JOURNAL OF MATERIALS SCIENCE 23 (1988) 343–346

X-ray photoelectron spectroscopy study of perovskite-type mixed oxides ($La_{1-x}A'_xCoO_3$)

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The surface states of the perovskite-type cerium-, thorium- and strontium-doped lanthanum cobalt oxides ($La_{1-x}Ce_xCoO_3$, $La_{1-x}Th_xCoO_3$, $La_{1-x}Sr_xCoO_3$, $x = 0$ to 0.03) have been investigated using X-ray photoelectron spectroscopy (XPS). The binding energy differences (ΔBE) between $Co2p_{3/2}$ and O1s of lattice oxygen have a maximum value at $x = 0.02$ in both $La_{1-x}Ce_xCoO_3$ and $La_{1-x}Th_xCoO_3$. From this result, it is expected that the bonding state between the surface cobalt and lattice oxygen is mostly ionic at this point. The valence band (VB) spectra change greatly at $x = 0.02$ on both cerium- and thorium-doped samples. We speculate that the high spin trivalent cobalt ion is dominant at $x = 0.02$ on the surface. On the other hand, the ΔBEs between $Co2p_{3/2}$ and O1s of lattice oxygen decrease with increasing x in $La_{1-x}Sr_xCoO_3$. It is expected that the bonding states become covalent in proportion to x. The change of the VB spectra for $La_{1-x}Sr_xCoO_3$ near the Fermi level (E_F) can be explained by the formation of the impurity level.

1. Introduction

Perovskite-type mixed oxides (ABO_3) have been investigated widely for their crystal structures, magnetic and catalytic properties [1–3]. In our previous papers, we reported the catalytic and magnetic properties of $La_{1-x}Ce_xCoO_3$ [4], $La_{1-x}Th_xCoO_3$ [5, 6] and $La_{1-x}Sr_xCoO_3$ [5]. In this study, we investigate the surface states, especially the VB structures, of $La_{1-x}A'_xCoO_3$ (A' = cerium, thorium, strontium, $x = 0$ to 0.03) using XPS.

2. Experimental procedure

All $La_{1-x}Ce_xCoO_3$, $La_{1-x}Th_xCoO_3$ and $La_{1-x}Sr_xCoO_3$ ($0 \leqslant x \leqslant 0.03$) compounds were prepared by heating the precipitate which was obtained from mixtures of metal acetates of lanthanum, cerium, strontium, cobalt and thorium nitrate solution, at 1673 K for 5 h. The phases of the products were determined by XRD using Cu$K\alpha$ radiation (Philips APD-10).

The XPS spectra were recorded on a V.G. ESCA LAB-5 electron spectrometer with Al$K\alpha$ or Mg$K\alpha$ radiation. The binding energies (BE) were corrected by using the value of 285.0 eV for the C1s level resulting from the contaminated carbon. Then, the core-level BEs of palladium, silver and gold foils were measured. The $Pd3d_{5/2}$, $Ag3d_{5/2}$ and $Au4f_{7/2}$ BEs were 335.4, 368.3 and 84.0 eV relative to the Fermi level, respectively [7]. The experimental errors were within ± 0.1 eV. The normal operating vacuum pressure was less than 3×10^{-8} Pa. The XPS spectra were measured at room temperature without any additional surface treatment.

The $OKL_{23}L_{23}$ Auger electron spectra were also recorded on the same instrument in the constant analyser energy mode.

3. Results and discussion

3.1. X-ray measurement of $La_{1-x}A'_xCoO_3$

The X-ray powder diffraction patterns of all $La_{1-x}A'_xCoO_3$ (A' = cerium, thorium, strontium, $x = 0$ to 0.03) samples were indexed on the basis of the perovskite-type structure, and no other phases were found. The crystal structure was rhombohedral in all samples.

3.2. Surface states of $La_{1-x}A'_xCoO_3$

Fig. 1 represents the ΔBE, calculated from the XPS spectra for both $Co2p_{3/2}$ and O1s of lattice oxygen, against x in $La_{1-x}A'_xCoO_3$ (A' = cerium, thorium). The ΔBE in both $La_{1-x}Ce_xCoO_3$ and $La_{1-x}Th_xCoO_3$ had a maximum at $x = 0.02$. According to Frost *et al.* [8], the increase in the BE of cobalt for the cobalt halides from bromide to fluoride was due to the increase in ionicity of the compounds. Thus, the bonding state between the surface cobalt and lattice oxygen was most ionic at $x = 0.02$. Further substitution of cerium or thorium decreased the ionicity as shown in Fig. 1.

