

Crystal Structure, Oxygen Nonstoichiometry and Diffusion Mobility in Some Ferrites-Nickelites

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Abstract. Crystal structure, thermal expansion, oxygen non-stoichiometry, electrical conductivity and diffusion characteristics of two analogous $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ and $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ compositions were investigated depending on temperature (20–1000 °C) and oxygen partial pressure (0.6–2100 Pa). The found oxygen diffusion and oxygen exchange coefficients for the both compositions at similar conditions are near to each other and varied in the range of $1 \cdot 10^{-7}$ – $1 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ and $5 \cdot 10^{-6}$ – $1 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$, respectively.

Key words: double-B-site mixed nickelites-ferrites, electrical conductivity, oxygen non-stoichiometry, chemical diffusion, oxygen exchange

I. INTRODUCTION

$\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ and $\text{PrFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ perovskites are of interest to a wide variety of applications including electrodes and current collectors in Solid Oxide Fuel Cells (SOFCs), cells for gas electrolyzes, oxygen solid electrolyte sensors, oxygen pumps operative at intermediate temperatures et cetera [1]. A single phase compositions in the system $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$ are known at $x=0$ –0.8 [2,3] and in system $\text{PrFe}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ at $x=0.4$ –0.6 [1,4]. $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ was prepared and its crystal structure, conductivity and diffusion parameters were compared with analogous $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ composition at broad range of temperatures (20–1000 °C) and oxygen partial pressures 0.6–2100 Pa).

II. EXPERIMENTAL

$\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ and $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ powders were prepared by the solid-state reaction method. The constituent metal oxide powders Pr_6O_{11} (99% pure, Alfa Aesar), La_2O_3 (99.5% pure Merck), NiO (99% pure, Alfa Aesar) and Fe_2O_3 (Analytical Reagent, Reanal Hungary) were first ball-milled in an agate mill in stoichiometric amounts along with some minimum amount of ethanol for 24 hours. The resultant pastes were dried, ground in a mortar, and then calcined in air up to a temperature of 1000–1350 °C with a heating and cooling rate of 5 K/min. This powder has been analyzed at room temperature by XRD measurements (Siemens D5000 diffractometer, $\text{Cu K}\alpha$ radiation).

In situ high-temperature powder diffraction experiments were performed in the temperature range of 20–900 °C at the synchrotron facility HASYLAB@DESY (beamline B2 [5]). Diffraction data were collected in the Debye-Scherrer capillary geometry using the on-site readable image plate

detector [6].

Porous ceramic samples for conductivity and oxygen exchange measurements were prepared by sintering pressed bars (dimensions: 10 mm × 3 mm × 1.5 mm) in air at 1200 °C for 17 h, whereas gas dense ones for oxygen diffusion and oxygen exchange measurements by sintering of the similar bars at 1500 °C in air for 17 h.

Oxygen non-stoichiometry and electrical conductivity were investigated on the ceramic samples using a solid electrolyte measurement complex ZirOxSystem (Zirox, Greifswald, Germany) analogous to OXYLYT complex described elsewhere [7].

Chemical diffusion and oxygen surface exchange coefficients were determined by conductivity relaxation measurements of the gas dense samples after 50 K temperature jumps at constant oxygen concentration in gas phase [3,4], or after oxygen partial pressure jumps at constant temperatures from one equilibrium state to the other one.

III. RESULTS AND DISCUSSIONS

A. Crystal structure

The both $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ and $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ samples prepared at 1350 °C were black in colour and analyzed by powder diffraction of synchrotron radiation to be single-phase orthorhombic perovskite with *Pbnm* space group. $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ is stable and does not show any structural transformations in air in the temperature range 298–1173 K (Fig. 1).

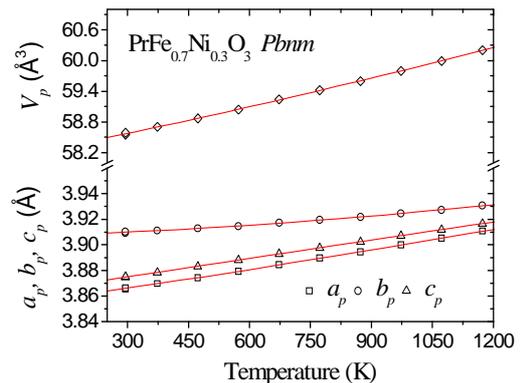


Fig. 1. Temperature dependence of cell dimensions in $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$. Lattice parameters and cell volume of the orthorhombic cell are normalized to the perovskite ones as follows: $a_p = a_o/\sqrt{2}$, $b_p = b_o/\sqrt{2}$, $c_p = c_o/2$, $V_p = V_o/4$.

In contrast, corresponding lanthanum sample $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ undergoes structural phase transition from orthorhombic to rhombohedral (*R-3c*) structure at around 790 K (Fig. 2). The analysis of the diffraction patterns in the vicinities of the transition temperature revealed the

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coexistence of both, orthorhombic and rhombohedral phases in the temperature range 713–873 K, which gives evidence of 1st-order character of the phase transition. This conclusion is also proved by a significant change of the cell volume occurred at the phase transition (see Fig. 2).

