

### NRC Publications Archive Archives des publications du CNRC

## Structure, stability and electrical properties of the La(2–x)SrxMnO4± $\delta$ solid solution series

Munnings, Christopher N.; Skinner, Stephen J.; Amow, Gisele; Whitfield, Pamela; Davidson, Isobel

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

#### Publisher's version / Version de l'éditeur:

https://doi.org/10.1016/j.ssi.2006.01.009 Solid State Ionics, 177, October, pp. 1849-1853, 2006

#### NRC Publications Record / Notice d'Archives des publications de CNRC:

https://nrc-publications.canada.ca/eng/view/object/?id=f2be87ec-d572-4c66-8e40-fbd22711297b https://publications-cnrc.canada.ca/fra/voir/objet/?id=f2be87ec-d572-4c66-8e40-fbd22711297b

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at <u>https://nrc-publications.canada.ca/eng/copyright</u> READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site https://publications-cnrc.canada.ca/fra/droits LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

**Vous avez des questions?** Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.







Available online at www.sciencedirect.com



SOLID STATE IONICS

Solid State Ionics 177 (2006) 1849-1853

www.elsevier.com/locate/ssi

# Structure, stability and electrical properties of the $La_{(2-x)}Sr_xMnO_{4\pm\delta}$ solid solution series

Christopher N. Munnings<sup>a</sup>, Stephen J. Skinner<sup>a,\*</sup>, Gisele Amow<sup>b</sup>, Pamela S. Whitfield<sup>b</sup>, Isobel J. Davidson<sup>b</sup>

<sup>a</sup> Department of Materials, Imperial College London, Prince Consort Road, London, SW7 2BP, UK <sup>b</sup> ICPET, NRC Canada, 1200 Montreal Road, Ottawa, Canada, K1A 0R6

Received 30 June 2005; received in revised form 9 January 2006; accepted 9 January 2006

#### Abstract

Single phase materials of the  $La_{(2-x)}Sr_xMnO_{4\pm\delta}$  ( $0.6 \le x \le 2.0$ ) solid solution series were prepared via solid state reaction. The structure of each material was examined at room temperature and determined to be tetragonal for all phases examined. An expansion in lattice volume was observed on increasing lanthanum content. The stability and thermal expansion of each member of the solid solution series was determined via the use of in situ high temperature X-ray diffraction. It was found that all materials remained stable up to a temperature of 800 °C. Thermal expansion coefficients were found to be in the region of  $15 \times 10^{-6} \text{ K}^{-1}$  for  $La_{(2-x)}Sr_xMnO_{4\pm\delta}$  compounds where x > 1.4. The electrical conductivity of each phase was also determined over a similar temperature range with a maximum value of ~6 Scm<sup>-1</sup> at 900 °C for the x = 1.8 phase. © 2006 Elsevier B.V. All rights reserved.

Keywords: K2NiF4; Cathode; SOFC; La-Sr-Mn; Electrical conductivity

#### 1. Introduction

The development of new mixed ionic-electronic conductors (MIECs) is important for many high temperature (400–1000 °C) applications such as sensors, oxygen pumps, separation membranes and solid oxide fuel cells [1,2]. With the increase in global energy consumption, however, it is MIECs used as electrodes in solid oxide fuel cells that are attracting greatest attention from the scientific community. The main area of study is the development of new materials that would allow the operation of solid oxide fuel cells below 700 °C. This would have several benefits including an increase in the thermodynamic efficiency, longer device operating life and reduction in production costs. To date, most investigations have concentrated on the development of materials of the perovskite structure type [3]. However, recent studies have also shown that K<sub>2</sub>NiF<sub>4</sub>-type oxides may offer viable alternatives. The majority of these investigations have concentrated on the suitability of Cu, Ni, Fe and Co substituted materials as possible electrodes [4-8]. These investigations have concluded that the La<sub>2</sub>NiO<sub>4+ $\delta$ </sub> based phases show great promise as possible cathode materials for solid oxide fuel cells operating at temperatures below 700 °C [7]. Despite the promising results little work has been reported on the closely related cobalt and manganese substituted phases with studies only recently revealing high levels of ionic diffusion (~2.5×10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup> at 500 °C) and promising levels of electronic conductivity (~25 Scm<sup>-1</sup> at 500 °C) in the pure La<sub>2</sub>CoO<sub>4+ $\delta$ </sub> phase [9,10]. The purpose of this study is to carry out a preliminary investigation of the structure, electrical conductivity and high temperature stability (up to 800 °C) of materials from the La<sub>2-x</sub>Sr<sub>x</sub>MnO<sub>4± $\delta$ </sub> solid solution series, enabling the evaluation of these materials as possible electrode materials for solid oxide fuel cells.