Figs 2 and 3 shown the VB spectra for $La_{1-x}Ce_xCoO_3$ and $La_{1-x}Th_xCoO_3$, respectively. All the spectra were similar, except $x = 0.02$ for both cerium- and thorium-doped samples. The peaks near the Fermi levels (E_F) almost disappeared for $x = 0.02$ in both $La_{1-x}Ce_xCoO_3$ and $La_{1-x}Th_xCoO_3$ samples.

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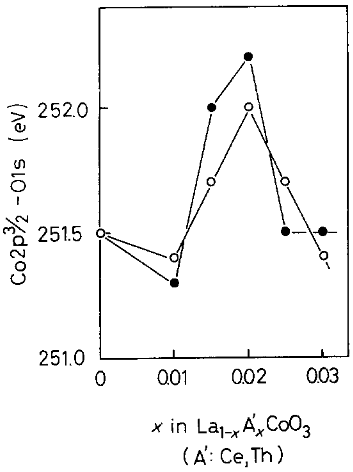

Figure 1 The BE difference between $\mathrm{Co2p_{3/2}}$ and O1s of lattice oxygen. (○) Ce, (●) Th.

The VB structures of $\mathrm{LaCoO_3}$ have been thoroughly investigated from both the experimental [9] and theoretical aspects [10, 11]. Veal and Lam [11] reported that the leading edge of the valence band XPS spectra near E_F is mainly due to the cobalt 3d-electron multiplet. Fig. 4 shows their results of calculated multiplet spectra. The peak near E_F decreased greatly with the shift from low spin trivalent cobalt state to high spin state.

On the other hand, Goodenough *et al.* [2] reported that the energy difference trivalent cobalt ions between the diamagnetic low-spin state ($\mathrm{Co^{III}}$) and the paramagnetic high spin state ($\mathrm{Co^{3+}}$), $E_{3+} - E_{\mathrm{III}}$, is less than 0.08 eV. They also reported that there are disordered $\mathrm{Co^{3+}}$ amongst the majority of $\mathrm{Co^{III}}$ in the interval $0 < T < 398$ K, namely, the low-spin state is dominant at room temperature.

From Figs. 2, 3 and 4, it was speculated that the low-spin state was also dominant on the surface of both cerium- and thorium-doped samples except $x = 0.02$. The XPS spectra of $x = 0.02$ for both cerium- and thorium-doped samples were different from the others, i.e. the peak near E_F decreased remarkably, indicating that the high-spin state is dominant on the surface at $x = 0.02$. If these considerations are reasonable, the electronic character of the surface cobalt has to be changed at $x = 0.02$. This speculation agreed with the results in Fig. 1, i.e. the bonding states between the surface cobalt and lattice oxygen changed and became mostly ionic at $x = 0.02$.

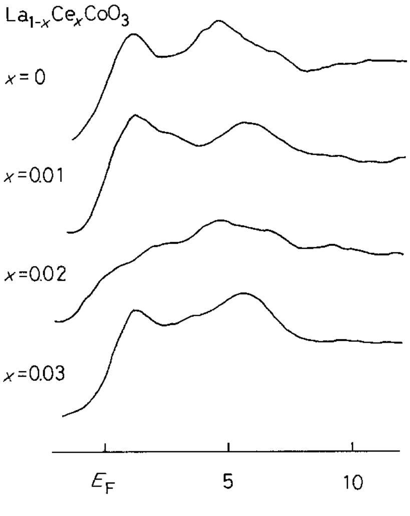

Figure 2 VB spectra for $\mathrm{La_{1-x}Ce_xCoO_3}$.

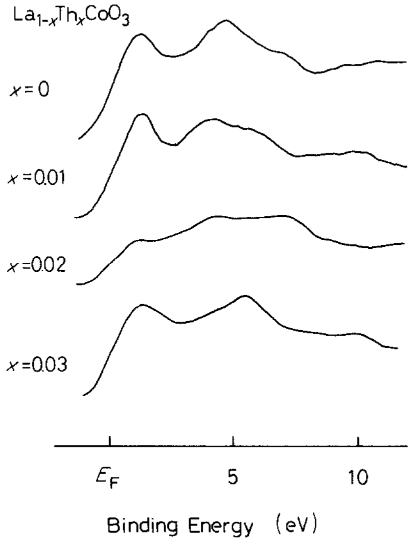

Figure 3 VB spectra for $\mathrm{La_{1-x}Th_xCoO_3}$.

