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High-temperature transport properties, thermal expansion and cathodic performance of Ni-substituted $LaSr_2Mn_2O_{7-\delta}$

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ABSTRACT

The substitution of manganese with nickel in $LaSr_2Mn_2O_{7-\delta}$, where the solubility limit corresponds to approximately 25% Mn sites, enhances the Ruddlesden–Popper phase stability at elevated temperatures and atmospheric oxygen pressure. The total conductivity of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ ($y = 0$–0.4) decreases with nickel additions, whilst the average thermal expansion coefficients calculated from dilatometric data in the temperature range 300–1370 K increase from $(11.4–13.7)\times 10^{-6}\,K^{-1}$ at $y = 0$ up to $(12.5–14.4)\times 10^{-6}\,K^{-1}$ at $y = 0.4$. The conductivity and Seebeck coefficient of $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$, analyzed in the oxygen partial pressure range 10^{-15}–0.3 atm at 600–1270 K, display that the electronic transport is n-type and occurs via a small polaron mechanism. Reductive decomposition is observed at the oxygen pressures close to Ni/NiO boundary, namely $\sim 2.3\times 10^{-11}$ atm at 1223 K. Within the phase stability domain, the electronic transport properties are essentially $p(O_2)$-independent. The steady-state oxygen permeability of dense $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$ membranes is higher than that of $(La,Sr)MnO_{3-\delta}$, but lower if compared to perovskite-like $(Sr,Ce)MnO_{3-\delta}$. Porous $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$ cathodes in contact with apatite-type $La_{10}Si_5AlO_{26.5}$ solid electrolyte exhibit, however, a relatively poor electrochemical performance, partly associated with strong cation interdiffusion between the materials.

1. Introduction

Manganese-based Ruddlesden–Popper (RP) phases possess an attractive combination of structural, magnetic and electrical properties, including the colossal magnetoresistance (CMR) effect [1–15]. One potential application of these materials relates also to porous cathodes of solid oxide fuel cells (SOFCs), the alternative power generation systems enabling to increase energy conversion efficiency. Several RP manganites and nickelates were evaluated recently for possible use in the intermediate-temperature SOFCs operating at 870–1070 K [5,16]; the higher-order RP phases, with general formula $A_{n+1}B_nO_{3n+1}$ where $n = 2$ or 3, were suggested as promising cathode materials [16].

This work is focused on synthesis and characterization of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ system at elevated temperatures necessary for the fuel cell fabrication and operation. The parent compound, $LaSr_2Mn_2O_7$, has a layered $n = 2$ RP structure which can be described as a succession of perovskite bilayers alternating with rock-salt (La,Sr)O sheets along the crystallographic *c*-axis. Since the first observations of CMR in bilayered manganites in 1990s [1], the crystal chemistry, electrical and magnetic properties of $LaSr_2Mn_2O_7$ and related oxide systems, $La_{2-2x}Sr_{1+2x}Mn_{2-y}B_yO_{7-\delta}$ (*B*—transition metal cation), were extensively studied at temperatures below 350 K (e.g. [6–15] and references cited). Information on the high-temperature properties of these materials is, however, almost absent. $LaSr_2Mn_2O_7$ was reported to be nearly oxygen-stoichiometric in air [10]. Due to equal concentrations of Mn^{3+} and Mn^{4+} cations, a highest conductivity level in the $La_{2-2x}Sr_{1+2x}Mn_2O_{7-\delta}$ family can be expected for this compound. As the solubility of strontium and manganese cations in the corresponding sublattices of $La_3Ni_2O_{7-\delta}$ is very low [17,18], the present study was centered on the Mn-rich part of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ system. Taking into account the superior electrode behavior of numerous RP nickelates (e.g. [5]), doping of $LaSr_2Mn_2O_7$ with nickel might be expected to enhance the oxygen-ionic transport and electrochemical activity. Attention was also focused on other properties relevant for potential applications in SOFC cathodes, including the electronic conduction, thermal expansion and phase stability. The cathodic performance of porous electrodes was evaluated in contact with $La_{10}Si_5AlO_{26.5}$ solid electrolyte [19]. The ionic conductors based on apatite-type $La_{10-x}(SiO_4)_6O_{2\pm\delta}$ may provide serious advantages for the intermediate-temperature SOFCs owing to a substantially high oxygen diffusivity and relatively low costs [20]; however, data on their behavior in high-temperature electrochemical cells are still scarce.

