Solid State Ionics 279 (2015) 53–59

Contents lists available at ScienceDirect

Solid State Ionics

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

Synthesis, oxygen nonstoichiometry and total conductivity of $(La,Sr)_2(Mn,Ni)O_{4\pm\delta}$

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A R T I C L E I N F O

Article history:
Received 25 December 2014
Received in revised form 22 July 2015
Accepted 22 July 2015
Available online 10 August 2015

Keywords:
K_2NiF_4-type structure
Oxygen nonstoichiometry
Mixed conductors
Manganites–nickelates
p-type conductivity
Seebeck coefficient

A B S T R A C T

The series of complex oxides, $La_{2\text{-}x}Sr_xNi_{1\text{-}y}Mn_yO_{4\text{-}\delta}$ ($x = 0.7–1$, $y = 0.1, 0.2, 0.3, 0.5, 0.7$), were synthesized via glycine–nitrate and citrate–nitrate combustion techniques followed by sintering at 1350–1400°C in air. All single-phase compounds have the K_2NiF_4-type structure (sp.gr. *I4/mmm*). The unit cell volume increases with *y* and decreases with *x* in $La_{2\text{-}x}Sr_xNi_{1\text{-}y}Mn_yO_{4\pm\delta}$. At room temperature, the solid solutions $LaSrNi_{1\text{-}y}Mn_yO_{4\pm\delta}$ ($y = 0.1, 0.3, 0.5$, and 0.7) show a small excess of oxygen ($\delta > 0$) which increases with the manganese doping level *y*. Total conductivity and Seebeck coefficient were determined in air from room temperature to 1100°C, with the maximum value ~100 S/cm for $La_{1.2}Sr_{0.8}Ni_{0.9}Mn_{0.1}O_{4\pm\delta}$ and $La_{1.3}Sr_{0.7}Ni_{0.9}Mn_{0.1}O_{4\pm\delta}$. The conduction is temperature activated for all phases under study. Seebeck coefficient has tendency to decrease from low temperature to high temperature and predominantly adopts slightly negative values varying from −15 to −5 μV/K.

1. Introduction

In the series of the Ruddlesden–Popper phases $La_{n+1}Ni_nO_{3n+1}$, the member $La_2NiO_{4+\delta}$ ($n = 1$) and its derivatives $La_{2\text{-}x}A_xNi_{1\text{-}y}Me_yO_{4\pm\delta}$ (A – AEM and Me – 3*d*-transition metal) are still of great interest due to mixed oxygen ionic and electronic conductivity discovered in $La_2NiO_{4+\delta}$ [1–3]. The crystal structure of such phases belonging to tetragonal K_2NiF_4-type structure (sp.gr. *I4/mmm*) is usually represented as the alternation of one rock-salt LaO layer with one perovskite-like $LaNiO_3$ layer. $La_2NiO_{4+\delta}$-based materials exhibit high values of oxygen ionic conductivity due to oxygen diffusion via interstitial sites along the LaO layers [1–14]. Another advantage of K_2NiF_4-type phases is reasonable TEC compatibility with solid oxide electrolytes and high electrocatalytic activity under oxygen reduction that allows them to be considered as promising alternative cathode materials in IT-SOFC's [4–14]. They can also be considered as membranes for natural gas conversion or oxygen separation [3,7,15,16].

$La_{2\text{-}x}Sr_xNiO_{4\pm\delta}$ and $La_2Ni_{1\text{-}x}Me_xO_{4+\delta}$ solid solutions were intensively studied during the last three decades [1–24]. Interstitial oxygen was shown to be gradually depleted with *x* in $La_{2\text{-}x}Sr_xNiO_{4\pm\delta}$: this leads to an increase in total conductivity and to a decrease in oxygen ion transport [1,21,22]. In contrast to A-site (Sr for La), Ni-sublattice substitution in $La_2NiO_{4+\delta}$ moderately effected mixed ionic/electronic conductivity [2,3,5,10,11,14].

A number of earlier works were focused on manganites $La_{2\text{-}x}Sr_xMnO_{4\pm\delta}$ [25–27] due to their thermodynamic stability at high temperatures under reducing atmosphere (H_2–N_2) compared to nickelates $La_{2\text{-}x}Sr_xNiO_{4\pm\delta}$ and their ability to absorb sufficient amounts of oxygen ($\delta \sim 0.42$) in an oxidizing atmosphere at ~500°C.

Rare efforts were undertaken to study the A_2BO_4 phases, with simultaneous substitution in both A- and B-sites. For example, $LaSrNi_{1\text{-}x}Mn_xO_{4\pm\delta}$ was investigated as catalyst for NO direct decomposition [28]. The high-spin state of Ni^{+3} ions and their high thermodynamic stability under reducing atmosphere (Ar, 1300°C) were established by Millburn for $LaSrNi_{0.5}Mn_{0.5}O_{4\pm\delta}$ [29].