#### 2. Experimental

Materials were prepared through the solid state reaction of  $La_2O_3$  (Alfa Aesar 99.999%), SrCO<sub>3</sub> (Alfa Aesar 99.999%) and MnO<sub>2</sub> (Alfa Aesar 99.999%).  $La_2O_3$  was first dried at 1000 °C for 16 h to remove any moisture. Stoichiometric amounts of each starting material were then weighed out and mixed under

<sup>\*</sup> Corresponding author. Tel.: +44 20 7594 6782; fax: +44 20 7594 6757. *E-mail address:* s.skinner@imperial.ac.uk (S.J. Skinner).

acetone in an agate mortar and pestle until a fine homogeneous grey powder was obtained. This powder was uniaxially pressed into discs of approximately 10 mm diameter. Compositions where x>1 were heated under flowing Argon for 12 h at 1300 °C. This process was repeated until a single phase material, as determined by X-ray diffraction, was obtained. Samples with higher lanthanum contents were prepared in a similar manner but heated under flowing forming gas (5% H<sub>2</sub>/N<sub>2</sub>) at 1100 °C for 12 h.

Electrical conductivity was measured through the use of standard 4 point DC Van der Pauw measurements at temperatures of up to 900 °C. Each conductivity measurement was carried out on a single ceramic plate approximately 20 mm square. Each square was uniaxially pressed into shape and then sintered for 12 h under identical conditions to that of the original synthesis.

Thermogravimetric analysis of each material was carried out at temperatures of between room temperature and 800 °C in flowing air using a Stanton Redcroft STA-780 TG-DTA. Samples were slowly cooled to room temperature and then examined via X-ray diffraction.

In situ high temperature X-ray diffraction studies were conducted on a Phillips X'pert system using Cu K $\alpha$  radiation. Samples were heated in a Bühler type furnace with a beryllium

window in static air up to 800 °C with measurements taken at 100 °C intervals. Heating and cooling rates were set at 60 °C/ min. Once cooled, the process was repeated to gain a true value of thermal expansion of the oxidised material. Indexing and lattice parameter determinations of the diffraction data were carried out using the program DICVOL [11,12].

#### 3. Results and discussion

#### 3.1. Structure

X-ray diffraction data recorded from each sample confirmed that single phase samples of  $La_{2-x}Sr_xMnO_{4\pm\delta}$  ( $0.6 \le x \le 2.0$ ) had been produced, having been evaluated against reference patterns. The calculated lattice parameters were also, where possible, compared with values from the literature [13,14] and were found to be in good agreement with previous data obtained from samples prepared in a similar manner to those used in this study. Variation in the lattice parameters reported by other authors can generally be explained by the variation in sample preparation technique which will lead to a variation in anion stoichiometry. Direct chemical determination of the Mn valence, and hence anion stoichiometry, has been precluded by the insolubility of these materials in solvents up to and



Fig. 1. Variation of lattice parameter with mol% lanthanum dopant of as synthesised  $La_{2-x}Sr_xMnO_{4\pm\delta}$  (0.8  $\leq x \leq 2.0$ ).

