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X-Ray Photoelectron Spectroscopy Study of $(Ca_{1-x}La_x)MnO_{2.97}$ $(0.1 \leqq x \leqq 0.4)$

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The X-ray photoelectron spectroscopy (XPS) of perovskite-type $(Ca_{1-x}La_x)MnO_{2.97}$ $(0.1 \leqq x \leqq 0.4)$ was measured at room temperature. From the absolute values of the binding energy difference (ΔBE) of Ca2*p*-O1*s*, La3*d*-O1*s*, and Mn2*p*-O1*s*, both the chemical bonding of Mn–O and Ca–O become more covalent, and that of La–O becomes more ionic with increasing x. The electron transfer of the Mn–O–Mn path is dominant, and the electrical properties are strongly influenced by the decrease of the electron transfer of the Mn–O–(Ca,La)–O–Mn path.

Introduction

$(Ca_{1-x}La_x)MnO_{2.97}$ $(0 \leqq x \leqq 0.4)$ has the perovskite-type structure and exhibits *n*-type semiconductor below room temperature (*1*). Below 125 K, the electrical resistivity follows the Mott's $T^{-1/4}$ law indicating the possible occurrence of variable hopping of electrons due to Anderson localization (*2, 3*). Above ca. 400–450 K, a metal–insulator transition is encountered. From the results of DTA measurements, this transition occurs without the crystallographic change. On the other hand, the magnetic susceptibility has a deflection point at ca. 450–500 K. From the results of the electrical and magnetic measurements, the mechanism of the metal–insulator transition in these manganates is explained by the band model proposed by Goodenough (*4*).

Taguchi and Shimada measured the X-ray photoelectron spectroscopy (XPS) of perovskite-type $CaMnO_{3-\delta}$ at room temperature (*5*). The binding energies of $Ca2p_{1/2}$ and $Ca2p_{3/2}$ slightly decrease with decreasing oxygen content. On the other hand, the binding energy of $O1s_{1/2}$ increases with decreasing oxygen content. Since the spectrum of $Mn2p_{3/2}$ is broad, the binding energy is independent of the oxygen content. From the results of the binding energy difference (ΔBE), the chemical bonding of Mn–O becomes more covalent, and that of Ca–O becomes more ionic with decreasing oxygen content. The electron transfer in the Mn–

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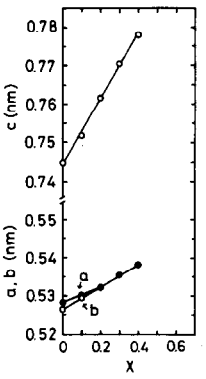

FIG. 1. Cell constants vs composition in the system $(Ca_{1-x}La_x)MnO_{2.97}$. (The cell constants of $x = 0$ are given the values reported by Poppelmeier *et al.* (*7*))

O–Mn path can take place easily in the perovskite-type $CaMnO_{3-\delta}$.

In the present study, XPS of $(Ca_{1-x}La_x)MnO_{2.97}$ ($0.1 \leqq x \leqq 0.4$) is measured to examine the electron transfer from O1*s* to Ca2*p*, La3*d* and Mn2*p*. These results will provide information regarding the electrical properties of the perovskite-type manganates.

Experimental

Samples were prepared using a standard ceramic technique. Powders of $CaCO_3$, La_2O_3, and $MnCO_3$ were weighed in the desired proportions and milled for a few hours with acetone. After the mixed powders were dried at 100°C, they were calcined in air at 800°C, then fired at 1300°C for 24 hr in a flow of pure oxygen gas. The oxygen-deficient materials obtained in this way were annealed at 600–700°C in air for 50 hr.

The phases of the samples were identified by X-ray powder diffraction with filtered CuKα radiation. The cell constants of the samples were determined using Si as a standard material. The oxygen content in each sample was determined by the oxidation–reduction method (*6*). XPS measurements were carried out for Ca2*p*, La3*d*, Mn2*p*, and O1*s* levels of the samples using AlKα radiation ($h\nu$ = 1486.6 eV) at room temperature. The energy calibration was made against the C1*s* peak from the usual contamination.

Results and Discussion

X-ray powder diffraction patterns of all samples are completely indexed as the perovskite-type structure. The oxygen content of all samples annealed at 600–700°C in air is determined to be 2.97 ($\delta = 0.03$) from the chemical analysis. The relation between the cell constants and the composition is shown in Fig. 1. In Fig. 1, the cell constants of $x = 0$ are given the values of the single crystals reported by Poeppelmeier *et al.* (*7*). The cell constants increase with increasing x, and the crystal structure changes from orthorhombic to tetragonal symmetry at $x = 0.2$. The tetragonal cell constants also increase with increasing x in the range $0.2 \leqq x \leqq 0.4$. Since the ionic radii of Ca^{2+} and La^{3+} ions are 0.132 and 0.135 nm, respectively (*8*), the monotonic increase in the cell constants is explained by the difference of the ionic radii between Mn^{3+} and Mn^{4+}.