The present work is aimed to study the simultaneous substitution in both La- and Ni-sublattices of the La_2NiO_4 phase while the substituents are of a different nature: Sr in A-site is an acceptor-type and Mn serves as a donor-type dopant. We reported the synthesis procedure, crystal structure, high-temperature total conductivity, Seebeck coefficient, and oxygen nonstoichiometry of $La_{2\text{-}x}Sr_xNi_{1\text{-}y}Mn_yO_{4\pm\delta}$ solid solutions.

2. Experimental

The solid solutions were prepared by glycine–nitrate (GNT) and citrate–nitrate (CNT) combustion techniques. The starting materials were $Ni(CH_3COO)_2 \times 4H_2O$ (Acros Organics, 99%), $SrCO_3$ (Aldrich, ≥99.9%), $La(NO_3)_3 \times 6H_2O$ (Vekton, 99.95%), MnO_2 (Panreac, 99%), chemical pure grade $C_2H_5NO_2$ (Ecros), and citric acid monohydrate $C_6H_8O_7 \times H_2O$ (Vekton). Before weighing, MnO_2 was annealed at 700 °C for 10 h in air to form stoichiometric Mn_2O_3; and $SrCO_3$ was annealed at 500 °C for 5 h to remove absorbed gases.

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http://dx.doi.org/10.1016/j.ssi.2015.07.017
0167-2738/

In both techniques the starting materials taken in the appropriate ratios were dissolved in nitric acid. Primarily, manganese sesquioxide, Mn_2O_3, was dissolved in concentrated nitric acid under heating. Crystalline oxalic acid dihydrate $H_2C_2O_4 \times 2H_2O$ (chemical pure grade, Astra) was required as a reductant of Mn^{3+} (in Mn_2O_3) to Mn^{2+} (in solution). The as-prepared solutions were dried and then decomposed forming dark grey powders. Afterwards, a solid state reaction was carried out at 1100 °C in air for 24 h with 2–3 intermediate grindings. The powders obtained were uniaxially pressed into bars and sintered at 1350–1400 °C for 60 h in air.

The phase composition of the samples was analyzed at room temperature (RT) by powder XRD using Equinox 3000 (FWHM ~0.05° at 2θ) and DRON-6 (FWHM ~0.15° at 2θ) instruments with Cu–Kα radiation. The high-temperature XRD was performed in air using HT-chamber HDK-S1 (Edmund Buhler) and HTK 1200N (Anton Paar) installed on DRON-6 and Equinox 3000 diffractometers, respectively.

The refinement of the XRD patterns was implemented by both the Le Bail technique (profile-matching mode) and the Rietveld method using FullProf program [30].

The absolute values of oxygen content (4 ± δ) in the $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4\pm\delta}$ samples were calculated from the results of the dichromate titration technique. The average oxidation state ($z+$) of 3d-transition metals, Mn and Ni, is directly related to the oxygen content as follows: $La^{3+}_{2-x}Sr^{2+}_x(Ni_{1-y}Mn_y)^{z+}O^{2-}_{3+0.5(z-x)}$, where $\delta = 1 - 0.5 \times (z - x)$. During the dissolution of the known amount of $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4\pm\delta}$ oxide in the concentrated hydrochloric acid with the known excess amount of the Mohr's salt $(NH_4)_2Fe(SO_4)_2 \times 6H_2O$, the following red/ox reaction takes place:

$$M^{z+} + (z-2)\,Fe^{2+} \rightarrow M^{2+} + (z-2)\,Fe^{3+} \qquad (1)$$

where M — (Ni, Mn).

The quantity of the Mohr's salt that had been left as an excess was then titrated by potassium dichromate $K_2Cr_2O_7$ solution with a precisely fixed concentration (~0.1 N). The end point was determined potentiometrically using the automatic titration apparatus Akvilon (ATP-02). The titration technique was tested using manganese oxides: Mn_2O_3, MnO_2, and the complex oxide $LaSrNiO_4$.

Temperature dependencies of oxygen nonstoichiometry were determined by TGA using Netzsch STA 409 PC instrument. A powder oxide sample was placed in the alumina crucible already annealed at 1000 °C. Equilibrium mass changes of the oxide sample were measured at temperatures from 1150 °C to RT with steps of 100 °C in air flow at the rate of 50 ml/min, using the empty alumina crucible as a reference material.

