

# Oxygen permeability, electronic conductivity and stability of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_3$ -based perovskites

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## Abstract

The electrical properties of perovskite-type  $(\text{La}_{0.3}\text{Sr}_{0.7})_{1-y}\text{CoO}_{3-\delta}$  ( $y=0-0.03$ ) and  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{M}_{0.2}\text{O}_{3-\delta}$  ( $\text{M}=\text{Al}, \text{Ga}$ ), promising parent materials of dense mixed-conducting membranes for oxygen separation, were studied in the oxygen partial pressure range from  $10^{-14}$  to 0.5 atm. The steady-state oxygen permeation fluxes through cobaltite ceramics at 973–1223 K are limited by both bulk ionic conductivity and surface exchange kinetics. The substitution of cobalt with  $\text{Al}^{3+}$  or  $\text{Ga}^{3+}$  increases cubic perovskite unit cell volume, oxygen deficiency and Seebeck coefficient, whereas the thermal expansion, p-type electronic conductivity and oxygen permeability decrease. The creation of A-site cation vacancies, compensated by  $\text{Co}^{4+}$  formation, leads to higher p-type electronic conductivity and thermal expansion at temperatures above 700 K, whilst the ionic transport in A-site deficient cobaltite is lower than that in  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ . Reducing oxygen pressure down to approximately  $10^{-5}$  atm results in transition into brownmillerite-type phases having essentially  $p(\text{O}_2)$ -independent electrical properties until decomposition, which occurs at  $p(\text{O}_2)$  values  $10^2$  to  $10^4$  times higher compared to CoO/Co boundary. The average thermal expansion coefficients of cobaltite ceramics in air are  $(15.9-19.6) \times 10^{-6} \text{ K}^{-1}$  at 300–750 K and  $(27.9-29.7) \times 10^{-6} \text{ K}^{-1}$  at 750–1240 K.

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## 1. Introduction

The use of mixed-conducting ceramic membranes for oxygen separation from air and partial oxidation of light hydrocarbons may provide substantial economic and environmental advantages with respect to the conventional industrial processes [1–6]. However, developments of the membrane technologies are still limited due to materials science-related problems. The membrane materials should satisfy numerous requirements, including high ambipolar conductivity determined by the bulk ionic and electronic transport, fast oxygen surface exchange kinetics within a wide  $p(\text{O}_2)$  range, thermodynamic and dimensional stability under operation conditions, and suitable thermo-mechanical properties. One attractive group of mixed conductors relates to the phases derived from  $(\text{Sr},\text{La})\text{CoO}_{3-\delta}$  cobaltites

with  $\text{ABO}_3$  perovskite-type structure, which exhibit very high oxygen ionic and electronic conductivities and, thus, oxygen permeability [3,7–10]. For  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  series, the maximum ionic transport is observed at  $x \approx 0.7$  [7–10]; greater oxygen fluxes were obtained only for  $\text{SrCo}(\text{Fe})\text{O}_3$ - and  $\text{BaCo}(\text{Fe})\text{O}_3$ -based ceramics having insufficient physicochemical and thermo-mechanical stability [3,8,12–16]. Further increase of strontium content in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ , at  $x > 0.7$ , leads to decreasing oxygen transport due to progressive association of defects and phase separation [10]. Oxygen transport through  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  ceramics is determined by both ambipolar conductivity and surface exchange [9,11].

The present work is focused on the effects of A-site cation deficiency and B-site doping on the oxygen ionic and electronic transport in  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ . For this study, perovskite-type  $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.97}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Al}_{0.2}\text{O}_{3-\delta}$  and  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$  were selected as model compositions. The choice of two latter compounds was based on the data on ferrite systems  $(\text{Sr},\text{La})(\text{Fe},\text{M})\text{O}_{3-\delta}$  ( $\text{M}=\text{Ga}, \text{Al}$ ), where a substantial improvement in phase stability and thermo-mechanical

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Table 1  
Properties of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ -based ceramics

Composition	Relative density (%)	Unit cell parameter, $a$ (nm)	Average linear thermal expansion coefficient in air		Activation energy for the oxygen permeation fluxes <sup>a</sup>	
			$T$ (K)	$\bar{\alpha} \times 10^6$ ( $\text{K}^{-1}$ )	$T$ (K)	$E_a$ (kJ/mol)
$\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$	92.6	0.3836	300–750	$19.6 \pm 0.5$	1023–1153	$77 \pm 5$
			750–1100	$28.8 \pm 0.5$		
$(\text{La}_{0.3}\text{Sr}_{0.7})_{0.97}\text{CoO}_{3-\delta}$	97.5	0.3837	390–640	$17.5 \pm 0.3$	1073–1173	$106 \pm 12$
			790–1160	$29.7 \pm 0.5$		
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Al}_{0.2}\text{O}_{3-\delta}$	97.2	0.3846	390–790	$17.4 \pm 0.2$	1103–1173	$124 \pm 2$
			790–1240	$28.3 \pm 0.4$		
$\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$	96.5	0.3871	360–710	$15.9 \pm 0.5$	1073–1223	$78 \pm 11$
			710–1030	$27.9 \pm 0.4$		

