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X-ray absorption investigation of the valence state and electronic structure of $La_{1-x}Ca_xCoO_{3-\delta}$ in comparison with $La_{1-x}Sr_xCoO_{3-\delta}$ and $La_{1-x}Sr_xFeO_{3-\delta}$

O. Haas [a],*, Chr. Ludwig [b,c], U. Bergmann [d], R.N. Singh [e], A. Braun [f], T. Graule [f]

[a] Energy and Material Research Consulting, CH-6648 Minusio, Switzerland
[b] General Energy Research, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
[c] École Polytechnique Fédérale de Lausanne, ENAC-IIE, CH-1015 Lausanne, Switzerland
[d] Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA
[e] Banaras Hindu University, Chemistry Department, Varanasi 221005, India
[f] Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, CH-8600 Duebendorf, Switzerland

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ABSTRACT

3*d* metal K-shell X-ray absorption spectra of perovskites with the composition $La_{1-x}Ca_xCoO_{3-\delta}$ ($x=0$, 0.2, 0.4, 0.5, 0.6, 0.8), $La_{1-x}Sr_xCoO_{3-\delta}$ ($x=0$, 0.1, 0.2, 0.3, 0.4, 0.5) and $La_{1-x}Sr_xFeO_{3-\delta}$ ($x=0$, 0.2, 0.4, 0.5, 0.6, 0.8) are compared on the basis of pre-edges, white line features and extended fine structures. The measurements were performed at 300 K and for $La_{1-x}Ca_xCoO_{3-\delta}$ also at temperatures as low as 10–20 K. Going to low-temperature the measurements indicate an increase in t^*_{2g} and a decrease in e^*_g orbital occupancy, which is most accentuated in the $LaCoO_3$ sample. Virtually no Co K-edge shift was observed for the $La_{1-x}Ca_xCoO_{3-\delta}$ and $La_{1-x}Sr_xCoO_{3-\delta}$ compounds and the Co–O distances are also not significantly reduced when La^{3+} is partially substituted by Ca^{2+} or Sr^{2+}. From the pre-edge features of these perovskites we are tended to conclude that the t^*_{2g} orbitals are less, and the e^*_g orbitals are more occupied with increasing x in the Ca and Sr substituted compounds, whereas the total *d*-electron density is not changing. These results indicate that cobalt prefers a valence state of 3^+ in these Co perovskites. This could also be confirmed with iodometric titrations. The Fe perovskites behave differently. In contrast to the Co perovskites, for $La_{1-x}Sr_xFeO_{3-\delta}$ perovskites the Fe K-edge is shifted, the pre-edge features intensity is increasing and the Fe–O bond length is decreasing with increasing x. The valence states of the iron in the $La_{1-x}Sr_xFeO_{3-\delta}$ perovskites in fact increase as much as x increases.

1. Introduction

$La_{1-x}Ca_xCoO_{3-\delta}$, $La_{1-x}Sr_xCoO_{3-\delta}$ and $La_{1-x}Sr_xFeO_{3-\delta}$ perovskites have attractive electronic and ion-conduction properties, which offer applications in numerous domains. They are used as a catalyst in redox processes. $LaCoO_3$ for instance exhibits catalytic activity above 1000 K, where carbon monoxide can be oxidized and NO_x can be decomposed [1]. $La_{1-x}Ca_xCoO_{3-\delta}$ and $La_{1-x}Sr_xCoO_{3-\delta}$ can be used in oxygen diffusion electrodes as a catalyst to reduce and to evolve oxygen [2–4]. The oxygen-ion-conducting and electron-conducting properties of such perovskites can be used in high temperature fuel cell cathodes [5–8]. They show also promises for thermoelectric devices [9] and have interesting magnetic properties, e.g. high magneto-resistance or even negative magneto-resistance [10]. Magnetic anomalies and its temperature dependency [11–13] are another area of interest of these perovskites.