Table 1 Calculated thermal expansion values for selected compositions of the solid solution series  $La_{2-x}Sr_xMnO_{4\pm\delta}$  ( $0 \le x \le 1.4$ )

x	TEC/K <sup>-1</sup> , a/b	$TEC/K^{-1}$ , c	TEC/K <sup>-1</sup> , total
2.0	$17.8 \times 10^{-6}$	$14.0 \times 10^{-6}$	$16.5 \times 10^{-6}$
1.8	$16.5 \times 10^{-6}$	$13.9 \times 10^{-6}$	$15.6 \times 10^{-6}$
1.6	$13.2 \times 10^{-6}$	$15.7 \times 10^{-6}$	$14.0 \times 10^{-6}$
1.4	$13.5 \times 10^{-6}$	$18.3 \times 10^{-6}$	$15.1 \times 10^{-6}$

including conc.  $H_2SO_4$ . This also precludes the use of ICP-MS to determine cation concentrations in the materials and, hence, in combination with thermogravimetric analysis, the oxygen stoichiometry and thus Mn valence.

The overall effect of the addition of lanthanum to the structure was an increase in the lattice volume which is most likely caused by the substitution of the divalent Sr with trivalent La resulting in a reduction of the manganese, thus increasing the atomic radius and resulting in an increase in the lattice parameter. One point of interest is the manner in which the expansion occurs. For the first three compositions (x=2, 1.8 and 1.6) the *c*-parameter remains relatively stable with only a slight decrease observed, Fig. 1. Previous studies of the closely related lanthanum nickel/cobalt system (La<sub>2</sub>Ni<sub>1-x</sub>Co<sub>x</sub>O<sub>4+ $\delta$ </sub>, 0 ≤ x ≤ 1) [9] and  $Sr_2MnO_{4-\delta}$  [13] have both suggested that the cparameter in this structure type is largely dependant on the ionic radii, and hence the oxidation state, of the transition metal ion. Therefore the absence of a sharp increase in *c*-parameter suggests that the oxidation state of the manganese ion remains reasonably constant for these initial compositions. The increase in *a*-parameter (over the initial three compositions) is most likely a result of the filling of oxygen vacancies, which have been shown to occupy the manganese planes within this material [13]. The increase in the *c*-parameter from the 30% lanthanum doped composition onwards suggests a reduction of manganese on increasing lanthanum content. The sharp rise in *c*-parameter on transition from the x=1.2 to x=1.0 composition is not unexpected as phases containing 50% or more lanthanum were synthesised under flowing forming gas, as opposed to argon, thus the corresponding decrease in the *a*-parameter can be attributed to the likely presence of oxide ion vacancies forming in the manganese planes.

#### 3.2. Stability

The stability and thermal expansion of each phase were assessed through the use of high temperature X-ray diffraction. It was possible to obtain thermal expansion coefficients for 0%, 10%, 20% and 30% lanthanum doped materials. The total thermal expansion coefficient, referred to in Table 1, is the combined average thermal expansion coefficient expected for a randomly orientated polycrystalline sample. Materials with higher lanthanum contents showed a considerable increase in peak width making accurate determination of the lattice parameters, and hence thermal expansion coefficients, impossible from the data obtained in this study. The exact reason for this peak broadening is unclear but it is likely to be a result of either i) orthorhombic distortion, ii) decomposition or iii) mixed phases due to the variable cation valence.

The first two options are unlikely as samples examined at room temperature via X-ray diffraction after both thermogravimetric and electrical conductivity measurements do not display similar levels of peak broadening. This leads to the most likely explanation being that the material consists of several different phases each with a unique oxygen stoichiometry. This would not be unreasonable as the heating and cooling rates used in the high temperature X-ray furnace are at least six times more rapid than can be expected from a standard furnace used in the electrical conductivity measurements or the thermogravimetric analysis. It is therefore important that future work on these compositions considers the collection and evaluation of rapidly



Fig. 2. Electrical conductivity variation with temperature for the phases  $La_{2-x}Sr_xMnO_{4\pm\delta}$  (0.6  $\leq x \leq 2.0$ ).



Fig. 3. Variation of lattice parameter with mol% lanthanum dopant of oxidised  $La_{2-x}Sr_xMnO_{4\pm\delta}$  (0.8  $\leq x \leq 2.0$ ).

acquired high resolution diffraction data using synchrotron diffraction techniques.

The overall stability of these materials below 800 °C was found to be good with no decomposition products or processes observed during any of the experiments carried out in this study.

