

# Defect structure and oxide ion transport in Sr- and Cr-doped $\text{LaCoO}_{3-\delta}$

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## ABSTRACT

The results of oxygen nonstoichiometry,  $\delta$ , measured by means of coulometric technique as a function of oxygen partial pressure,  $p_{\text{O}_2}$ , in temperature range  $1223 \leq T, K \leq 1323$  are presented for the perovskite-type doped with chromium solely  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  and simultaneously doped both with strontium and chromium  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  cobaltites. The limit stability of the latter was found to exceed that of undoped cobaltite  $\text{LaCoO}_{3-\delta}$  on six orders of magnitude of  $p_{\text{O}_2}$  at a given temperature. The modeling of the defect structure of these perovskites was carried out and its adequate model was found. Chemical and self-diffusion coefficients of oxygen vacancies and oxygen ionic conductivity and ionic transport numbers were measured for the first time for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  as a function of oxygen partial pressure  $p_{\text{O}_2}$  and temperature in the ranges  $-4 \leq \log(p_{\text{O}_2}, \text{atm}) \leq 0$  and  $1223 \leq T, K \leq 1323$ , respectively. The additional substitution of Sr for La in  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  was shown to lead to noticeable increase of ionic conductivity and oxygen chemical diffusion coefficient at given values of oxygen partial pressure and temperature as compared to lanthanum cobaltite doped with chromium solely. Self-diffusion coefficient of oxygen vacancies and their mobility in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  were found to be dependent on oxygen partial pressure and nonstoichiometry unlike undoped and doped with chromium lanthanum cobaltites.

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## 1. Introduction

Lanthanum cobaltite-based oxides are the-state-of-the-art materials for high temperature electrochemical devices such as solid oxide fuel cells (SOFCs) [1–3], oxygen membranes [4–6]. They also find an application as cathodes [7] for  $\text{CO}_2$ -lasers and catalysts [8,9]. The known disadvantage of these materials is their low stability at high temperatures and low oxygen partial pressures [10,11]. The substitution of low reducible 3d metal, for instance Cr, for Co is believed to lead to dramatic growth of thermodynamic stability of lanthanum cobaltite. So far, however, there are no data on limits of thermodynamic stability of Cr-doped lanthanum cobaltites. It is worth noting that doping with Cr was shown to be accompanied by significant oxide ion conductivity decrease as compared to undoped lanthanum cobaltite [12]. Hence simultaneous doping with Cr on B-site and with Sr on A-site can be expected to be a way to increase oxide ion conductivity retaining required thermodynamic stability of doped lanthanum cobaltite at the same time. It is necessary to note that defect structure of solid oxides is of key importance for understanding their properties such as electronic and ionic transport. However, neither data on defect structure of  $\text{LaCoO}_{3-\delta}$  simultaneously doped with Sr and Cr nor those on its oxide ion conductivity are available to date.

The priority goals of the present work were, therefore, (i) to measure oxygen nonstoichiometry of the perovskites  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Cr}_y\text{O}_{3-\delta}$

( $x=0, 0.3$ ;  $y=0.3$ ) as a function of oxygen partial pressure and temperature, (ii) to carry out model analysis of their defect structure on the basis of reliable data on oxygen nonstoichiometry, (iii) to determine oxygen chemical diffusion coefficient and oxygen ionic conductivity of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  as a function of oxygen partial pressure at different temperatures by means of polarization technique.

## 2. Experimental

Powder samples of  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_3$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  were prepared by pyrolysis of the corresponding polymer–salt compositions according to the technique described elsewhere [12]. The phase composition of all samples prepared was determined by means of X-ray diffraction, XRD, with a Dron-6 diffractometer using  $\text{Cu K}\alpha$  radiation. XRD showed no indication for the presence of a second phase.

The single phase powders were pressed into tablets of 6 mm diameter and 0.9 mm thickness and then sintered at 1500 °C for 24 h in air. Relative density of sintered samples was 95%.

The original coulometric titration set up used for oxygen nonstoichiometry measurements is described in detail elsewhere [13]. Absolute value of  $\delta$  for both oxides was determined using model calculation described in detail elsewhere [14]. Thermodynamic stability limits of  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  were determined by use of an electromotive force (emf) method. On finishing complete cycle of the Coulometric titration measurements the Coulometric set up was used as an emf one. The emf method is described elsewhere [15]. Complete cycle of the emf measurements was followed by fast cooling of the cell with the sample

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in order to determine a composition of the oxide sample after its decomposition using XRD analysis.

