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Electric and Magnetic Properties of Cobaltites with layered Perovskite Structure

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The effects of alkaline earth ion substitution on electric and magnetic properties of layered cobaltites, $La_{1.4}A_{0.6}CoO_{4+\delta}$ (A=Ca, Sr, Ba) were investigated in the present paper. Lattice constants and oxygen content, 4-δ, increase with increasing radius of A-ion. The electric and magnetic properties depend on the average valence of Co ion rather than lattice expansion. With increasing radius of A-ion, the activation energy of semiconduction decreases and electric conductivity is improved so that antiferromagnetic correlation between magnetic moments of Co ions is suppressed. The lattice expansion does not change the spin states of Co ions and the effective Bohr magneton, which is experimentally derived, decreases because the fraction of Co^{2+} and Co^{3+} ions is changed due to increasing oxygen content.

Key words: Cobaltite, Layered perovskite Structure, Electric resistivity, Magnetic Susceptiblitiy

1. INTRODUCTION

The electronic properties of transition metal oxides have been improved by controlling carrier number, such as the superconducting transition temperature of cuprate superconductors. However, it has been found that several electronic properties can be controlled by the modification of crystal structure of these oxides, of which carrier number is fixed. For example, the ferromagnetic transition temperature of perovskite-type manganites (R,Sr)MnO_3 (R=rare earth ions) decreases with decrease in radius of R ion [1]. Perovskite-type cobaltite $LaCoO_3$ shows the magnetic transition at 90 K from intermediate spin state ($t_{2g}{}^5e_g{}^1$) to low spin state ($t_{2g}{}^6$) of Co^{3+} ion when reducing temperature [2]. The transition temperature increases under application of physical pressure [3]. Therefore, the spin state of Co ions is changed readily by external stimulation, such as temperature and pressure so that the cobaltites are expected to show various electronic properties.

In the present study, we prepared layered cobaltites $La_{1.4}A_{0.6}CoO_{4-\delta}$ (A=Ca, Sr, Ba) which have K_2NiF_4 type (layered perovskite type) structure. It is expected that the lattice constants, that is, length of Co-O bond changes with radius of A-ion. We investigated the effect of A-ion on the electric and magnetic properties of these cobaltites.

2. EXPERIMENTALS

The samples were prepared by a conventional ceramic technique. The starting materials, La_2O_3 (99.9%), $CaCO_3$ (99.9%), $SrCO_3$ (99.9%), $BaCO_3$ (99.9%) and CoO (99.9%) were weighed and mixed thoroughly with an agate mortar and ethanol. The mixtures were calcined at 1100°C for 12 h. The calcined samples were ground well and pelletized by a cold isostatic pressing under a pressure of 1 GPa. The pellets were sintered at 1300 °C for 12 h. The atmosphere during the calcination and the sintering was N_2 gas flow for Ca containing and Sr containing samples, O_2 gas flow for Ba containing sample.

The oxygen content was measured by iodometric titration. The crystal structures of the samples were refined by the Rietveld method using the program RIETAN [?]. X-ray diffraction intensities were collected at intervals of 0.02 degree in 2θ by means of X-ray diffractometer (RINT2500VHF, Rigaku Co., Japan).

The electric resistivity was measured by dc four probe method below room temperature. The magnetic susceptibility was measured by means of a vibrating sample magnetometer (Riken Denshi Co., Japan) under a magnetic field of 5 kOe in the temperature range between 10 K and 300 K.