#### 3.3. Electrical conductivity

The electrical conductivity for each phase was determined in air at temperatures of up to approximately 900 °C, Fig. 2. The peak conductivity for the solid solution series examined was determined to be ~6 Scm<sup>-1</sup> at 900 °C. All of the compositions investigated displayed semi-conducting behaviour, with the electrical conductivity increasing with temperature closely mirroring the behaviour in the related La<sub>2</sub>Ni<sub>1-x</sub>Co<sub>x</sub>O<sub>4+δ</sub> ( $0 \le x \le 1$ ) solid solution series [9]. Within the transition metal doped series it would be expected that the electrical conduction would be dominated by the transition metal–oxygen–transition metal exchange interactions in the basal plane [9]. It was therefore expected that on increasing the inter-atomic distances within the a/b basal plane a loss in electron mobility and thus a drop in electrical conductivity would be observed. Comparing the lattice parameters obtained from the oxidised material after thermogravimetric analysis, Fig. 3, shows that on increasing lanthanum content there was indeed an expansion in the a/b plane that corresponds to a decrease in the electrical conductivity across the same range. However, it should be noted that although the atomic spacing appears to be an important factor in controlling electrical conductivity in these materials it does not explain the comparatively poor performance of the Sr<sub>2</sub>MnO<sub>4±δ</sub> phase which, despite having a more compact basal plane, still maintains a conductivity lower than other members of the solid solution series with more diffuse a/b basal planes. In order to gain a more in depth understanding of the electrical properties of this material and a more detailed model of the conduction process further study is obviously required.

#### 4. Conclusion

Materials of composition  $La_{2-x}Sr_xMnO_{4\pm\delta}$  (0.6  $\leq x \leq 2.0$ ) show good stability over a wide range of oxygen partial pressures and temperatures. The thermal expansion is also comparable to most commonly available electrolyte materials. However, these materials do not exhibit high enough electrical conductivity to be used as a cathode material in a solid oxide fuel cell with the low levels of electrical conductivity ruling out the use of this material for use in most applications where mixed ionic/electronic conductivity is required.

#### Acknowledgements

The authors would like to thank the British Council and the National Research Council of Canada for funding this work through the joint Science and Technology programme, grant reference 00CRP12.

#### References

- [1] B.C.H. Steele, Solid State Ionics 134 (2000) 3.
- [2] S.J. Skinner, J.A. Kilner, Materials Today 6 (2003) 30.

- [3] A. Petric, P. Huang, F. Tietz, Solid State Ionics 135 (2000) 719.
- [4] V.V. Kharton, D.M. Bochkov, A.V. Kovalevsky, A.P. Viskup, E.N. Naumovich, Solid State Ionics 120 (1999) 281.
- [5] V.V. Kharton, A.P. Viskup, A.V. Kovalevsky, E.N. Naumovich, F.M.B. Marques, Solid State Ionics 143 (2001) 337.
- [6] S. Skinner, C. Munnings, G. Amow, P. Whitfield, I. Davidson, Electrochemical Society Series: SOFC VIII (Paris), 2003, p. 552.
- [7] S.J. Skinner, J.A. Kilner, Solid State Ionics 135 (2000) 709.
- [8] A.J. Jennings, S.J. Skinner, Solid State Ionics 152-153 (2002) 663.
- [9] G. Amow, P. Whitfield, I. Davidson, R.P. Hammond, C. Munnings, S. Skinner, Solid State Chemistry of Materials IV (Boston), 2002, p. 347.
- [10] C. Munnings, S.J. Skinner, G. Amow, P. Whitfield, L.J. Davidson, Solid State Ionics 176 (2005) 1895.
- [11] G. Vanhoyland, F. Bouree, M.K. Van Bael, J. Mullens, L.C. Van Poucke, Journal of Solid State Chemistry 157 (2001) 283.
- [12] A. Boultif, D. Louer, Applied Crystallography 37 (2004) 724.
- [13] L.J. Gillie, A.J. Wright, J. Hardermann, G. Van Tendeloo, C. Greaves, Journal of Solid State Chemistry 167 (2002) 145.
- [14] R.K. Li, C. Greaves, Journal of Solid State Chemistry 153 (2000) 34.