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M. Imamura, H. Shimada, N. Matsubayashi, T. Sato, A. Nishijima. O K-Edge XANES Study on Perovskite-Type $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$. Journal de Physique IV Proceedings, 1997, 7 (C2), pp.C2-917-C2-918. 10.1051/jp4:1997280 . jpa-00255363

HAL Id: jpa-00255363

<https://hal.science/jpa-00255363>

Submitted on 1 Jan 1997

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O K-Edge XANES Study on Perovskite-Type $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$

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Abstract: The O K-edge XANES was applied to the characterization of the oxygen species in the perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ of which XPS spectra showed the presence of at least two kinds of oxygen species. By comparing the PEY, TEY, and FY spectra, the π^* and σ^* features of the surface species were successfully extracted from the complicated spectra. The result suggested that the surface species was anionic dioxygen which presumably occupied the defect of the oxide.

1. Introduction

The strontium-doped lanthanum cobalt oxides ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$) with perovskite-type structure have been of great scientific interest because of their high catalytic activities for the oxidation of hydrocarbons and the decomposition of nitrogen oxides. Their catalytic activities were reported to be correlated with the desorption properties of oxygen in conjunction with oxygen-deficient lattice structures around cobalt [1]. However, very few studies have been conducted on the electronic structures of these materials perhaps because of the complexity of the ternary oxide system. In the present paper, we apply x-ray absorption near edge structure (XANES) to the characterization of the surface oxygen.

2. Experimental

The O K-edge XANES were measured at the BL13C [2] of the Photon Factory. The energy resolution of the monochromator was set at about 1500. The photon energy was calibrated using L_3 absorption edges of titanium (453.8 eV) and chromium (574.1 eV) metal foils. The spectra were recorded in a high vacuum chamber [3] under the base pressure of 3×10^{-7} Pa monitoring the fluorescence yield (FY), the total electron yield (TEY), and the partial electron yield (PEY) with a retarding voltage of 350 eV. The spectra were normalized by the photocurrent of a gold mesh located in the upstream of the sample. The x-ray photoelectron spectra (XPS) were measured using a hemispherical electrostatic analyzer attached to the chamber.

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ samples with three different values of x ($x=0, 0.2, 0.4$) were prepared by a modified sol-gel method [4] and pressed into small disks. Before introduction into the vacuum chamber, the samples were annealed at 500°C for one hour under dry air to remove CO_3^{2-} possibly formed after calcination.

3. Results and Discussion

Figure 1 shows the O1s XPS spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ with different excitation energies. Evidently, the feature at the high binding energy (O_S) is ascribed to the surface species, that at the low energy (O_L) ascribed to the lattice oxygen. Figure 2 displays the XANES spectra of the same sample measured with the TEY, PEY and FY modes. To analyze the complicated spectra, iterative curve fitting analyses have been carried out using the arc tangent step function and the Voigt profile [5, 6] which is the convolution of a Gaussian and Lorentzian envelop. Table 1 summarizes the least fitting results of the TEY and PEY spectra. The peak positions and intensities are referenced to the position and height of the step function. The fitting analysis has not been applied to the FY spectrum, because the FY spectrum is smeared by the self absorption effect.

Two features below the threshold are assigned to $1s-\pi^*$ transitions, those between 0 eV and +15 eV assigned to $1s-\sigma^*$ transitions [5]. Other features above +20 eV are likely induced by the multiple scattering of the excited electrons, that are not discussed in the present paper because of the complexity. Considering the analysis depth of the FY, TEY, and PEY methods, the features with relatively high intensities in the PEY spectrum are ascribed to the surface species. Comparing the relative intensities of the two π^* features, they are almost similar in both TEY and PEY spectra. However, in the FY spectrum with the largest analysis depth, the feature (1) at -1.4 eV has higher intensity and the feature (2) at -0.1 eV appears

Table 1: Result of curve fitting analyses of XANES spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$.

mode \ feature	π^*		σ^*				MS	
	1	2	3	4	5	6	7	8
TEY position/ eV *	-1.4	-0.1	4.1	6.6	10.4	14.0	21.6	36.6
TEY intensity	1.36	2.62	0.56	6.14	3.21	12.3	3.91	16.4
PEY position/ eV *	-1.4	-0.1	4.1	6.7	10.3	14.0	21.1	36.8
PEY intensity	0.87	1.80	0.43	4.39	3.26	8.90	3.02	16.8
PEY/TEY ratio	0.63	0.68	0.76	0.71	1.01	0.72	-	-

* relative to the step energy (530.0 eV)

Figure 1: O 1s XPS spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$.

Figure 2: O K-edge XANES spectra of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$.

as a shoulder at the higher energy side, which is assigned to the surface species. For the σ^* region, the feature (5) at +10.3 eV is most likely assigned to the surface species. Thus, the adsorbed oxygen species is suggested to give a π^* feature at 529.9 eV and a σ^* feature at 540.3 eV. Comparing to the literature [7], these energy values are almost identical with those of anionic dioxygen (O_2^-) in alkali-metal superoxide, which has a π^* feature at 529 eV and two σ^* features at about 535 eV and 540 eV. In Fig. 2, the first σ^* feature is not observed because it is overlapped with the large features (3) and (4). In conclusion, it is suggested that the surface oxygen species is the anionic dioxygen bounded weakly, probably occupying the oxygen-deficient site of the oxide lattice.

Acknowledgment

This work has been performed under the approval of the Photon Factory Advisory Committee (No. 95G232).

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