fraction is negligible, suggesting that Sr solubility in the system sharply decreases for Sr content >0.50 per formula unit.

Iodometric titration shows that the samples with low Sr content (x = 0.1, 0.25) are able to accommodate some oxygen excess, while samples with $x \ge 0.5$ are sub-stoichiometric or oxygen deficient. The δ values are 0.17, 0.14, 0.036, -0.031 for x = 0, 0.1, 0.25 and 0.5, respectively. This is in agreement with the results obtained by previous researchers¹⁸ and is due to the hole-doping effect induced by the introduction of Sr into the La sublattice, implying the oxidation of Ni²⁺ to Ni³⁺ to preserve the charge neutrality and reducing the trend to incorporate interstitial oxygen into the crystal structure.

The crystal structure refinement was performed from highresolution NPD data collected at room temperature and wavelength $\lambda = 1.494$ Å. For the x = 0 sample, the orthorhombic Fmmm model proposed by Jorgensen et al.6 was considered. La was located at 8i (0,0,z) positions, Ni at 4a (0,0,0) sites, and the four crystallographically independent oxygen atoms, O1-O4, at 8e (1/4, 1/4, 0), 8i (0, 0, z), 32p (x, y, z) and 16j (1/4, 1/4, z), respectively. The O4 site corresponds to interstitial oxygen atoms. The insertion of these additional oxygen atoms into the lattice causes a displacement of the axial O2 from its normal location to a new axial O3 position. This is indeed observed, since the refinement of oxygen site occupancies allows us to detect a large vacancy concentration at the O2 positions. In agreement to this, the occupancy of one O4 interstitial position would be expected to displace four neighbouring O2 atoms into the O3 axial site. Fig. 2 shows the local defect structure created by the insertion of the O4 interstitial oxygens. The refinement of the La₂NiO_{4+ δ} structure



Fig. 1 XRD patterns of $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$), collected with Cu-Ka radiation.



Fig. 2 View of the K_2NiF_4 structure showing the localization of the interstitial atoms (O4) in the LaO rock salt layer. In the NiO₆ octahedra, O1 represents the equatorial atoms whereas O2 and O3 are the axial oxygens.

Table 1 Structural parameters after the Rietveld refinement of NPD data for La₂NiO₄₊₆ at RT. Space group *Fmmm*, a = 5.4563(2) Å, b = 5.4630(2) Å, c = 12.7049(3) Å and V = 78.70(2) Å³ with $\chi^2 = 1.78$, $R_p = 2.75$, $R_{wp} = 3.61$, $R_{exp} = 2.71$ and $R_1 = 3.70$

Atom	Site	x	у	Ζ	$B/Å^2$	f_{occ}
La	8i	0	0	0.3592(2)	1.01(3)	1
Ni	4a	0	0	0	1.05(4)	0.5
01	8e	0.25	0.25	0	1.36(5)	1
O2	8i	0	0	0.1752(9)	1.8(1)	0.64(2)
O3	32p	-0.055(5)	-0.059(5)	0.172(2)	1.8(1)	0.36(2)
O4	16j	0.25	0.25	0.223(2)	1.1(5)	0.09(2)

based on this model led to a good fit between the calculated and observed NPD profiles ($R_{\text{Bragg}} = 3.70$). Table 1 summarises the structural parameters obtained for this x = 0 sample.

The subsequent analysis of the NPD patterns along the series for x > 0 evidenced the existence of a structural transition from the orthorhombic *Fmmm* to the tetragonal *I4/mmm* symmetries upon the incorporation of Sr into the crystal lattice. In order to correlate the different structures obtained, the *F4/mmm* setting was used¹⁹ instead of the standard *I4/mmm* space group setting.²⁰ In *F4/mmm*, La, Sr and O2 atoms are located at 8e (0,0,z) sites, Ni at 4a (0,0,0), O1 at 8c (1/4, 1/4, 0), O3 at 32m (*x*,*y*,*z*) and the interstitial O4 atoms at 16e (1/4,1/4,1/4) positions. We observed a similar behaviour to that described by Jorgensen *et al.*⁶ concerning the displacement of the O3 oxygen atoms with the insertion of the interstitial O4 oxygens. In this regard, the complementary occupancies of the axial O2 positions and the displaced axial O3 oxygens were constrained to 1.00, and the isothermal factors were also constrained.