We speculated that the crystalline electric field around cobalt ions on the surface, which is nearest to cerium or thorium ions, may be weakened in the composition range of $x \leqslant 0.02$, because their ionic radii are smaller than that of lanthanum. Further substitution with the smaller ionic radii components may bring about shrinkage of the lattice in the whole crystal. Consequently, the crystal field on the surface also seemed to be intensified. The trivalent low-spin cobalt ions also become dominant at the surface.

3.3. Surface states of $\mathrm{La_{1-x}Sr_xCoO_3}$

Fig. 5 shows the ΔBE, calculated from the XPS spectra for both $\mathrm{Co2p_{3/2}}$ and O1s of lattice oxygen, plotted against x in $\mathrm{La_{1-x}Sr_xCoO_3}$. The ΔBE in $\mathrm{La_{1-x}Sr_xCoO_3}$ decreased with increasing x, i.e. the bonding state between the surface cobalt and lattice oxygen became covalent in proportion to x. Goodenough [2] reported from his measurements of both magnetic susceptibility and electrical conductivity, that the relation between the cobalt and oxygen in $\mathrm{La_{1-x}Sr_xCoO_3}$ became covalent by strontium substitution. This result in the bulk states seemed to agree with our results for the surface states of $\mathrm{La_{1-x}Sr_xCoO_3}$.

Fig. 6 shows the VB spectra for $\mathrm{La_{1-x}Sr_xCoO_3}$ ($x = 0$ to 0.03). The leading edges of the VB spectra

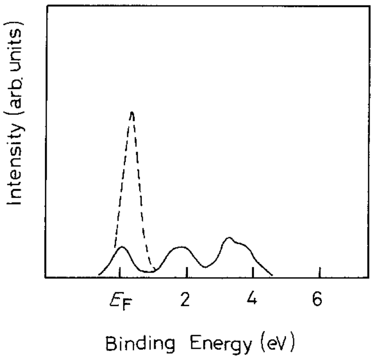

Figure 4 XPS final-state multiplet of $\mathrm{LaCoO_3}$ for trivalent cobalt ions taken from [11]. (– – –) Low spin, (——) high spin.

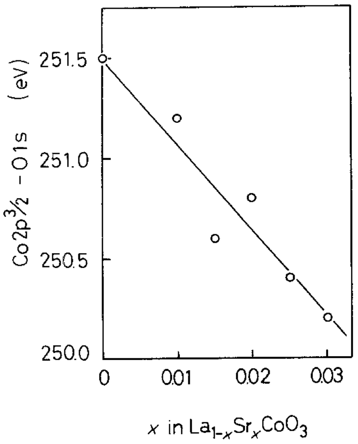

Figure 5 The BE difference between $Co2p_{3/2}$ and O1s of lattice oxygen.

near E_F for the strontium-doped samples were enhanced and the slopes of these were decreased in comparison to $LaCoO_3$ ($x = 0$).

For examining the effect of further strontium substitution on the VB spectra, we prepared samples calcined at 1123 K for 5 h. All $La_{1-x}Sr_xCoO_3$ samples ($x = 0$ to 0.5) were indexed on the basis of the perovskite-type structure, and no other phases were found.

We examined the ionic properties of $La_{1-x}Sr_xCoO_3$ ($x = 0$ to 0.5) from a different point of view, i.e. using the Auger parameter. Table I shows the Auger parameter (α_a) of lattice oxygen in these samples. The Auger parameter of oxygen (α) is defined as

$$\alpha = \mathrm{BE\,(O1s)} + \mathrm{KE\,(O\,KLL)}. \qquad (1)$$

In a practical point of view, α is convenient because it is independent of the absolute energy calibration and of the sample charging. If two compounds ar examined, the difference can be designated as follows

$$\Delta\alpha = 2R_{ex}\,(\mathrm{O\,2p}) \qquad (2)$$

by Kowalczyk *et al.* [12] and Wagner [13]. The value of $1/2$ ($\Delta\alpha$) is equivalent to the difference in extra-atomic relaxation energy for a singly charged final state of the atom under study in the two compounds. Bahl *et al.* [14] reported that in an ionic bond, the extra-atomic relaxation energy shift was a useful scale of ionicity of the bond. Then, the increase of the Auger parameter implies that the ionicity of the bond decreases. As shown in Table I, the lattice oxygen became covalent by substituting strontium for lanthanum, which is the same result as in Fig. 5.