3. RESULTS and DISCUSSION

All samples were confirmed to have tetragonal K_2NiF_4-type structure (space group: *I4/mmm*) by X-ray diffraction study. Refined crystallographic parameters are listed in Table 1, 2 and 3 for Ca containing, Sr containing and Ba containing samples, respectively. Lengths of a axis and c axis increase with increasing radius of A-ion. The oxygen content ($4+\delta$) also increases, *i.e.*, 3.99, 4.02 and 4.05 for Ca containing, Sr containing and Ba containing samples, respectively. Bond lengths calculated from the crystallographic parameters are summarized in Table 4. La ions and A ions are coordinated by nine oxygen ions. Bond lengths between La, A ions and oxygen ions increase, consequently, space around La and A ions is extended with radius of A ion. It seems that the excess oxygen is easier to be included in the crystalline lattice and the tetragonal lattice is consequently stabilized with increasing radius of A-ion. In fact, a stoichiometric cuprate La_2CuO_4 has orthorhombically distorted K_2NiF_4-type structure, while oxidized one, $La_2CuO_{4+\delta}$, has tetragonal K_2NiF_4-type

Table 1 Refined crystallographic parameters for $La_{1.4}Ca_{0.6}CoO_{3.99}$.

Atom	Site	*x*	*y*	*z*
La, Ca	4*e*	0	0	0.3611(4)
Co	2*a*	0	0	0
O1	4*c*	0.5	0	0
O2	4*e*	0	0	0.170(4)

a=0.381924(5) nm, c=1.23005(4)nm
R_{wp}=15.74%, R_p=11.81%

Table 2 Refined crystallographic parameters for $La_{1.4}Sr_{0.6}CoO_{4.02}$.

Atom	Site	*x*	*y*	*z*
La, Sr	4*e*	0	0	0.3626(4)
Co	2*a*	0	0	0
O1	4*c*	0.5	0	0
O2	4*e*	0	0	0.167(3)

a=0.383323(4) nm, c=1.25229(2) nm
R_{wp}=13.80%, R_p=10.83%

Table 3 Refined crystallographic parameters for $La_{1.4}Ba_{0.6}CoO_{4.05}$.

Atom	Site	*x*	*y*	*z*
La, Ba	4*e*	0	0	0.3609(4)
Co	2*a*	0	0	0
O1	4*c*	0.5	0	0
O2	4*e*	0	0	0.170(4)

a=0.385988(4) nm, c=1.28083(1)nm
R_{wp}=15.74%, R_p=11.81%

Table 4 Bond lengths (nm) and aspect ratio, *t*, of CoO_6 octahedron for $La_{1.4}A_{0.6}CoO_{4+\delta}$ (A=Ca, Sr and Ba).

	A		
	Ca	Sr	Ba
La, A – O1 (×4)	0.2562(3)	0.2576(3)	0.2627(3)
La, A – O2 (×4)	0.2728(7)	0.2736(5)	0.2758(7)
La, A – O2 (×1)	0.235(5)	0.245(4)	0.245(5)
Co – O1 (×4)	0.190962(3)	0.191662(2)	0.192994(2)
Co – O2 (×2)	0.209(5)	0.209(4)	0.218(5)
*t**	1.10(3)	1.09(2)	1.13(3)

*(Co-O2)/(Co-O1)

structure [4]. Aspect ratio of CoO_6 octahedron slightly increases when replacing Sr ion to Ba ion.

All samples show semiconductive behavior below room temperature. Figure 2 indicates the logarithmic electric resistivity as a function of reciprocal temperature. The electric resistivity at a fixed temperature decreases one order or more of magnitude by replacing Ca ion to Sr ion and by replacing Sr ion to Ba ion. The temperature dependence of the electric resistivity, ρ, is well described as thermally activated conduction process, *i.e.*, $\rho=\rho_0\exp(E_a/kT)$, where ρ_0 is the pre-exponent factor, E_a is the activation energy and k is the Boltzmann's constant. The activation energies are obtained by fitting the results to the equation, and are 0.44 eV, 0.32 eV and 0.26 eV for Ca, Sr and Ba containing samples, respectively. The electric conduction is improved with increasing A-ion's radius in view of the activation energy. The length of a axis is equal to the twice of equatorial Co-O bond length. It has been expected that the expansion of the Co-O bond suppress the electric conductivity of the layered cobaltite, because the bond expansion decreases the degree of overlapping between Co 3*d* orbital and O 2*p* orbital. The change in the electric conductivity, so, the activation energy is explained by increasing carrier number due to the excess oxygen.

