Solid State Ionics 292 (2016) 38–44

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Synthesis and oxygen transport properties of $La_{2-y}Sr_yNi_{1-x}Mo_xO_{4+\delta}$

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ARTICLE INFO

Article history:
Received 15 December 2015
Received in revised form 20 April 2016
Accepted 10 May 2016
Available online 21 May 2016

Keywords:
Lanthanum nickelate, Sr- and Mo-substitution
Electrical conductivity
Oxygen diffusion
Surface exchange
Electrical conductivity relaxation

ABSTRACT

$La_2NiO_{4+\delta}$-based materials (LN) with tetragonal K_2NiF_4-type structure exhibit high electronic and oxygen ion conductivity. In this work synthesis, phase relations and oxygen transport properties are reported for the system $La_{2-y}Sr_yNi_{1-x}Mo_xO_{4+\delta}$ where $0.0 \le y \le 0.4$ and $0.0 \le x \le 0.1$. The solubility of Mo in LN is low, but becomes enhanced by Sr substitution on the A-site. $La_{1.8}Sr_{0.2}Ni_{0.95}Mo_{0.05}O_{4+\delta}$ (LSNM) bar shaped samples were subjected to electrical conductivity relaxation (ECR) for assessment of oxygen bulk diffusion (D_{chem}), oxygen surface exchange (k_{chem}) and electronic conductivity. The p-type conductivity was 50 $S \cdot cm^{-1}$ at 900 °C, which is lower than both LN and LSN (Sr = 0.2). On the other hand, k_{chem} was enhanced by one order of magnitude compared with LN at all temperatures, while D_{chem} was lower at T > 700 °C and higher at T < 700 °C.

1. Introduction

Mixed conductors derived from nickelates with K_2NiF_4-type structure, $La_2NiO_{4+\delta}$ (LN) and doped LN-compounds have attracted much attention as promising materials for intermediate-temperature solid oxide fuel cell (IT-SOFC) cathodes and ceramic membranes for oxygen separation as well as applications involving partial oxidation of light hydrocarbons [1–9]. The advantages of LN-based materials include favorable oxygen transport properties (surface exchange and bulk diffusion) combined with moderate thermal- and chemical expansion and high electrocatalytic activity [10–13].

The K_2NiF_4-type structure of LN is tetragonal (space group I4/mmm or F4/mmm), and corresponds to alternating layers of perovskite- and rock salt structure [14–19]. The oxygen ion transport may occur by a combination of vacancy diffusion in the perovskite layer and via interstitial sites between the rock-salt and perovskite layers [18,20,21].

In order to estimate characteristic features of the oxygen transport and conductivity in LN based compounds, a simplified model may be considered [22–24]. As we will investigate the properties at relatively high partial pressures of oxygen we disregard the presence of oxygen vacancies and assume that the main point defects in $La_2NiO_{4+\delta}$ are interstitial oxygen ions (O_i'') and electron holes ($h^\cdot$, originating from the presence of Ni^{3+}). Hence the following defect equilibria may be formulated:

$$\frac{1}{2}O_2 = O_i'' + 2\left[Ni_{Ni}^{\cdot}\right] = O_i'' + 2h^{\cdot} \quad (1)$$

corresponding to the equilibrium constant, K_p':

$$K_p' = \frac{\left[O_i''\right][h^{\cdot}]^2}{P_{O_2}^{\frac{1}{2}}}. \quad (2)$$

Charge balance is formulated in Eq. (3):

$$2\left[O_i''\right] = [h^{\cdot}]. \quad (3)$$

And substituting Eq. (3) into Eq. (2) gives:

$$P_{O_2}^{1/2} = K_p[h^{\cdot}]^3 \quad (4)$$

where K_p is a constant. Since the electronic conductivity, σ, is proportional to the concentration of charge carriers the following proportionality should apply for the non-substituted case:

$$\sigma \propto [h^{\cdot}] \propto P_{O_2}^{\frac{1}{6}}. \quad (5)$$

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http://dx.doi.org/10.1016/j.ssi.2016.05.006
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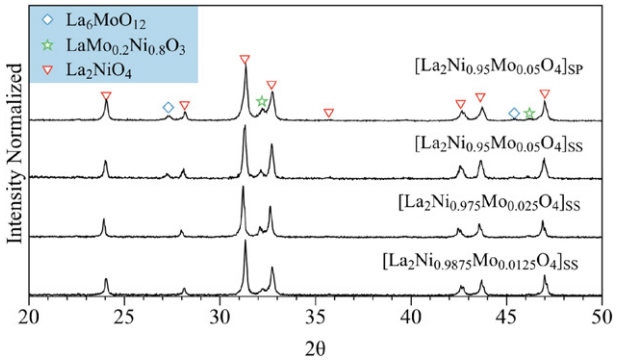