For the determination of chemical diffusion coefficient and ionic conductivity the following electrochemical cell was used:



The technique of polarization measurements and corresponding experimental setup is described in detail elsewhere [12].

Depolarization (relaxation)  $U_d$  voltages of aforementioned cell (Eq. (1)) can be expressed [12] as a long time solution of Fick's second law

$$U_d(t) = -\frac{jL t_e}{\sigma_{\text{O}^{2-}}} \left( \frac{8}{\pi^2} \exp(-t/\tau) \right), \quad (2)$$

where  $j$ ,  $L$ ,  $t_e$ ,  $\sigma_{\text{O}^{2-}}$  and  $t$  are current density, sample thickness, electronic defects transport number, oxide ion conductivity, and time, respectively.  $\tau$  in Eq. (2) is a relaxation time defined as  $\tau = \frac{L^2}{\pi^2 \tilde{D}}$ , where  $\tilde{D}$  is oxygen vacancies chemical diffusion coefficient. As can be seen  $\ln|U_d - U_\infty|$  is linear function of  $t$  with slope coefficient,  $k = -\frac{1}{\tau} = -\frac{\pi^2 \tilde{D}}{L^2}$ . Oxygen vacancies chemical diffusion coefficient and oxygen ionic conductivity can be, therefore, calculated from the plot  $\ln|U_d - U_\infty|$  vs.  $t$ . Chemical diffusion coefficient, in turn, is related to so-

called thermodynamic enhancement factor,  $\left( \frac{\partial \ln P_{\text{O}_2}}{\partial \ln[V_{\text{O}^\bullet}]} \right)_{T=\text{const}}$ , by the following equation

$$\tilde{D}_{V_{\text{O}^\bullet}} = -D_{V_{\text{O}^\bullet}} \left( \frac{\partial \ln P_{\text{O}_2}}{\partial \ln[V_{\text{O}^\bullet}]} \right)_{T=\text{const}}, \quad (3)$$

where  $D_{V_{\text{O}^\bullet}}$  is oxygen vacancies self-diffusion coefficient. Then partial oxygen conductivity can be expressed using Nernst–Einstein equation as

$$\sigma_{V_{\text{O}^\bullet}} = \frac{(z_i F)^2 D_{V_{\text{O}^\bullet}} B}{RT} \delta = z_i F U_{V_{\text{O}^\bullet}} B \delta, \quad (4)$$

where  $\delta$ ,  $B$ ,  $z_i=2$ ,  $F$ , and  $U_{V_{\text{O}^\bullet}}$  are oxygen nonstoichiometry, a conversion constant, oxygen vacancy charge, Faraday constant, and oxygen vacancies mobility, respectively.

Derivative  $\left( \frac{\partial \ln P_{\text{O}_2}}{\partial \ln[V_{\text{O}^\bullet}]} \right)_{T=\text{const}}$  was determined from the isothermal dependencies of oxygen nonstoichiometry vs. oxygen partial pressure measured in the present work by coulometric titration technique.

The polarization current of 0.1–0.3 mA/cm<sup>2</sup> was used in the present work in order to voltage drop on the cell did not exceed 10–100 mV. Depolarization voltage was measured by Agilent 34401 A voltmeter.

### 3. Results and discussion

Oxygen nonstoichiometry of  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  measured as a function of  $p_{\text{O}_2}$  and temperature is given in Fig. 1a and b, respectively. According to Zuev et al. [16], addition of Co to  $\text{LaCrO}_3$  acts as an acceptor dopant. Substitution of Cr for Co in the lanthanum cobaltites can be, therefore, resulted in the formation of somewhat  $\text{Cr}^{4+}$  amount according to the reaction



where  $\text{Cr}_{\text{Co}}^{\times}$ ,  $\text{Co}_{\text{Co}}^{\times}$ ,  $\text{Cr}_{\text{Co}}^{\bullet}$ , and  $\text{Co}_{\text{Co}}^{\prime}$  denote  $\text{Cr}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cr}^{4+}$ , and  $\text{Co}^{2+}$ , respectively, using the Kröger–Vink notation. Taking into account the charge disproportionation involving the transfer of an electron between adjacent  $\text{Co}_{\text{Co}}^{\times}$  sites