For the samples $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0.1,²¹ 0.25 and 0.5) the refinement in this teragonal model led to good reliability R_{Bragg} factors (~3%). As is shown in Table 2 and Fig. 3, in this compositional range *a* and *b* unit-cell parameters decrease with the Sr content while *c* increases leading to an overall decrease of



Fig. 3 Variations of lattice parameters for the system $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$) as a function of strontium content: (a) *a* and *b* parameters; (b) *c* parameter; (c) unit cell volume, *V*.

the volume cell. This is in agreement with the expected oxidation of Ni^{2+} to Ni^{3+} upon chemical doping with Sr. The decrease in the volume cell also reveals the minor tendency to accommodate excess of oxygen of this materials as the Sr content increases. In our case, the introduction of the interstitial position (O4) in the refinement was only required for Sr content lower than 0.5 per formula unit.

The analysis of the diffraction data of the Sr-rich members of the series, $La_{1.25}Sr_{0.75}NiO_{4+\delta}$ and $LaSrNiO_{4+\delta}$ reveals a very poor fitting between the experimental and the calculated NPD

Table 2 Structural parameters after the Rietveld refinement of NPD data for $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0.1, 0.25 and 0.5) at RT. Space group *F4/mmm*, La, Sr and O2 at 8e (0,0,z) sites, Ni at 4a (0,0,0), O1 at 8c (1/4,1/4,0), O3 at 32m (x,y,z) and O4 at 16e (1/4,1/4,1/4) positions

		$La_{1.9}Sr_{0.1}NiO_{4+\delta}$	$La_{1.75}Sr_{0.25}NiO_{4+\delta}$	$La_{1.5}Sr_{0.5}NiO_{4+\delta}$	
a = b/Å		5.45243(7)	5.4288(2)	5.40079(9)	
c/Å		12.6927(2)	12.7032(5)	12.7331(3)	
$V/\text{\AA}^3$		377.24(1)	374.39(2)	371.41(1)	
La (Sr)	Ζ	0.3616(1)	0.3614(2)	0.3616(2)	
	$B/Å^2$	0.50(2)	0.41(4)	0.42(2)	
Ni	$B/Å^2$	0.62(3)	0.68(4)	0.43(3)	
01	$B/Å^2$	0.79(3)	0.70(6)	0.41(4)	
O2	Ζ	0.1742(3)	0.176(2)	0.1736(2)	
	$B/Å^2$	0.48(7)	0.1(1)	1.15(4)	
O3	x = y	-0.5233(1)	-0.041(5)		
	Z	0.1742(2)	0.171(2)		
	$B/Å^2$	0.48(7)	0.1(1)		
O4	$B/Å^2$	5(1)	1(1)		
χ^2		5.41	12.7	11.70	
$R_{\rm p}$ (%)		4	5.98	5.53	
R_{wp} (%)		5.31	8.29	7.49	
$R_{\rm exp}$ (%)		2.28	2.32	2.19	
$R_{\rm I}$ (%)		3.19	3.47	3.14	

profiles due to the appearance of extra features or shoulders in the experimental profile (Fig. 4(a)). Attempts to refine these data in less symmetric space groups did not improve the fitting. Preliminary studies in LaSrNiO₄ revealed the coexistence of



Fig. 4 Observed (points) and calculated (full curve) neutron diffraction profiles for $La_{1.25}Sr_{0.75}NiO_{4+\delta}$ using (a) a single phase *F4/mmm* model, and (b) a two phase *F4/mmm* model. In both cases, the second row of tick marks indicate the Bragg reflections of a NiO impurity.

three tetragonal K₂NiF₄ phases with different Sr contents and slightly different unit-cell parameters.²² In the present case, the introduction of two tetragonal phases allowed us to satisfactorily improve the profile fitting. Fig. 4(b) illustrates the final refinement for La_{1.25}Sr_{0.75}NiO_{4+δ}, successfully performed with a three-phase model consisting on two tetragonal K₂NiF₄ phases and one NiO minor impurity phase. Table 3 lists the structural parameters obtained for both tetragonal phases present in La_{1.25}Sr_{0.75}NiO_{4+δ} and LaSrNiO_{4+δ} samples. It is worth remarking that the materials formulated as La_{2-x}Sr_xNiO_{4+δ} (x = 0.5, 0.75 and 1) were refined with an oxygen sub-stoichiometric model according with the results obtained from iodometric analysis; hence O4 was not defined and the axial positions O2 and O3 were not split.