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2. Experimental

Submicron powders of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ ($y = 0$–0.6) were prepared by the glycine-nitrate process (GNP), a self-combustion technique using metal nitrates as oxidant and glycine as a fuel and chelating agent [21]. In the course of GNP, aqueous glycine-nitrate solutions containing metal cations in the stoichiometric proportions were dried and heated until auto-ignition. The foam-like products were ground, annealed in air at 1173 K for 2 h in order to remove organic residues, and then ball-milled. Ceramic samples were pressed uniaxially at 350–400 MPa and sintered in air at 1673–1823 K for 10–40 h. After sintering and polishing, all materials were annealed at 1273 K for 2 h and slowly (1–2 K/min) cooled down to room temperature in order to achieve equilibrium with atmospheric oxygen. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-B diffractometer (Cu$K\alpha$, $2\Theta =$ 10–100°, step 0.02°). A Hitachi S-4100 scanning electron microscope (SEM) with a Rontec UHV detection system for the energy dispersive spectroscopy (EDS) was used for microstructural studies. Thermogravimetric analysis (TGA, Setaram SetSys 16/18) was performed in a flow of dried air in continuous heating/cooling regime (2 K/min). The dilatometric studies were carried out using a vertical Linseis L75 instrument (accuracy $\pm 2\,\mu m$, sample length of 10–12 mm) in air. General characterization of the ceramic materials included also determination of steady-state oxygen permeation fluxes (j) as function of temperature and oxygen partial pressure gradient, and measurements of the total conductivity (σ, 4-probe DC) and Seebeck coefficient (α). The equipment and experimental procedures used for materials characterization were described elsewhere ([19,22,23] and references therein). The electrical properties were studied at 600–1270 K in the oxygen partial pressure range 10^{-15}–0.3 atm; the criteria for equilibration after a change in either oxygen pressure or temperature included the relaxation rates of the conductivity and Seebeck coefficient less than 0.05%/min and 0.001 μV/(K min), respectively. The investigations of steady-state electrode polarization were carried out by the 3-electrode technique in cells with symmetrical working and counter electrodes (WE and CE); the cell geometry was selected according to Ref. [24]. The porous WEs (sheet density of 18.4 mg/cm^2) were made of single-phase $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$ powder annealed in air at 1423–1593 K for 40 h with several intermediate milling steps; the powder was suspended in ethanol and deposited onto dense $La_{10}Si_5AlO_{26.5}$ substrates, followed by the final annealing step at 1503 K for 2 h. The counter and reference electrodes, both made of porous Pt, were sintered at 1273 K for 0.5 h. The processing conditions of $La_{10}Si_5AlO_{26.5}$ electrolyte ceramics were described elsewhere [19]. The polarization experiments were performed in the galvanostatic mode using an AUTOLAB PGSTAT302 instrument at 873–1073 K in atmospheric air. The values of the ohmic and polarization resistances were determined from the impedance spectra collected in the frequency range from 10 mHz to 1 MHz; the relaxation times after a change in the WE potential were 30–70 min. The phase composition and microstructure of the electrode layers before and after electrochemical measurements were examined by XRD and SEM/EDS.