The XPS of the Ca2*p* level of $(Ca_{1-x}La_x)MnO_{2.97}$ is shown in Fig. 2. The binding energies of $Ca2p_{1/2}$ and $Ca2p_{3/2}$ slightly increase with increasing x. The satellite peaks on the high binding energy side of the Ca2*p* peaks are separated from the main peaks by ca. 1.2 eV, and this value is independent of the composition. In $CaMnO_{3-\delta}$, the energy difference between the Ca2*p* peak and the satellite peak increases from 1.2 to 2.0 eV with decreasing oxygen content (*5*). From these results, it is considered that the energy differences between the main peak and the satellite peak is strongly influenced by the oxygen content in the perovskite-type manganate.

Figure 3 shows the XPS of the $La3d_{5/2}$ level. The binding energy of $La3d_{5/2}$ slightly

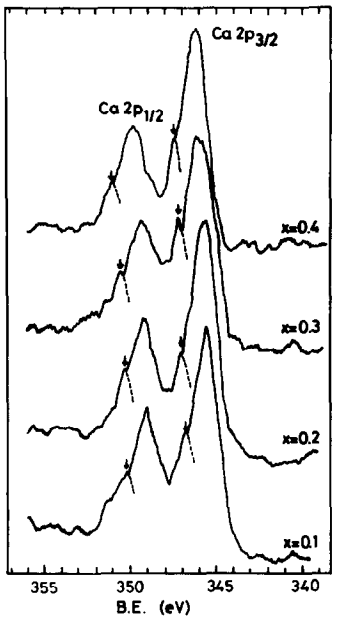

FIG. 2. XPS spectra of the Ca2*p* level in the system $(Ca_{1-x}La_x)MnO_{2.97}$.

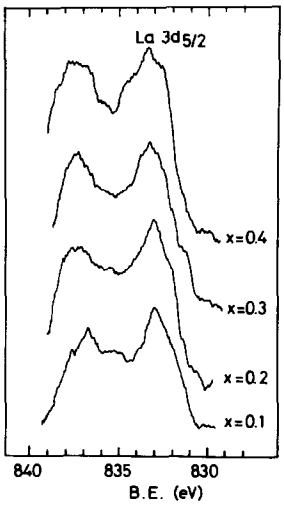

FIG. 3. XPS spectra of the La3*d* level in the system $(Ca_{1-x}La_x)MnO_{2.97}$.

increases with increasing x. The satellite peak on the high binding energy side of the La3*d* level is separated from the main peak by ca. 4 eV. Lam *et al.* reported the electronic structure of $LaBO_3$ (B = Ti, Cr, Mn, Fe, and Co) using the XPS measurement (*9*). In the La3*d* spectra of $LaBO_3$, the satellite peaks are observed on the high binding energy side of the main peaks by ca. 4 eV. The satellite is interpreted in terms of the excitation of an electron from the anion valence band into the lanthanium *f* band. From these results, it is considered that the present satellite of the La3*d* peak in $(Ca_{1-x}La_x)MnO_{2.97}$ is due to the excitation of the electron in analogy with $LaBO_3$.

Figure 4 shows the XPS of the Mn2$p_{3/2}$ level. The Mn2$p_{3/2}$ peak is broad and the binding energy is independent of the composition. The binding energy of Mn2$p_{3/2}$ in $LaMn^{3+}O_3$ and $Mn^{4+}O_2$ is ca. 642.0 and 642.4 eV, respectively (*9, 10*). These values are also shown in Fig. 4. Kowalczyk *et al.* reported that the Mn2$p_{3/2}$ peak in MnF_2 was broad and asymmetric toward the high binding energy site, and this asymmetry was discussed in terms of multiplet splitting

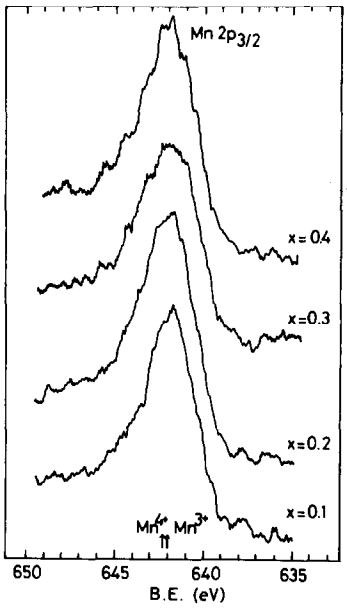

FIG. 4. XPS spectra of the Mn2*p* level in the system $(Ca_{1-x}La_x)MnO_{2.97}$.

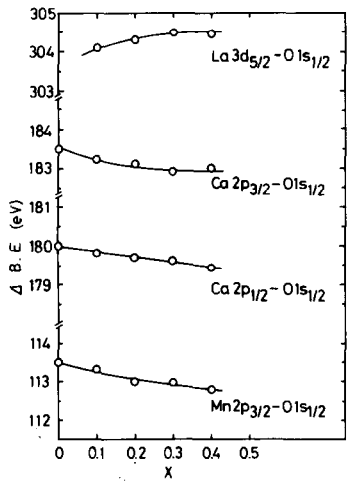

FIG. 5. Absolute values of the binding energy difference (ΔBE) of Ca2*p*-O1*s*, La3*d*-O1*s*, and Mn2*p*-O1*s* in the system $(Ca_{1-x}La_x)MnO_{2.97}$.