Fig. 1. Diffractograms of $La_2Ni_{1-x}Mo_xO_{4+\delta}$ with x = 0.0125, 0.025, and 0.05. All SS-samples are sintered at 1300 °C while SP-sample is sintered at 1400 °C. The presence of the major phase is compared with the characteristic reflections for tetragonal La_2NiO_4.

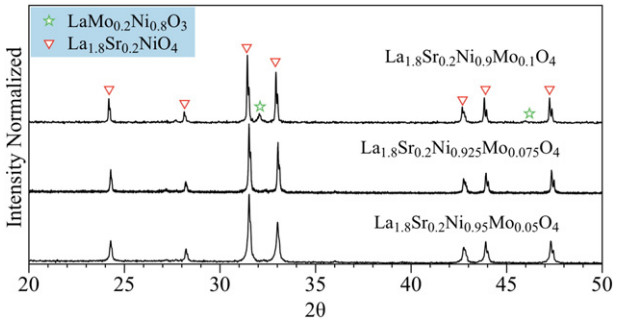

Fig. 2. XRD-data for $La_{1.8}Sr_{0.2}Ni_{1x}Mo_xO_{4+\delta}$ (SS-samples) with x = 0.05, 0.075 and 0.1. All samples are sintered at 1300 °C. The major LN phase is compared with the characteristic reflections for $La_{1.8}Sr_{0.2}NiO_4$.

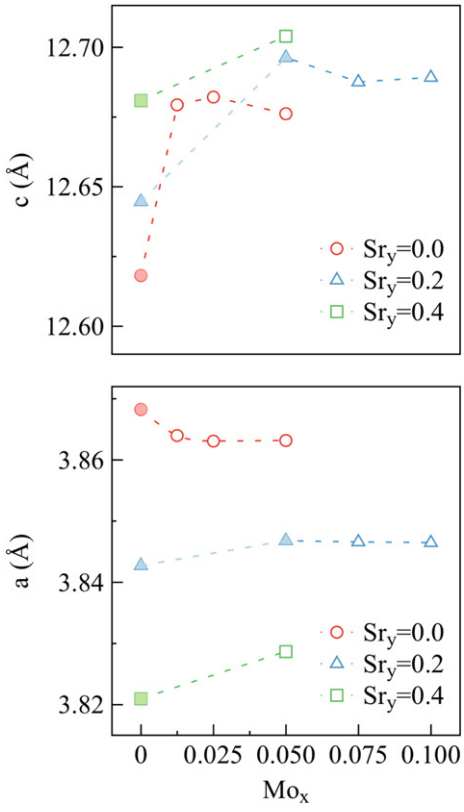

Fig. 3. Variation in cell parameter for $La_{2-y}Sr_yNi_{1-x}Mo_xO_{4+\delta}$ with Mo-content for compositions with 0.0, 0.2 and 0.4 Sr. Cell parameters for La_2NiO_4 is taken from [14]. Samples are heat treated at T = 1300 °C. Filled symbols indicate single phase while open symbols indicate the presence of secondary phases. Magnitude of error will typically be within the size of the symbols given in the figures.

Substituting divalent Sr for trivalent La on A-site and hexavalent Mo for divalent Ni on B-site in $La_{2-y}A_yNi_{1-x}B_xO_{4+\delta}$, the electroneutrality may be formulated viz.:

$$2\left[O_i''\right] + [Sr'_{La}] = [h^{\cdot}] + 4[Mo_{Ni}^{\cdots}]. \quad (6)$$

Eqs. (1) to (6) will form the basis for discussing the behavior of conductivity for both non-substituted and substituted LN.