3. Results and discussion

XRD analysis of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ ($y = 0$–0.4) ceramics sintered at 1773 K in air, showed the formation of tetragonal $Sr_3Ti_2O_7$-type structure (Figs. 1A, D and 2A). However, whilst $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$ is single-phase, XRD patterns of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ ($y = 0$–0.2) indicate the presence of secondary perovskite-type component. Longer sintering time at this temperature resulted only in a larger fraction of the perovskite phase impurity, as illustrated by Fig. 1B. Single-phase $LaSr_2Mn_2O_{7-\delta}$ and $LaSr_2Mn_{1.8}Ni_{0.2}O_{7-\delta}$ ceramics were only obtained after sintering at lower temperatures, such as 1723 K (Figs. 1C and E), insufficient to achieve density higher than 90% (Table 1). Attempts to prepare single-phase $LaSr_2Mn_{1.4}Ni_{0.6}O_{7-\delta}$ failed. The samples of this composition comprise a major perovskite phase after sintering at 1823 K (Fig. 2C), and melt at 1873 K. In addition to the $Sr_3Ti_2O_7$-type solid solution, $LaSr_2Mn_{1.4}Ni_{0.6}O_{7-\delta}$ ceramics sintered at 1673–1773 K comprise also a K_2NiF_4-type phase impurity (Figs. 2D–F); increasing the duration of thermal treatment has rather a negligible effect on the intensity of secondary phase reflections. Therefore, the solubility limit of nickel cations in $LaSr_2Mn_2O_{7-\delta}$ at atmospheric oxygen pressure corresponds to approximately 25% manganese sites.

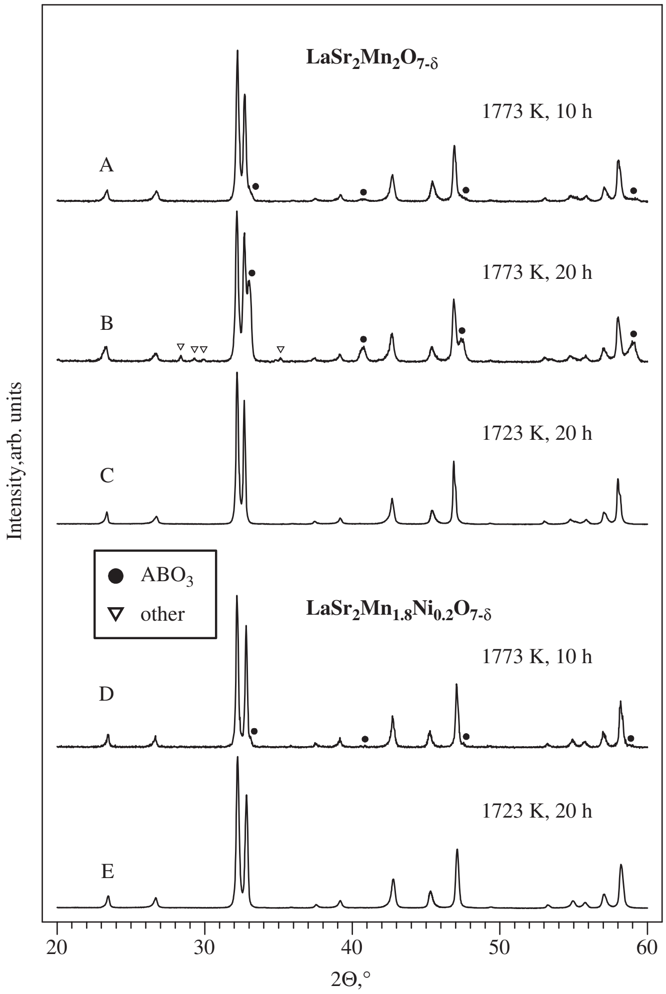

Fig. 1. XRD patterns of $LaSr_2Mn_2O_{7-\delta}$ (A–C) and $LaSr_2Mn_{1.8}Ni_{0.2}O_{7-\delta}$ (D and E) ceramics sintered under different conditions.

The crystal structure of $LaSr_2Mn_{2-y}Ni_yO_{7-\delta}$ ($y = 0$–0.4) was refined in $I4/mmm$ space group. The substitution of manganese with nickel leads to a lattice contraction along the ab planes and to an expansion along the c-axis (Table 1). As a result, the unit cell volume decreases on doping. Due to an enhanced thermodynamic stability of the $n = 2$ RP phase containing 20% Ni at elevated temperatures which makes it possible to sinter gas-tight ceramic materials with density higher than 95% in air (Table 1), the maximum attention in this work was focused on $LaSr_2Mn_{1.6}Ni_{0.4}O_{7-\delta}$.