(*11*). From these results, it is concluded that the present broad $Mn2p_{3/2}$ peak in $(Ca_{1-x}La_x)MnO_{2.97}$ is due to the mixed valency of both Mn^{3+} and Mn^{4+} ion and the multiplet structure in analogy with MnF_2.

The binding energy of O1*s* in $(Ca_{1-x}La_x)MnO_{2.97}$ is ca. 529.1 eV, and this value slightly increases with increasing x. Figure 5 shows the absolute values of the binding energy difference (ΔBE) of Ca2*p*-O1*s*, La3*d*-O1*s*, and Mn2*p*-O1*s*. Δ BE of both Ca2*p*-O1*s* and Mn2*p*-O1*s* decreases with increasing x. On the other hand, Δ BE of La3*d*-O1*s* increases with increasing x. Johnson reported that the binding energies of $O1s_{1/2}$ in BeO, MgO, and CaO were 532.1, 530.0 and 529.6 eV, respectively (*12*). The binding energy of $O1s_{1/2}$ increases with increasing electronegativity of the alkaline earth metal ion. Carver *et al.* reported that the binding energies of $Mn2p_{3/2}$ in MnO, MnS, MnF_2, $MnCl_2$, $MnBr_2$, and MnI_2 were 641.7, 640.5, 642.8, 642.1, 642.2, and 642.1 eV, respectively (*10*). Since the electronegativity of the anion is as follows, $O^{2-} > S^{2-}$, $F^- > Cl^- > Br^- > I^-$, it is expected that the binding energy of $Mn2p_{3/2}$ decreases with increasing covalency of the Mn–X (X = O, S, F, Cl, Br, and I) bond. Citrin discussed the binding energy of Ru^{2+} and Ru^{3+} in $[(NH_3)_5Ru(pyr)Ru(NH_3)_4]^{4+,5+,6+}$ salt from XPS measurements (*13*). Ru^{2+} and Ru^{3+} 3*d* electron binding energy in the [2+,3+] salt slightly converged with respect to those in the [2+,2+] and the [3+,3+] salts, and this convergence is understood in the results by the increase of the electron transfer between Ru^{2+} and Ru^{3+}. From these results, it is concluded that the chemical bonding of both Ca–O and Mn–O becomes more covalent with increasing x. On the other hand, the chemical bonding of La–O becomes more ionic with increasing x.

The electrical resistivity (ρ) at room temperature and the activation energy (ΔE) of $(Ca_{1-x}La_x)MnO_{2.97}$ are listed in Table I (*1*, *14*). With increasing x, both ρ and ΔE abruptly decrease and have minimum values at ca. $x = 0.1$, and then gradually increase. In the perovskite-type $(Ca_{1-x}La_x)MnO_{2.97}$, two paths of the electron transfer are considered. One is Mn–O–Mn and the other is Mn–O–(Ca,La)–O–Mn. Though the distance of Mn–O–Mn increases with increasing x as shown in Fig. 1, it is apparent from the results of XPS measurements that the chemical bonding of Mn–O becomes more covalent and the electron

TABLE I

THE ELECTRICAL RESISTIVITY (ρ) AT ROOM TEMPERATURE AND THE ACTIVATION ENERGY (ΔE) IN THE SYSTEM $(Ca_{1-x}La_x)MnO_{2.97}$ (Refs. *1*, *14*)

x	$\log \rho_{\text{room temp.}}$ (Ω cm)	ΔE (eV)
0	2.98	ca. 3.0
0.05	−0.62	0.04
0.1	−0.94	0.05
0.2	−0.84	0.12
0.3	−0.76	0.18
0.4	−0.36	0.19

transfer of the Mn–O–Mn path is dominant. The chemical bonding of Ca–O becomes more covalent, but that of La–O becomes more ionic with increasing x. From these results, it is considered that the electron transfer in both Mn–O–Mn and Mn–O–(Ca,La)–O–Mn paths easily takes place in the range $0 \leqq x \leqq 0.1$. On the other hand, the electron transfer in the Mn–O–(Ca,La)–O–Mn path becomes difficult with increasing La^{3+} ion content. Consequently, both the electrical resistivity and the activation energy have minimum values at ca. $x = 0.1$.

It is concluded that the chemical bonding of both Mn–O and Ca–O becomes more covalent and that of La–O becomes more ionic with increasing x in the system $(Ca_{1-x}La_x)MnO_{2.97}$. The electron transfer of the Mn–O–Mn path is dominant and that of the Mn–O–(Ca,La)–O–Mn path decreases with increasing x. The electrical properties are strongly influenced by these two paths of electron transfer.

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