It is evident that the coexistence of two K₂NiF₄ phases for high x > 0.5 values is due to Sr segregation giving rise to Srrich and Sr-poor phases. The Sr content of each phase could not be refined from the neutron profiles given the similar scattering lengths of La and Sr atoms. However, we can estimate the Sr contents of each particular sample from the unit-cell parameters vs. composition diagrams published elsewhere.23 Therein, for the samples with nominal compositions $La_{1.25}Sr_{0.75}NiO_{4+\delta}$ and LaSrNiO_{4+ δ}, the majority phases present a lower Sr content, with an approximate value of x = 0.6 and 0.5, respectively. The minority phases in both samples have an approximate Sr content of x = 0.8and x = 0.6, respectively. This means that the sample with nominal composition LaSrNiO₄ has, in fact, a lower Sr content than that with nominal x = 0.75, suggesting that the incorporation of Sr has reached a plateau under the synthesis conditions for x = 0.75. In fact, Fig. 3 shows that the *a* parameter and the volume display a broad minimum and maximum at x = 0.75.

Table 4 lists the interatomic distances obtained for each sample. The Ni–O1 and Ni–O2 bond lengths are plotted vs. Sr content in Fig. 5. The Ni–O1 bond length (Fig. 5(a)) decreases with the Sr content up to x = 0.75, which in fact corresponds to the Srrichest sample. This decrease is concomitant with the progressive oxidation of Ni²⁺ to Ni³⁺, and can be related to the observed

Table 3 Structural parameters after the Rietveld refinement of NPD data for $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0.75 and 1) with two tetragonal *F4/mmm* phases in each material at RT. La, Sr and O2 at 8e (0,0,z) sites, Ni at 4a (0,0,0) and O1 at 8c (1/4,1/4,0), positions

0()

Table 4Interatomic distances for the system $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$) system determined from Rietveld refinement of power neutron diffraction

Bond length/ x	0	0.1	0.25	0.5	0.75(1)	0.75(2)	1(1)	1(2)
$La(Sr)-O1 \times 4$	2.632(1)	2.608(1)	2.605(2)	2.598(2)	2.598(3)	2.586(7)	2.564(4)	2.647(5)
La(Sr)–O2	2.34(1)	2.379(4)	2.35(3)	2.393(4)	2.412(7)	2.46(2)	2.495(8)	2.34(2)
La(Sr)–O2 × 4^a	2.766(2)	2.7639(7)	2.756(5)	2.7374(6)	2.728(1)	2.721(2)	2.735(1)	2.718(2)
$La(Sr) - O2 \times 2$	2.763(2)	~ /						
La(Sr)–O3	2.42(2)	2.413(2)	2.44(2)					
La(Sr)–O3	2.46(3)	2.4992(3)	2.54(3)					
La(Sr)–O3	2.48(2)							
La(Sr)–O4	2.59(1)	2.3923(9)	2.384(2)					
La(Sr)–O4	2.19(1)	~ /						
$Ni-O1 \times 4$	1.9303(1)	1.9277(0)	1.9194(0)	1.9095(0)	1.9063(0)	1.9109(2)	1.9081(1)	1.9099(2)
Ni–O2 \times 2	2.22(1)	2.211(4)	2.24(3)	2.211(3)	2.180(6)	2.06(1)	2.158(6)	2.14(2)
Ni–O3	2.22(2)	2.2475(0)	2.19(2)					
For the $x = 0$ compound, defined in <i>Fmmm</i> , the multiplicity of La(Sr)–O2 distances is 2.								

shrinkage of the *a* and *b* parameters. The Ni–O2 distances for x = 0, 0.1 and 0.25 must be averaged with Ni–O3, since O2 and O3 are both axial positions slightly split as a consequence of the introduction of the O4 interstitials. An overall decrease of the Ni–O2 axial bond lengths (Fig. 5(b)) is also observed, indicating the mentioned charge transfer effect upon substitution of La³⁺ by Sr²⁺.