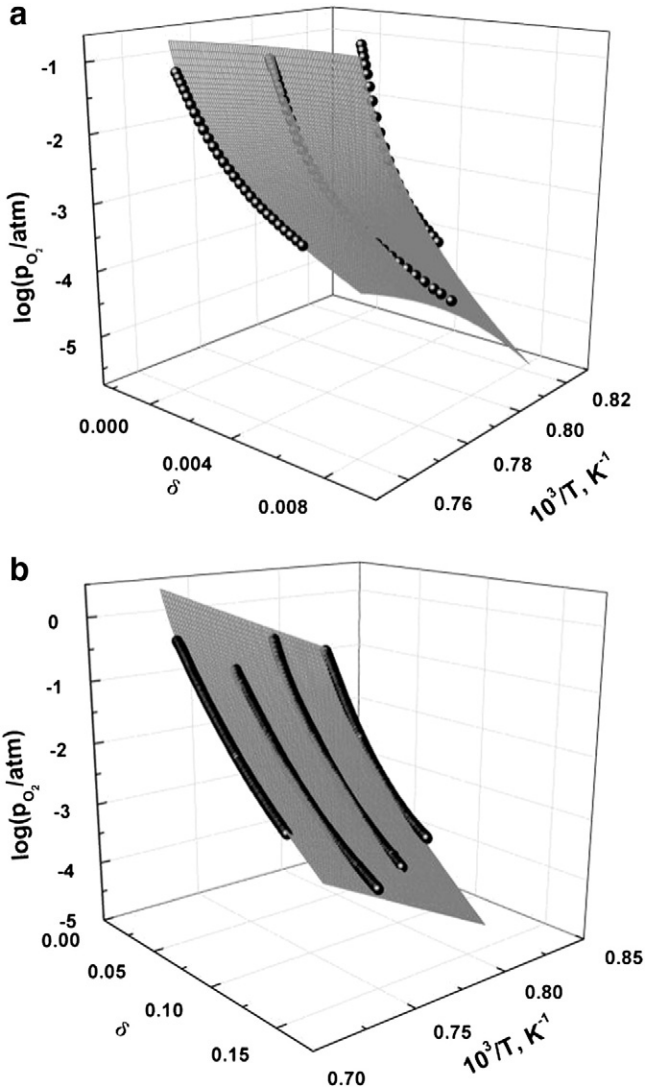


Fig. 1. Oxygen nonstoichiometry measured (points) and 3D fitting results (surface) of the defect structure modeling for  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  (a) and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  (b).

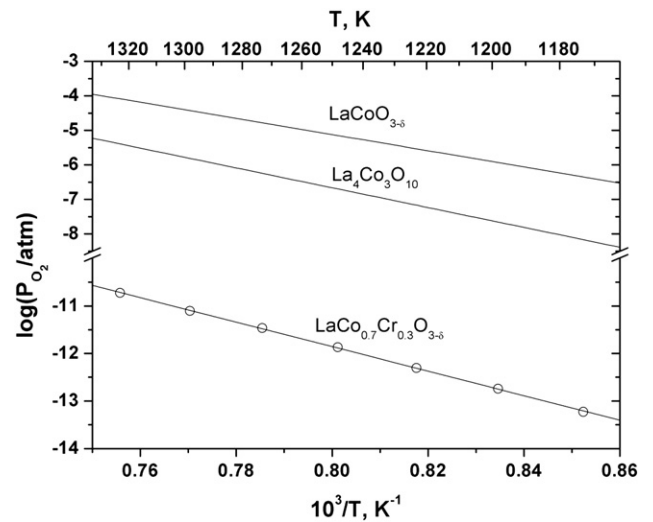


Fig. 2. Thermodynamic stability limits of  $\text{LaCoO}_{3-\delta}$  [15],  $\text{La}_4\text{Co}_3\text{O}_{10}$  [15] and  $\text{LaCo}_{0.7}\text{Cr}_{0.3}\text{O}_{3-\delta}$  (this work).

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