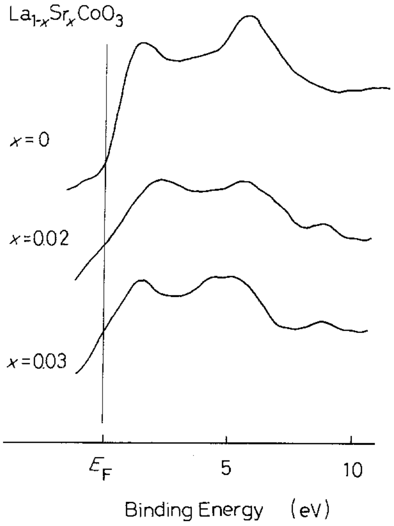

Figure 6 VB spectra for $La_{1-x}Sr_xCoO_3$ calcined at 1673 K.

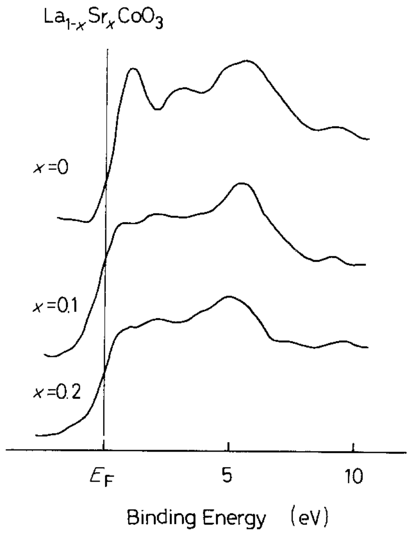

Figure 7 VB spectra for $La_{1-x}Sr_xCoO_3$ calcined at 1123 K.

The VB spectra near E_F for $La_{-x}Sr_xCoO_3$ (x = 0 to 0.2) are shown in Fig. 7. The VB structures of $La_{1-x}Sr_xCoO_3$ have been studied intensively by Raccah and Goodenough [15]. Fig. 8 shows their "3d" band models for $La_{1-x}Sr_xCoO_3$ [15]. According to them, the Co^{IV} ions (or "3d" holes) introduced by initial Sr^{2+} ions remain tightly bound to the strontium and its nearest-neighbour cobalt ions, which act as a relatively deep acceptor complex as shown in Fig. 8a. These bound holes belong to all the cobalt atoms that are nearest neighbours to a Sr^{2+} ion. As x increases, the acceptor complexes interact to form "impurity bands" and ferromagnetism within a Sr^{2+} region. In the compositional range $x > 0.1$, the Sr^{2+}-rich regions become joined together to form a continuous impurity band region throughout the crystal (Fig. 8b). From this

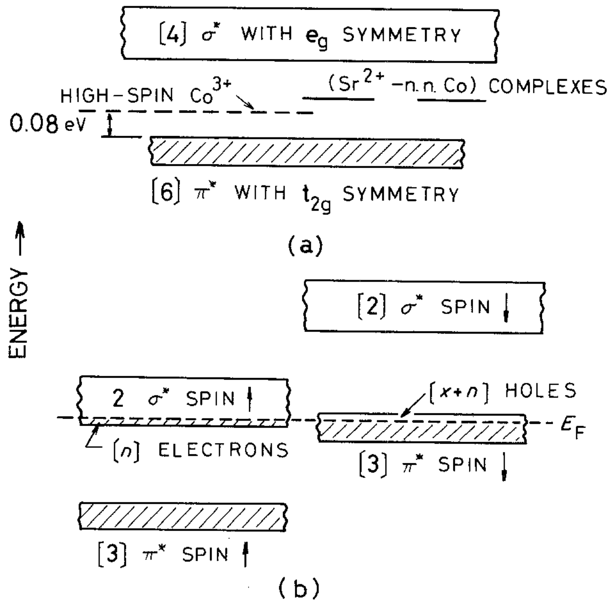

Figure 8 Schematic "3d" bands for (a) initial Sr^{2+} ions in $LaCoO_3$ and (b) Sr^{2+}-rich, ferromagnetic regions taken from [15].

TABLE I The Auger parameter (α_a) of the lattice oxygen in $La_{1-x}Sr_xCoO_3$ calcined at 1123 K

x	0	0.1	0.3	0.5
α_a (eV)	1042.7	1043.0	1043.3	1043.4

model, we speculated that the change of the VB spectra near E_F of $La_{1-x}Sr_xCoO_3$ was related to the formation of the impurity level, i.e. the leading edges of the VB spectra near E_F for the strontium-doped ones were enhanced in proportion to the increase of the impurity level.

Acknowledgements

The authors thank Mr Yamada, Mr Maki and Mr Matsumoto for their support in this work. We also thank Professor Misono, Tokyo University and Dr Kido, Osaka Municipal Technical Research Institute, for their helpful advice.

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Received 13 April
and accepted 29 June 1987