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XAS structural characterization of $La_{1-x}A_xCoO_3$ doped with calcium and barium as a function of temperature

Washington C.M. Gomes [a,*], Dulce M.A. Melo [a,b], Patrícia M. Pimentel [a], Erika P. Marinho [a], Marcus A.F. Melo [a,b], Ricardo S. Nasar [a]

[a] *Universidade Federal do Rio Grande do Norte, Laboratório de catalise e refino, Instituto de Química, Av. Senador Salgado Filho, 3000, CEP 59078-970 Natal, RN, Brazil*
[b] *Universidade Federal do Rio Grande do Norte, Laboratório de catalise e refino, Departamento de engenharia de materiais, Campus I, Natal, RN, Brazil*

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ABSTRACT

The temperature dependence of $La_{0.8}Ba_{0.2}CoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ perovskite structures was investigated, and the $LaCoO_3$ structure was analyzed at room temperature. These materials were characterized by X-ray absorption spectroscopy (XAS) at the cobalt K-edge, and both the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed. The correlated Einstein model was used in the EXAFS data analysis. These materials were prepared by the combustion method. The structures of $LaCoO_3$ at room temperature and of the Ca^{2+}- and Ba^{2+}-doped samples in the temperature range of 50 K–298 K the CoO_6 octahedron have a distorted monoclinic *I*2/a symmetry. However, the Ba^{2+}-doped sample the CoO_6 octahedron has a slightly distorted rhombohedral R-3c symmetry at 50 K, 220 K and 260 K. The $La_{0.8}Ca_{0.2}CoO_3$ structure does not vary much with temperature and has a more distorted Co octahedron and higher local thermal disorder.

1. Introduction

Lanthanum cobaltite ($LaCoO_3$) perovskite has attracted the attention of the scientific community since the 1950's due to its fascinating physical properties and catalytic activity [1–14]. Cobaltites are promising materials for use in solid oxide fuel cells, oxygen membrane separations, catalysis and oxygen sensors [13–16]. Fine $LaCoO_3$ films grown on substrates have also been shown to have potential for future applications [12,17–19]. Cobaltites are similar to manganites and cuprates in that the structures of these families of mixed valence compounds are determined by many interactions, i.e., coupling interactions due to Hund's rule, double exchange interactions and crystal-field interactions. However, cobaltites are unique because of the number of possible spin states [18,19]. In $LaCoO_3$ perovskite, the Co^{3+} ion has six 3d electrons, allowing it to adopt low-spin (LS) ($t_{2g}^6e_g^0$, LS = 0), intermediate-spin (IS) ($t_{2g}^5e_g^1$, IS = 1) and high-spin (HS) ($t_{2g}^4e_g^2$, HS = 2) states with total electron spins of S = 0, 1 and 2, respectively [4,12,18]. In its fundamental state, $LaCoO_3$ perovskite is an insulating, non-magnetic, low-spin material at 4 K [4]; however, at temperatures of 90 K and 500 K, it undergoes transitions to the intermediate-spin excited state [4–8] and to the high-spin state, respectively [9–12]. On the other hand, when some of the La^{3+} ions are replaced by a divalent alkaline earth metal (A = Ca^{2+}, Sr^{2+} or Ba^{2+}) to give a $La_{1-x}A_xCoO_3$ structure, these materials start to exhibit spin-glass behavior and complex spin-state transitions. Divalent cation doping (A) results in the strong suppression of the non-magnetic, low-spin fundamental state by facilitating a spin transition at low temperatures. Usually, a small doping concentration can lead to spin-glass behavior, whereas a high doping concentration ($x \geq 0.2$) leads to ferromagnetic ordering [20,21].

The symmetry of Ca^{2+}- and Sr^{2+}-doped $La_{1-x}A_xCoO_3$ crystalline structures is highly debated. Kriener et al. [20] determined that $La_{0.8}Ca_{0.2}CoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ belong to the orthorhombic Pnma space group and the rhombohedral R-3c space group, respectively [20]. Yet, Wang et al. [21] placed these structures in the monoclinic *I*2/a space group [21]. The undoped $LaCoO_3$ structure was determined to fall in the rhombohedral R-3c space group [22,23]. However, this interpretation is inconsistent with a cooperative Jahn-Teller (JT) distortion of the IS Co^{3+} ion, which is strongly JT active [21,24,25]. High-resolution X-ray studies showed that $LaCoO_3$ has a distorted monoclinic symmetry with three different short-range Co-O distances, which is consistent with JT distortions [24,25].