<sup>a</sup> The permeation fluxes correspond to the oxygen pressure gradient of 0.209/0.066 atm and the membrane thickness of 1.00 mm.

properties was achieved due to iron substitution [6,17,18]. In the case of Ga-doped ferrites, local lattice distortions near statistically distributed  $\text{Ga}^{3+}$  may also partially suppress oxygen-vacancy ordering, thus increasing ionic conductivity [18]. The creation of A-site cation vacancies has often analogous influence on the ionic transport and simultaneously enhances the stability in  $\text{CO}_2$ -containing atmospheres [19]; both these effects are extremely important for the practical applications of membrane materials. Although previous work [9] showed a decrease in the oxygen permeability of  $(\text{Sr},\text{La})\text{CoO}_{3-\delta}$  ceramics containing 5–10% vacancies in the A sublattice, the results on  $\text{SrFeO}_3$ -based compounds [19] indicate that this level of A-site deficiency may be excessive for any positive influence on the ionic conduction. Particular emphasis in this work is given to the properties determining applicability of mixed conductors, namely oxygen permeation, thermal expansion and phase stability; the defect chemistry of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ -based compositions is analyzed using the results on oxygen partial pressure dependencies of total conductivity and Seebeck coefficient, in combination with thermogravimetric data.

## 2. Experimental

The submicron powders of  $(\text{La}_{0.3}\text{Sr}_{0.7})_{0.97}\text{CoO}_{3-\delta}$ ,  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Al}_{0.2}\text{O}_{3-\delta}$  and  $\text{La}_{0.3}\text{Sr}_{0.7}\text{Co}_{0.8}\text{Ga}_{0.2}\text{O}_{3-\delta}$  were synthesized via the glycine-nitrate process (GNP), a self-combustion technique using nitrates of metal components as an oxidant and glycine as a fuel and chelating agent [20]. This synthesis method is suitable to obtain very fine and homogeneous multicomponent oxide powders, especially when the solid-state reaction is stagnated due to kinetic reasons. For the synthesis, stoichiometric amounts of metal nitrates were dissolved in distilled water, before adding glycine. The amount of glycine was twice the stoichiometric one, calculated assuming the only gaseous reaction products to be  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The solutions were dried until self-ignition; the resultant foam-like powders were annealed in air at 1073–1273 K for 2 h to remove residual carbon and then ball-milled. The synthesis conditions of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ , used in this work for comparison, were reported elsewhere [11]. The disc-shaped samples (12–18 mm in diameter) were uniaxially pressed at 250–400 MPa; gas-tight ceramics were sintered in air at 1423–1553 K for 2 h and slowly

(2–3 K/min) cooled to equilibrate with atmospheric oxygen at low temperatures. The density of ceramic materials was higher than 92% of their theoretical density calculated from the X-ray diffraction (XRD) results, Table 1.

Formation of single perovskite phases was verified by the XRD analysis performed using a Rigaku Geigerflex D/MAX-B diffractometer (Cu  $\text{K}\alpha$  radiation); the Fullprof software [21] was used to calculate unit cell parameters and to verify lattice symmetry. In order to assess phase changes on heating and under reduction, the powdered samples were annealed at 1023–1273 K in flowing  $\text{O}_2$ -Ar and  $\text{H}_2$ - $\text{H}_2\text{O}$ - $\text{N}_2$  mixtures, where the oxygen partial pressure was controlled using an oxygen sensor; these treatments were followed by quenching and XRD inspection. Transmission electron microscopy (TEM, Hitachi H-9000) and scanning electron microscopy (SEM, Hitachi S-4100), both combined with energy dispersive spectroscopy (EDS), were used for the microstructural studies. Dilatometric data were collected in air using alumina Linseis L70/2001 and Bahr DIL801L dilatometers (heating rate of 5 K/min). Thermogravimetric and differential thermal analyses (TG/DTA) were carried out on Setaram LabSys TG-DTA16 and Setaram SetSys 16/18 instruments in a flow of air or 10%  $\text{H}_2$ -90%  $\text{N}_2$  mixture. The total electrical conductivity (4-probe DC) and Seebeck coefficient were measured as functions of temperature and oxygen partial pressure, as described elsewhere [22]. The steady-state oxygen permeation fluxes were determined at 873–1223 K; the description of the measurement techniques used is found in Refs. [7,15,16]. For all permeation data reported in this work, the feed-side oxygen partial pressure ( $p_2$ ) was fixed at 0.21 atm (atmospheric air).

## 3. Results and discussion

### 3.1. General characterization

XRD studies confirmed that all studied materials are single-phase and have cubic perovskite structure (space group  $Pm\bar{3}m$ ) characteristic of the parent compound,  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  [10,11]. Selected examples of the XRD patterns are shown in Fig. 1. Note that the incorporation of aluminum cations may promote formation of vacancy-ordered microdomains with brownmillerite-like structure, which is undetectable by XRD

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