X-ray absorption spectroscopy (XAS) is a very valuable tool to study electronic and structural properties of materials. XAS has been developed over several decades, and standardized methods for data analysis are now available for near edge absorption (XANES), the extended X-ray absorption fine structure region (EXAFS) and its surface version (SEXAFS). Synchrotron radiation has extended the possibilities of these methods, since much higher X-ray intensities are available allowing faster measurements and the detection of lower concentrations. In many cases XAS, particularly based on hard X-rays with a large attenuation depth, can be used as an *in-situ* analytical tool [14] and has therefore tremendous advantages over most high-vacuum analytical methods. We used XAS to study the valence state and to obtain information about the electronic configuration of these Co and Fe perovskites. The valence states govern most of the physico-chemical properties of these perovskites. The valence state of the transition metal cation can be manipulated by partial substitution of La^{3+} using divalent earth metal ions like Ca^{2+} or Sr^{2+}. Especially the valence state of iron in such perovskites is substantially influenced by substitution of La with Ca^{2+} or Sr^{2+}.

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* Corresponding author.
E-mail address: otto.haas@bluewin.ch (O. Haas).

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Electrochemical methods can also be used to change the valence state [15]. The valence state may also depend on the oxidizing or reducing conditions during preparation [16]. The citric acid precursor method in example may lead to reduced perovskites since the citric acid is carbonized when the sample is fired and at high temperature this carbon may act as a reducing agent and influence the valence state. This is not the case if oxides are used as starting materials, but if they are heated too high, deoxygenation may also take place [17].

There are several publications about XAS investigations on $La_{1-x}Ca_xCoO_{3-\delta}$ [18–24], whereas to our knowledge low-temperature XAS studies were only performed on $LaCoO_3$ [18,20] and on $La_{1-x}Sr_xCoO_{3-\delta}$ [18,25]. XAS investigations on $La_{1-x}Sr_xFeO_{3-\delta}$ [26–29] and $La_{1-x}Sr_xCoO_{3-\delta}$ [30–35] should also be mentioned. In our former publications about $La_{1-x}Ca_xCoO_{3-\delta}$ [22] and $La_{1-x}Sr_xFeO_{3-\delta}$ [26] we discussed our XAS data together with the existing literature of these perovskites. In addition to these measurements we investigated now the $La_{1-x}Ca_xCoO_{3-\delta}$ series at low temperature (10–20 K) together with $La_{1-x}Sr_xCoO_{3-\delta}$ samples obtained from Prof. Singh. We think it is of general interest to compare the $La_{1-x}Sr_xCoO_{3-\delta}$ series and the cold measurements of the $La_{1-x}Ca_xCoO_{3-\delta}$ series with the former results obtained from $La_{1-x}Ca_xCoO_{3-\delta}$ and $La_{1-x}Sr_xFeO_{3-\delta}$ series presented in [22,26]. Concerning our new $La_{1-x}Sr_xCoO_{3-\delta}$ measurements we like to compare our work with the existing literature as follows:

Jiang et al. [25] investigated $La_{1-x}Sr_xCoO_{3-\delta}$ in a somewhat lower x range than we did but at room temperature and low temperature. They concentrated on a discussion about the Jahn–Teller effect in these perovskites and discussed the possibility of a core-hole potential interaction on the Co K-edge energy. It should be mentioned that their nanoparticle samples do not show the same x dependency of the Co K pre-edge as we present here. Toluemonde et al.'s work [18] is probably closest to our investigation and argumentation of the $La_{1-x}Sr_xCoO_{3-\delta}$ series but, they concentrated more on the O K edge and made no EXAFS investigation. In contradiction to Jiang et al. and our investigation, Toluemonde et al. suggested a mixed (LS–IS Co^{3+}/IS Co^{4+}) cobalt configuration. Hueso et al. [33] describe the influence of calcination to the crystal structure and electronic structure of $LaCoO_3$ and $La_{0.5}Sr_{0.5}CoO_{2.75}$. They confirmed our result obtained from the Co K pre-edge features with their O K-edge XAS spectra but have no Co K pre-edge discussion in their paper. They, however, introduced an interesting argument why Sr substitution of La would lead to a low field high spin configuration. None of the mentioned publications made a comparison of $La_{1-x}Sr_xCoO_{3-\delta}$ with $La_{1-x}Sr_xFeO_{3-\delta}$ and $La_{1-x}Ca_xCoO_{3-\delta}$. Piovano et al. [34] describe the electrochemical intercalation of oxygen ions in Brownmillerite phase $SrMO_{2.5}$. These experiments cannot be compared with our perovskites, where lanthanum is partially substituted by Sr. In fact their Co and Fe K pre-edge features behave completely different. The main focus of the present publication is the determination of the valence states of Co and Fe in the investigated perovskites with X-ray absorption spectroscopy. But we also discuss the influence of temperature and lanthanum substitution by Ca or Sr on the electronic structure and valence state of these perovskites.