The aim of this work is to examine the temperature dependence of the structures of $La_{1-x}A_xCoO_3$ perovskite doped with Ca^{2+} and Ba^{2+} (x = 0.2) in the range of $50\ K \leq T \leq 298\ K$. The room-temperature structure of $LaCoO_3$ was also investigated. X-ray absorption

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* Corresponding author.
E-mail address: wascmg@yahoo.com.br (W.C.M. Gomes).

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spectroscopy (XAS) at the cobalt K-edge was used to characterize the materials. To better understand the temperature dependence of the structural properties of $La_{1-x}A_xCoO_3$ ($A = Ca^{2+}$ and Ba^{2+}) and $LaCoO_3$, the EXAFS (extended X-ray absorption fine structure) region of the X-ray absorption spectra, which is especially suitable for probing the local atomic-scale structure around the cobalt ion [26–29], was analyzed using the correlated Einstein model for the vibrational and structural disorder. Stereochemical structural information was obtained from the XANES (X-ray absorption near edge structure) region of the XAS spectrum, and geometrical information about the Co local environment (i.e., first coordination sphere) was obtained from the EXAFS (extended X-ray absorption fine structure) region of the spectrum [29–32].

2. Materials and methods

Chemical reagents: Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 98%, Vetec, Fine Chemicals Vetec LTDA, BR), lanthanum (III) nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$, 99.9%, Sigma-Aldrich, Sigma-Aldrich LTDA, BR), calcium nitrate hexahydrate ($Ca(NO_3)_2 \cdot 6H_2O$, 99.99%, Sigma-Aldrich, Sigma-Aldrich LTDA, BR), barium nitrate hexahydrate ($Ba(NO_3)_2 \cdot 6H_2O$, 99%, Vetec, Fine Chemicals Vetec LTDA, BR), and urea ($(NH_2)_2CO$, PA, Vetec, Fine Chemicals Vetec LTDA, BR) were used. Deionized water was used to prepare all the perovskite structures.

Polycrystalline $LaCoO_3$, $La_{0.8}Ca_{0.2}CoO_3$ and $La_{0.8}Ba_{0.2}CoO_3$ perovskite structures were prepared by the combustion method in the principles of the chemistry of propellants [33,34]. The stoichiometric amounts of the metal nitrate and urea required to prepare these materials were calculated, mixed and dissolved in a minimal amount of deionized water [33,34]. The mixture was heated at approximately 80 °C until it became viscous. Next, the temperature was increased to approximately 300 °C until the system ignited. The ignition and the accompanying release of a large amount of gases led to the formation of a porous black ash in the container. The combustion products were milled by hand in an agate mortar to produce the as-prepared powders. The powders were calcined at 900 °C for 6 h to obtain the perovskite crystalline structures [35].

X-ray absorption spectroscopy measurements were performed at the XAS beam line of the Synchrotron Light National Laboratory (LNLS) in Campinas, Brazil. The prepared samples were pressed into pellets and placed in the sample holder to obtain the spectra. The $La_{0.8}Ca_{0.2}CoO_3$ and $La_{0.8}Ba_{0.2}CoO_3$ spectra were collected at 50 K, 150 K, 220 K, 260 K and 298 K, and the $LaCoO_3$ spectrum was collected at room temperature. Each sample was measured three times to check the repeatability and noise level of the spectra. The radiation was monochromatized using a Si(1 1 1) single crystal. The data acquisition set up consisted of three ionization chambers (incident I_o, transmittance I_t, and reference I_r detectors). The reference channel was primarily used for internal calibration of the edge position, using pure Co foil for the Co K-edge. Analyses were carried out in the transmittance mode at the cobalt K-edge. The EXAFS raw data were analyzed with the IFEFFIT program [36] using standard procedures [37]. The EXAFS function $\chi(k)$ was multiplied by k^3 to compensate for the damped EXAFS oscillations in the high k region. Next, the k^3-weighted $\chi(k)$ data in k-space ranging from 3.5 to 10 $Å^{-1}$ at the Co K-edge were Fourier transformed from k (wave vector) space to R (radial coordinate) space to separate the contributions of various coordination shells. The data analysis was performed using the IFEFFIT software [36]. The amplitudes and phase shifts were obtained from *ab initio* calculations using FEFF8.2 [38]. The amplitude reduction factor $S_o^2(K)$ was determined using a standard cobalt metal foil (0.808 ± 0.06) and was used for all fittings.