It is reported in the literature that substitution on B-site with a higher valent element results in a higher concentration of interstitial oxygen, which may be beneficial for the oxygen diffusivity [11,17,20,21,23–26], while incorporation of a divalent Sr on A-site suppress the oxygen diffusivity [11–13,23]. However, doping with Sr increases the overall conductivity, and EIS studies on Sr-substituted LN show a lower area specific resistance values compared with the non-substituted compound, which is advantageous for IT-SOFC applications [27,28].

The aim of the present work was to assess the phase relations in LN substituted with Sr and Mo and investigate the effect on electrical conductivity and oxygen transport properties (D_{chem} and k_{chem}) as measured by the method of electrical conductivity relaxation (ECR).

Table 1
Synthesis methods, sintering temperature and phases observed according to XRD-analysis for the nominal stoichiometry: $La_{2-y}Sr_yNi_{1-x}Mo_xO_{4+\delta}$. Cell parameters obtained by Rietveld refinement for the major LN phase are also listed. Estimated errors in cell parameters are ±0.0015 Å and ±0.003 Å for a- and c-axis, respectively.

y	x	Method	T/°C	Major phase	Minor phases	a (Å)	c (Å)
0.0	0.05	SP	1400	$La_2Ni_{1-z}Mo_zO_{4+\delta}$	La_6MoO_{12}-$LaMo_{0.2}Ni_{0.8}O_3$	3.866	12.665
	0.0125	SS	1300	$La_2Ni_{1-z}Mo_zO_{4+\delta}$	$LaMo_{0.2}Ni_{0.8}O_3$	3.864	12.679
	0.025	SS	1300	$La_2Ni_{1-z}Mo_zO_{4+\delta}$	$LaMo_{0.2}Ni_{0.8}O_3$	3.863	12.682
	0.05	SS	1300	$La_2Ni_{1-z}Mo_zO_{4+\delta}$	La_6MoO_{12}-$LaMo_{0.2}Ni_{0.8}O_3$	3.863	12.676
0.2	0.05	SP	1250	$La_{1.8}Sr_{0.2}Ni_{0.95}Mo_{0.05}O_{4+\delta}$	–	3.848	12.695
	0.05	SP	1400	$La_{1.8}Sr_{0.2}Ni_{0.95}Mo_{0.05}O_{4+\delta}$	–	3.848	12.676
	0.05	SP	1500	$La_{1.8}Sr_{0.2}Ni_{0.95}Mo_{0.05}O_{4+\delta}$	–	3.849	12.675
	0.05	SS	1300	$La_{1.8}Sr_{0.2}Ni_{0.95}Mo_{0.05}O_{4+\delta}$	–	3.847	12.696
	0.075	SS	1300	$La_{1.8}Sr_{0.2}Ni_{1-z}Mo_zO_{4+\delta}$	$LaMo_{0.2}Ni_{0.8}O_3$	3.847	12.688
	0.1	SS	1300	$La_{1.8}Sr_{0.2}Ni_{1-z}Mo_zO_{4+\delta}$	$LaMo_{0.2}Ni_{0.8}O_3$	3.847	12.689
0.4	0.05	SP	1400	$La_{1.6}Sr_{0.4}Ni_{1-z}Mo_zO_{4+\delta}$	$SrMoO_4$	3.287	12.704
	0.05	SP	1500	$La_{1.6}Sr_{0.4}Ni_{1-z}Mo_zO_{4+\delta}$	$SrMoO_4$	3.830	12.702
	0.05	SS	1100	$La_{1.6}Sr_{0.4}Ni_{1-z}Mo_zO_{4+\delta}$	$SrMoO_4$	3.827	12.711
	0.05	SS	1200	$La_{1.6}Sr_{0.4}Ni_{1-z}Mo_zO_{4+\delta}$	$SrMoO_4$	3.826	12.708
	0.05	SS	1300	$La_{1.6}Sr_{0.4}Ni_{1-z}Mo_zO_{4+\delta}$	$SrMoO_4$	3.828	12.705
	0.05	SS	1400	$La_{1.6}Sr_{0.4}Ni_{1-z}Mo_zO_{4+\delta}$	$SrMo_4$	3.830	12.703