The total conductivity and Seebeck coefficient measurements were carried out simultaneously using the standard 4-probe DC technique with Pt wire leads. The dimensions of the rectangular-shaped samples were 2 × 2 × 25 mm. The sample was installed in the cell, which was placed inside a furnace and heated up to 1000–1100 °C in air. The measurements were performed at a given temperature until constant values of both electrical resistivity and thermo-emf were obtained, with cooling to next temperature (with steps 50 °C).

3. Results and discussion

3.1. Synthesis and crystal structure of $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4+\delta}$

The solid solutions $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4\pm\delta}$ were prepared by the GNT and CNT method mentioned in the experimental procedure. In order to obtain single-phase materials, high-temperature sintering at 1350–1400 °C was needed. Moreover, using GNT, we could not achieve single-phase materials for a number of compositions even after sintering at such high temperatures. Namely, in the $LaSrNi_{1-y}Mn_yO_{4+\delta}$ series, small amounts of La_2O_3 and perovskite phases were detected as impurities. With this in mind, CNT seems to be a more appropriate way to obtain single-phase $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4+\delta}$ materials.

XRD patterns of the single-phase $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4+\delta}$ samples are presented in Fig. 1. Observed differences in peak width and variations in relative intensities at the same Bragg position are caused by the differences in resolution of the XRD instruments (see experimental part), type of specimen (powder or sintered), and a texture for a number of samples, respectively. All single-phase oxides were indexed in the tetragonal space group *I4/mmm*. These results are in a good agreement with those reported earlier [1,23–29]. However, it should be noted that Millburn et al. [29] prepared the single-phase $LaSrNi_{0.5}Mn_{0.5}O_4$ only under dried deoxygenated argon flow at 1200–1300 °C, but not in air. This apparent contradiction can be attributed to a different synthesis temperature and to oxygen partial pressure. It is well known that the increase in temperature affects the oxidation state similarly, as a decrease in oxygen partial pressure. Therefore, the single-phase $LaSrNi_{0.5}Mn_{0.5}O_4$ can be prepared either at relatively high temperatures around 1400 °C in air (the present work) or at lower oxygen partial pressures and temperatures of 1200–1300 °C [29].

XRD profiles for single-phase $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4+\delta}$ solid solutions were refined in profile-matching mode followed by the Rietveld refinement. Fig. 2 shows the refined XRD pattern of $LaSrNi_{0.5}Mn_{0.5}O_4$ using profile-matching mode. As can be seen from Fig. 2, the calculated profile (black line) is in a good agreement with the observed one (red cycles), except of a very weak peak at 2θ ≈ 34.5°. Detailed inspection of XRD pattern for $LaSrNi_{0.5}Mn_{0.5}O_4$ revealed that this peak can be attributed neither to possible orthorhombic modification of the studied phases [26] nor to possible impurities such as perovskite phases, nickel oxide, strontium oxide (or carbonate), manganese oxides, and lanthanum oxide. It can be related to the most intensive peak of the sample holder material (α-Al_2O_3).

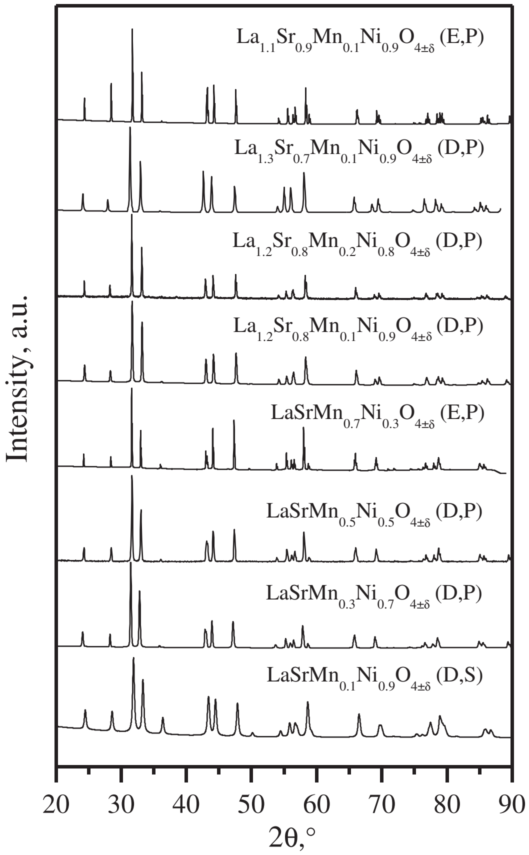

Fig. 1. XRD patterns of $La_{2-x}Sr_xNi_{1-y}Mn_yO_{4\pm\delta}$; symbols in parentheses denote: D – Dron-6, E – Equinox 3000, P – powder sample, and S – sintered samples.