Aiming to determine the mechanical compatibility of our materials with the other cell components, thermal expansion measurements of the dense ceramics were carried out in air in the temperature range 25–1000 °C. Fig. 6 illustrates the thermal expansion coefficients (TEC) obtained at 600 and 800 °C. It is remarkable that the observed values tend to increase with the introduction of Sr, exhibiting maximum values for the x = 0.75 compound. This might be ascribed to the increase of the shortest La–O2 distance with the Sr content, responsible for the cohesion between the perovskite and the rock-salt layer (see Table 4).

The total electrical conductivity (σ) of sintered ceramics was determined under air using the four-probe method in the temperature range 350–950 °C. Fig. 7 shows the σ vs. 1000/*T* curves. The electrical conductivity requirement for SOFC cathode material is about 100 S cm⁻¹ at the operating temperature. It is remarkable that the conductivity increases from 50 S cm⁻¹ (at 1000 °C) for the undoped $La_2NiO_{4+\delta}$ compound to values well above 100 S cm⁻¹ for most of the Sr-doped $La_{2-x}Sr_xNiO_{4+\delta}$ (0.5 $\leq x \leq 1$). The total electrical conductivity clearly increases with the Sr content up to 273 S cm⁻¹ at 600 °C for the sample with x = 0.75. Although the structural data have been collected at room temperature, and the conductivity measurements cover the range 350–950 °C, we are tempted to correlate the observed increase in conductivity with x to the contraction of the Ni–O1 equatorial bond lengths previously described. This can be understood as a result of the increment of charge carriers in the conduction band upon hole injection concomitant to the Sr chemical doping. We think that the hole injection effect together with the more basic character of Sr²⁺ vs. La²⁺ leads to more covalent, shorter Ni–O chemical bonds with a higher transfer integral which gives rise to an improved charge transport across the solid. The total conductivity is slightly lower for the sample with nominal composition LaSrNiO₄ than that of the x = 0.75 compound, since the actual Sr content is higher in this latter sample, as demonstrated in the neutron study. Fig. 7 shows a metal-insulator transition around 450 °C for La2NiO4+8, as described elsewhere in our previous work,24 whereas $La_{2-x}Sr_xNiO_{4+\delta}$ samples $(0.1 \le x \le 1)$ present a metallic behaviour in the studied temperature range.



Fig. 5 Variation of Ni–O bond lengths for the system $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$) as a function of strontium content: (a) Ni–O1; (b) Ni–O2.



Fig. 6 Evolution of the thermal expansion coefficient (TEC) for the system $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ($0 \le x \le 1$) as a function of strontium content calculated from dilatometric data in air at 600 and 800 °C.

4 Conclusions

A NPD study shows that, whereas $La_2NiO_{4+\delta}$ can be structurally defined in the orthorhombic *Fmmm* space group, the members of the series $La_{2-x}Sr_xNiO_{4+\delta}$ for moderate Sr contents, up to x = 0.5 can be refined in the tetragonal *F4/mmm*, and the Sr-



Fig. 7 Electrical conductivity for the system $La_{2-x}Sr_xNiO_{4+\delta}$ ($0 \le x \le 1$) in air at different temperatures.

rich members of the series (x = 0.75, 1) require the presence of two K_2NiF_4 type phases to explain the broadening of the highangle reflections, accounting for a Sr-segregation for x > 0.50. The structural parameters, in particular Ni-O bond lengths and (La,Sr)-O distances can be correlated with the physical properties, which allow us to propose the materials of the series La_{2-x} $Sr_x NiO_{4+\delta}$ ($0 \le x \le 1$) as appealing cathode-material candidates for IT-SOFC. The electronic conductivity values obtained is adequate for that required for cathode materials at SOFC. The highest conductivity was 273 S cm⁻¹ at 600 °C for La_{1.25}Sr_{0.75}NiO_{4+δ}. Their thermal expansion coefficients are close to that of the electrolytes usually utilized at SOFC (8YSZ, CGO) (11-13 × 10^{-6} K⁻¹). Although this magnitude increases with the Sr content, leading to values up to $17 \times 10^{-6} \text{ K}^{-1}$, high thermal stability is still retained. The presence of a majority Sr-rich phase and a minority Sr-deficient phase in the last members of the series could account for the change in conductivity behaviour observed for $La_{1.25}Sr_{0.75}NiO_{4+\delta}$ and $LaSrNiO_{4+\delta}$.