2. Materials and methods

2.1. Synthesis of perovskites

$LaCoO_3$ and $La_{1-x}Ca_xCoO_{3-\delta}$ perovskites were prepared using the citrate acid precursor method [2]. Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$ (Fluka) and $Co(NO_3)_2 \cdot 6H_2O$ (Fluka) were added to an aqueous 1 M citric acid solution. The solution was evaporated at 343 K using a rotary evaporator and dried for 3 days at 363 K. The resulting powder was first heated in air at 473 K for 2 h and then calcined in air for another 2 h at 973–1023 K.

$La_{1-x}Sr_xCoO_{3-\delta}$ perovskites were obtained by the malic acid precursor route as reported in the literature [36].

$La_{1-x}Sr_xFeO_{3-\delta}$ perovskites (LSF) were prepared using $La(OH)_3$ (Auer Remy, 99.99%), $SrCO_3$ (Fluka, 98%) and Fe_2O_3 (Fluka, 99%) in stoichiometric quantities corresponding to the desired LSF composition. The powder was homogenized during 15 h in the ball mill with 5 mm ZrO_2 balls using 40 wt% of distilled water and 2 wt% of Dolapix CE 64 (Zschimmer&Schwarz, Germany) as liquefier. Subsequently the slurry was dried in a rotary evaporator (Büchi type R-134). The annealing was performed in Al_2O_3 crucibles in a muffle furnace (Ceram-Aix FHT 175/30) using a heating rate of 300 K/h up to the annealing temperature, which was held for 4 h and then cooled down with a cooling rate of 300 K/h. The slow cooling rate allowed the sample to heal oxygen vacancies, introduced at high annealing temperatures. The annealing temperature was adjusted for different *A*-site compositions until phase purity was achieved. For the desired *A*-site variation of the $La_{1-x}Sr_xFeO_{3-\delta}$ perovskites, 1573 K was found to be the optimal annealing temperature for all *A*-site variations. The phase composition was determined by powder XRD analysis (PANalytical X'Pert PRO, Cu-$K\alpha$). After annealing, the powders were milled down to the desired particle size <1 μm by wet-ball milling. The slurry was finally dried with a rotary evaporator.

2.2. Iodometric titration

The perovskites were dissolved in 4 M HCl and titrated during dissolution. The titration was performed under rigorous oxygen exclusion using a 0.05 M $Na_2S_2O_3$ aqueous solution. The sample weight was corrected for water and CO_2 adsorption using thermogravimetry to evaluate the water and CO_2 contents. The procedure and the used apparatus have been described in a former publication [37].

2.3. X-ray absorption measurements

The powder samples of the perovskites were mixed with BN in a 1:5 ratio, and pressed to pellets for the X-ray absorption measurements. The Co amount per cm^2 in the pellet was adjusted to reach one absorption length using the X-ray absorption program offered by Lawrence Berkeley National Laboratory [38]. X-ray absorption measurements were carried out at beamline 9-3 at the Stanford Synchrotron Radiation Lightsource (SSRL), with the storage ring operating at 3 GeV beam energy and a beam current of 100 mA at the top of the fill. A Si(220) double-crystal monochromator was used for energy selection. The intensities of the incident and transmitted X-rays were monitored by nitrogen filled ionization chambers. The monochromator was scanned in energy from 200 eV below to 800 eV above the Co or Fe K absorption edge. The Co K edge X-ray absorption spectra of the $La_{1-x}Ca_xCoO_{3-\delta}$ perovskites were measured at 300 K and at about 10–20 K. A 7 μm thin Co or Fe foil was used as a reference. The foil and the $I_{\mathrm{reference}}$ detector were positioned behind the sample along the direction: {X-ray beam/I_o-detector/[sample]/$I_{\mathrm{sample}}-$detector/[metal foil]/$I_{\mathrm{reference}}-$detector}.

2.4. XAS data analysis

Reduction of the absorption data was performed with the software program WINXAS [39] using standard procedures. The resulting normalized $\chi(k)$ function was then transformed in the k-space and weighted with k^3 to account for dampening of oscillations with increasing k. The $k^3\chi(k)$ function was then