3. Results and discussion

3.1. XANES results

Fig. 1 shows the XANES spectra of the undoped and doped (Ca and Ba) cobalt compounds measured at the cobalt K-edge at room temperature. The main absorption edge is characterized by structures **B**, **C** and **D**, which are related to the transitions 1s-4p dipole transitions allowed by the electric dipole selection rule [39–43].

In all the spectra shown in Fig. 1, a subtle peak (structure **A**) is observed at the pre-edge. This peak has traditionally been assigned to the quadrupole transition from the level 1s level to an unoccupied 3d state, and its intensity is proportional to the magnitude of the distortion of the local structure around the metal ion absorber [44,45]. However, studies of the temperature dependence of the $LaCoO_3$ structure showed that the $\mathbf{A_1}$ and $\mathbf{A_2}$ intensities decrease with increasing temperature [39,40,46]. The expected deviation from centrosymmetry must be very small based on the results of Raccah and Goodenough [9] and of Maris et al. [24], which indicated that the $LaCoO_3$ structure belongs to the R-3 and *I*2/*a* space groups, respectively. The inset in Fig. 1 shows that structure **A** at the pre-edge is composed of two separate structures denoted $\mathbf{A_1}$ and $\mathbf{A_2}$. The pre-edge and main adsorption edge of the Ba^{2+}-doped sample are similar to those of the undoped structure, although structure **A** is narrower, the white-line intensity at structure **D** is slightly lower, and structures **C** and **D** occur at higher energies in the spectrum of the doped sample. In contrast, the spectrum of the Ca^{2+}-doped sample is significantly different from those of the other samples. For the Ca^{2+}-doped sample, the white-line intensity at structure **D** is considerably smaller, and structures **C** and **D** are shifted to higher energies. In addition, structure **A** is slightly wider in the $La_{0.8}Ca_{0.2}CoO_3$ spectrum than in the $La_{0.8}Ba_{0.2}CoO_3$ and $LaCoO_3$ spectra. These significant differences in the spectra shown in Fig. 1 can be attributed to the associated main line 1s-4p dipole-allowed transitions at the cobalt K-edge, but the small structures $\mathbf{A_1}$ and $\mathbf{A_2}$ correspond to the quadrupolar transitions from the Co 1s band to the 3d state due to the hybridization of the cobalt 3d band and the oxygen 2p band. All of these features result from the hybridizations of the Co_{3d} and O_{2p} orbitals and the Co_{4sp} and O_{2p} orbitals [40,42,43].

To investigate the temperature dependence of the $\mathbf{A_1}$ and $\mathbf{A_2}$ positions and intensities at the pre-edge, experiments were also performed at various temperatures for the Ca^{2+}- and Ba^{2+}-doped samples. As shown in Fig. 2, the main absorption edge features **B**,

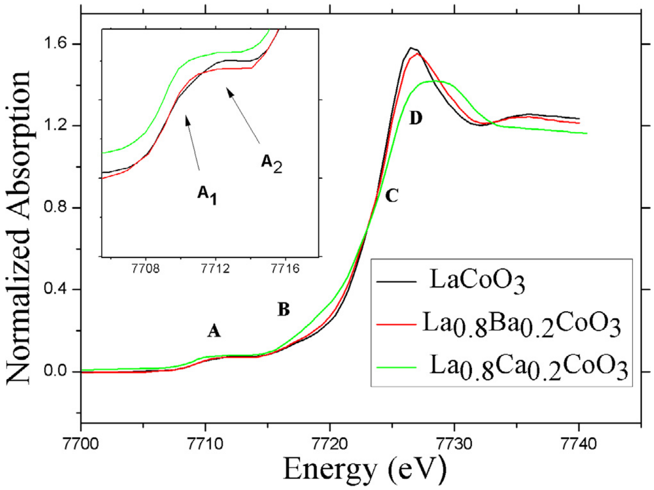

Fig. 1. XANES spectra of $LaCoO_3$, $La_{0.8}Ca_{0.2}CoO_3$ and $La_{0.8}Ba_{0.2}CoO_3$.