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References

- 1 O. Yamamoto, Electrochim. Acta, 2000, 45, 2423-2435.
- 2 P. Sing and N. Q. Minh, Appl. Ceram. Technol., 2004, 1, 5-15.
- 3 V. V. Kharton, A. P. Viskup, E. N. Naumovich and F. M. B. Marques, *J. Mater. Chem.*, 1999, **9**, 2623–2629.
- 4 A. Demourgues, A. Wattiaux, J. C. Grenier, M. Pouchard, J. L. Soubeyroux, J. M. Dance and P. Hagenmuller, J. Solid State Chem., 1993, 105, 458–468.
- 5 V. V. Kharton, A. P. Viskup, A. V. Kovalevsky, E. N. Naumovich and F. M. B. Marques, *Solid State Ionics*, 2001, 143, 337– 353.

- 6 J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards and D. G. Hinks, *Phys. Rev. B: Condens. Matter*, 1989, 40, 2187–2199.
- 7 A. Mehta and P. J. Heaney, *Phys. Rev. B: Condens. Matter*, 1994, **49**, 539–571.
- 8 D. E. Rice and D. J. Buttrey, J. Solid State Chem., 1993, 105, 197–210.
- 9 J. M. Bassat, P. Odier and J. P. Loup, J. Solid State Chem., 1994, 110, 124–135.
- 10 S. J. Skinner, Solid State Sci., 2003, 5, 419-426.
- 11 V. V. Kharton, A. A. Yaremchenko, A. L. Shaula, M. V. Patrakeev, E. N. Naumovich, D. I. Logvinovich, J. R. Frade and F. M. B. Marques, *J. Solid State Chem.*, 2004, **177**, 26–37.
- 12 J. P. Tang, R. I. Dass and A. Manthiram, *Mater. Res. Bull.*, 2000, 35, 411–424.
- 13 J. L. Routbort, S. J. Rothman, B. K. Flandermeyer, L. J. Nowicki and J. E. Baker, J. Mater. Res., 1988, 3, 116–121.
- 14 G. Xiao, M. Z. Cieplak, J. Q. Xiao and C. L. Chien, Phys. Rev. B: Condens. Matter, 1990, 42, 8752–8755.
- 15 M. J. Sayagués, M. Vallet-Regí, J. L. Hutchison and J. M. Gonzalez-Calbet, J. Solid State Chem., 1996, 125, 133–139.

- 16 P. Fischer, G. Frey, M. Koch, M. Koennecke, V. Pomjakushin, J. Schefer, R. Thut, N. Schlumpf, R. Buerge, U. Greuter, S. Bondt and E. Berruyer, *Physica B*, 2000, 46, 276.
- 17 J. Rodriguez-Carvajal, Physica B, 1993, 192, 55-69.
- 18 J. Rodriguez-Carvajal, M. T. Fernández-Diaz and J. L. Martinez, J. Phys.: Condens. Matter, 1991, 3, 3215–3234.
- 19 J. B. Goodenough and S. Ramaseshan, Mater. Res. Bull., 1982, 17, 383–390.
- 20 J. E. Millburn, M. A. Green, D. A. Neumann and M. J. Rosseinsky, J. Solid State Chem., 1999, 145, 401–420.
- 21 A. Aguadero, M. J. Escudero, M. Pérez, J. A. Alonso and L. Daza, J. Fuel Cell Sci. Technol., submitted for publication.
- 22 Y. Takeda, R. Kanno, M. Sakano, O. Yamamoto, M. Takano, Y. Bando, H. Akinaga, K. Takita and J. B. Goodenough, *Mater. Res. Bull.*, 1990, 25, 293–306.
- 23 A. Demourgues, A. Wattiaux, J. C. Grenier, M. Pouchard, J. L. Soubeyroux, J. M. Dance and P. Hagenmuller, J. Solid State Chem., 1993, 105, 458.
- 24 A. Aguadero, M. Perez, J. A. Alonso and L. Daza, J. Power Sources, 2005, 151, 52–56.