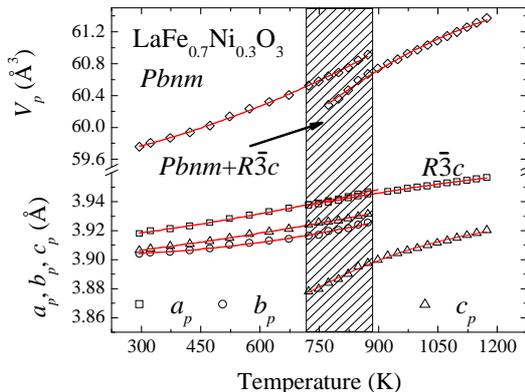


Fig. 2. Temperature dependence of cell dimensions in $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$. Lattice parameters and cell volumes of the orthorhombic and rhombohedral cells are normalized to the perovskite ones as follows: $a_p = a_o/\sqrt{2}$, $b_p = b_o/\sqrt{2}$, $c_p = c_o/2$, $V_p = V_o/4$; $a_p = a_r/\sqrt{2}$, $c_p = c_r/\sqrt{12}$, $V_p = V_r/6$.

One additional check-diffraction pattern of $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ was taken at room temperature after the heat treatment of the sample. The sample returned always to their initial state, which is the proof for transition reversibility and stability of the sample in the temperature range of 298–1173 K.

B. Oxygen diffusion mobility and surface exchange

Fig. 3 shows a typical result of relaxation experiment used in the calculation of oxygen diffusion and surface exchange characteristics on gas dense $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ ceramic sample in Ar/O_2 gas flow at temperature 900 °C. It demonstrates the fact that such stepwise measurements can yield reproducible and reversible results when switching between two oxygen partial pressures at constant temperature. The sample is allowed enough time to attain its new equilibrium state. For example, both oxidation steps (stepwise decreasing voltage U_1) and reduction ones (stepwise increasing voltage U_1) showed almost equal changes in conductivity and hence their diffusion characteristics were obtained and found to be comparable.

Fig. 4 illustrates the other relaxation scheme carried out on gas dense $\text{LaFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ ceramic sample in Ar/O_2 gas

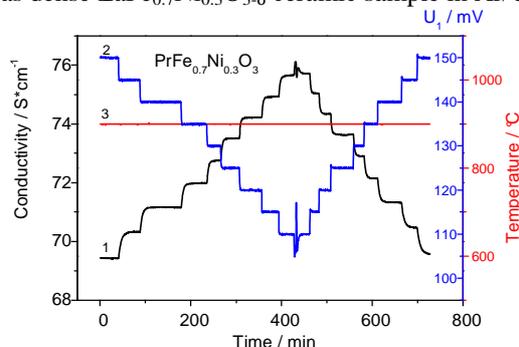


Fig. 3. Time dependence of conductivity (line 1), voltage on the input cell of a ZirOx device (line 2), and temperature (line 3) of the $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ ceramic sample.

flow at $p\text{O}_2$ of 56 Pa ($U_{1,750^\circ\text{C}} = 130$ mV). The conductivity relaxation changes were measured at constant oxygen concentration and stepwise temperature jumps of 50 K from 750 to 950 °C and back. Both experimental schemes gave the similar oxygen diffusion and exchange coefficients at the comparable conditions.

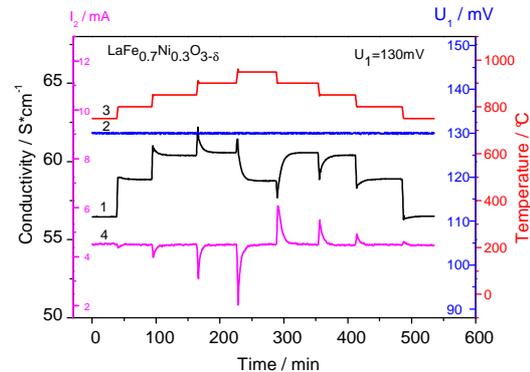


Fig. 4. Time dependence of conductivity (line 1), temperature of the $\text{PrFe}_{0.7}\text{Ni}_{0.3}\text{O}_{3-\delta}$ ceramic sample (line 3), voltage in the input cell (line 2) and titration current in output cell (line 4) of a ZirOx device.

At the used experimental conditions, oxygen diffusion and oxygen surface exchange coefficients of the both compositions are changed in the range of $(1 \cdot 10^{-7} - 1 \cdot 10^{-5}) \text{ cm}^2 \cdot \text{s}^{-1}$ and $(5 \cdot 10^{-6} - 1 \cdot 10^{-4}) \text{ cm} \cdot \text{s}^{-1}$, respectively.

Oxygen non-stoichiometry indexes of both compositions measured at low oxygen partial pressures (lower as 100 Pa) are varied between 0 and 0.05.

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