Figure 3 shows the temperature dependence of magnetic susceptibility. The magnetic susceptibility of Ca containing sample has a hump around 60 K. No humps are found in the magnetic susceptibility of Sr containing and Ba containing samples. One of the K_2NiF_4-type cobaltites, La_2CoO_4, shows antiferromagnetism with the Néel temperature T_N of 275 K [5]. The Sr ion substituted $La_{2-x}Sr_xCoO_4$ shows antiferromagnetism up to x=0.5 ($La_{1.5}Sr_{0.5}CoO_4$) and T_N is reported to decrease rapidly with Sr content, *e.g.*, T_N ~ 40 K for the x=0.5 cobaltite [6]. Thus, the hump is due to the antiferromagnetic transition and the Ca containing sample has T_N~60 K.

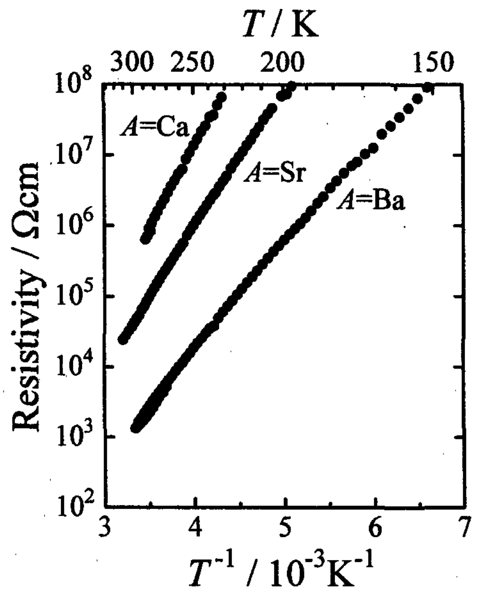

Figure 2 Temperature dependence of electric resistivity for $La_{1.4}A_{0.6}CoO_{4+\delta}$ (A=Ca, Sr, Ba).

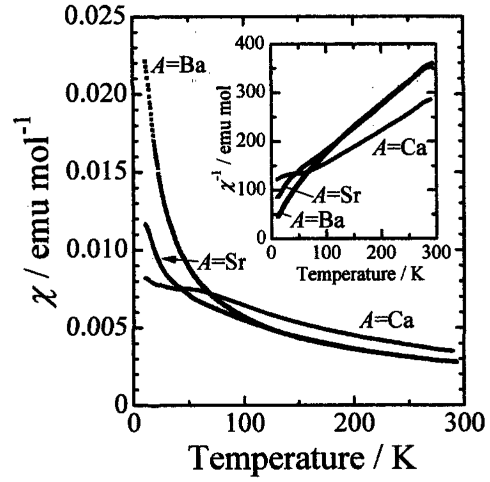

Figure 3 Temperature dependence of magnetic susceptibility for $La_{1.4}A_{0.6}CoO_{4+\delta}$ (A=Ca, Sr, Ba). The inset indicates temperature dependence of the reciprocal magnetic susceptibility.

The temperature dependence of reciprocal magnetic susceptibility (χ^{-1}) is shown in the inset of Figure 3. Linear relations between χ^{-1} and T are found from room temperature to 100 K. The magnetic susceptibility in this temperature range is fitted to the equation of $\chi=C/(T-\theta)+\chi_0$, where C is the Curie constant, θ is the Weiss temperature and χ_0 is the sum of the diamagnetic susceptibilities of ions. The χ_0 is calculated from the reported values [7]. These magnetic parameters are shown in Table 3. The Weiss temperatures are negative for all samples. The results show that the magnetic moments have antiferromagnetic correlation each other in the samples. The Weiss temperature increases toward 0 K with increasing radius of A-ion. The correlation is suppressed by the improvement of electric conductivity with increasing radius of A-ion.

The effective Bohr magneton ($p_{\mathrm{eff,\,exp}}$), estimated from the Curie constant, is found to decrease with increasing radius of A-ion, as shown in Table 3. The effective Bohr magnetons are evaluated to investigate the spin states of Co ions from the following equation:

$$p_{\mathrm{eff,cal}}{}^2 = f_{\mathrm{Co^{2+}},i}\, p_{\mathrm{Co^{2+}},i}{}^2 + f_{\mathrm{Co^{3+}},j}\, p_{\mathrm{Co^{3+}},j}{}^2 ,$$

where $f_{\mathrm{Co^{2+}},i}$ and $f_{\mathrm{Co^{3+}},j}$ are the fraction of Co^{2+} ion under spin state i and Co^{3+} under spin state j, therefore, $f_{\mathrm{Co^{2+}},i} + f_{\mathrm{Co^{3+}},j} = 1$. These fractions are calculated from the average valence of Co ions. $p_{\mathrm{Co^{2+}},i}$ and $p_{\mathrm{Co^{3+}},j}$ are the effective Bohr magnetons of Co^{2+} ion under spin state i (3.87 for high spin state [$t_{2g}{}^5e_g{}^2$] and 1.73 for low spin state [$t_{2g}{}^6e_g{}^1$])and Co^{3+} ion under spin state j (4.90 for high spin state [$t_{2g}{}^4e_g{}^2$], 2.83 for intermediate spin state [$t_{2g}{}^5e_g{}^1$] and 0.00 for low spin state [$t_{2g}{}^6$]), respectively. The calculated magnetons are closest to the experimentally derived ones for all samples, when it is assumed that the Co^{2+} ion under the high spin state and Co^{3+} ion under the intermediate spin state coexist. The lattice expansion due to the large A-ion does not affect the spin state of Co^{2+} and Co^{3+} ions.

4. CONCLUSION

We attempt to investigate the effect of lattice expansion on the electric and magnetic properties of layered cobaltite $La_{1.4}A_{0.6}CoO_{4-\delta}$ (A=Ca, Sr, Ba). The a-axis increases, in other word, the equatorial Co-O bond length increases with increasing radius of A-ion. However, the oxygen content (4-δ) simultaneously increases, that is, the average valence of Co ion increases with increase in radius of A-ion. The electric and magnetic properties of the cobaltites are affected by the average valence of Co ion rather than by the lattice

Table 5 Curie constant, C, Weiss temperature, θ, temperature independent susceptibility, χ_0, experimentally obtained effective Bohr magneton, $p_{\mathrm{eff,\,exp}}$, and calculated effective Bohr magneton, $p_{\mathrm{eff,\,cal}}$, for $La_{1.4}A_{0.6}CoO_{4+\delta}$ (A=Ca, Sr and Ba).

A	C / emu mol^{-1}K	θ / K	χ_0 / emu mol^{-1}*	$p_{\mathrm{eff,\,exp}}$ / μ_B	$p_{\mathrm{eff,\,cal}}$ / μ_B**
Ca	1.52	-131	-9.16×10^{-5}	3.49	3.31
Sr	1.13	-103	-9.60×10^{-5}	3.01	3.24
Ba	1.10	-94.1	-1.06×10^{-4}	2.97	3.18

*Calculated from the reported diamagnetic susceptibility [6].

**Calculated on the assumption that Co^{2+} ions are in the high spin state and Co^{3+} ions are in the intermediate spin state (see text).

expansion. Increase in the average valence decreases the activation energy so that the electric conductivity is improved. The improvement of the conductivity suppresses the antiferromagnetic correlation between the magnetic moments of Co ions. The change in the average valence indicates the change in the fraction of Co^{2+} ion and Co^{3+} ion in the samples. The change in the effective Bohr magnetons, which are experimentally derived, are well explained as the change in the fraction of Co^{2+} ion under high spin state and Co^{3+} ion under intermediate spin state.

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