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Reduction of perovskite oxide $LnCoO_3$(Ln = La–Eu) in a hydrogen atmosphere

TSUYOSHI ARAKAWA, NOBUHIKO OHARA, JIRO SHIOKAWA
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita-shi, Osaka-fu, Japan

The reduction of $LnCoO_3$(Ln = La–Eu) in a hydrogen atmosphere of 2×10^6 Pa at 25 to 600° C was investigated by X-ray diffraction and thermogravimetric analysis, which were carried out to pursue *in situ* the reaction of reduction of $LnCoO_3$. The amount of lattice oxygen consumed at 600° C increases on going from $LaCoO_3$ to $EuCoO_3$. It was shown that the reduction process proceeded through the formation of a series of oxygen-deficient structures in keeping the perovskite structures; for example, the final X-ray powder diffraction pattern of $NdCoO_{3-x}$($x = 1.1$) could be indexed on a cubic cell ($a = 0.39$ nm) and an orthorhombic cell ($a_0 = 0.522$ nm, $b_0 = 0.559$ nm, $c_0 = 0.795$ nm), the relationship with the cubic cell being $a_0 \simeq 2^{1/2}a_c$, $b_0 \simeq 2^{1/2}a_c$, $c \simeq 2a_c$.

1. Introduction

The perovskite structure is very commonly found in oxides of general formula ABO_3. These compounds have wide technical application, for example as electrode materials for fuel cells or batteries, as catalysts and as gas sensors [1–6]. Nakamura *et al.* [7] studied the stability of $LaBO_3$(B = vanadium, chromium, manganese, iron, cobalt, nickel) type perovskite oxides under reducing conditions. It has been reported that low-temperature reduction of $LaNiO_3$ under hydrogen led to new compounds such as $La_2Ni_2O_5$ and $LaNiO_2$ [8]. However, the change of the crystal symmetry of $LnCoO_3$(Ln = La–Eu) perovskite in a reducing atmosphere has rarely been observed. In this report, the chemical stability and the crystallographic properties of perovskites $LnCoO_3$ that were examined by X-ray diffraction at different degrees of reduction are presented.

2. Experimental details

The samples were prepared by the solid state reaction of dried Ln_2O_3(Ln = La–Eu) and CoO. The well ground mixtures of components were fired at 1300° C in air for 10 h. The X-ray diffraction patterns of these compounds showed perovskite $LnCoO_3$ peaks. No peaks corresponding to rare earth or the transition metal oxides were detected.

In order to avoid reoxidation after reduction, the measurements of X-ray diffraction were carried out to pursue *in situ* the reaction of $LnCoO_3$ under a hydrogen atmosphere as follows. The sample holder was mounted in a chamber with a beryllium metal plate as the X-ray window. Then the chamber was evacuated and the hydrogen pressure applied at 2×10^6 Pa in order to promote the reaction of reduction, as the temperature of this X-ray apparatus could not be raised to above 550° C.

A high pressure thermal gravimetric meter (Shinku Riko Co.) was used to measure the thermogravimetric behaviour of $LnCoO_3$ in the hydrogen atmosphere ($P_{H_2} = 2 \times 10^6$ Pa). Also, the weight-loss curves of $LnCoO_3$ were taken on a silica balance in a $10\,H_2 + 90\,He$ atmosphere, using a sample of 1.0×10^{-4} kg. The sensitivity was 10^{-7} kg. The gas flow rate was maintained at 36 $cm^3\,min^{-1}$.

3. Results and discussion

3.1. Thermogravimetric behaviour of $LnCoO_3$

When $LnCoO_3$ was heated in the temperature range of 25 to 600° C under a hydrogen atmosphere (2×10^6 Pa), the weight-loss showed. The individual weight-loss curves obtained are shown in Fig. 1. The weight-loss was due to loss of the lattice oxygen of $LnCoO_3$ as mentioned below. The overall reaction scheme can be written as follows;

$$LnCoO_3 + xH_2 \rightarrow LnCoO_{3-x} + xH_2O \qquad (1)$$

The temperature was selected to maintain x at less than 1.5. The weight change of $LaCoO_3$ commenced at about 300° C. When the isothermal reduction was carried at 390° C, a weight-loss of 0.5 wt % was observed. When the temperature was raised to about 500° C, the weight change took place. The weight-loss at 545° C was 6.0 wt %. For $NdCoO_3$, the weight-loss was 3.0 wt % at 400° C and 7.0 wt % at 435° C, respectively. The weight of $EuCoO_3$ decreased monotonously and the amount of oxygen consumed at 420° C was the largest. The magnitude of weight-loss for $LaCoO_3$ was the smallest among the rare earth cobaltates under the experimental conditions. Moreover, the thermogravimetric behaviour in the $10\,H_2 + 90\,He$ atmosphere was more clearly investigated by the measurement of the silica valence. The isothermal reductions were carried at 300, 400, 500 and 600° C, respectively. The amount of oxygen consumed in $LnCoO_3$ is summarized in Table I. Although the experimental conditions differed from those under the hydrogen atmosphere, the characteristics of the reduction were

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TABLE I The extent of the reduction of $LnCoO_3$

Catalyst	$-\Delta H$(kJ mol^{-1})*	Extent of reduction $x^{\dagger}$(° C)			
		300	400	500	600
$LaCoO_3$	281.8	0.25	0.25	0.77	0.77
$NdCoO_3$	272.7	–	0.24	1.04	1.04
$SmCoO_3$	265.7	–	0.18	0.51	1.30
$EuCoO_3$	255.8	–	–	1.27	1.27

*This value is estimated from the following equation [16]:

$$\Delta H(\text{metal–O}) = \frac{1}{C_n m}\left(H_f - H_s m - \frac{n}{2}D\right)$$

H_f = enthalpy of formation on one mole of oxide M_mO_n, H_s = sublimation energy of metal, D_0 = dissociation energy of O, C_n = coordination number of metal ions.

†We write the reduced form as $LnCoO_{3-x}$.

close to those under the experimental conditions in Fig. 1. The temperature at which the reduction of $LaCoO_3$ commenced was the lowest. Also, the amount of lattice oxygen consumed at 600° C increased on going from $LaCoO_3$ to $EuCoO_3$. It was understandable that the magnitude of reduction for $EuCoO_3$ at 600° C was larger than that for other $LnCoO_3$, as judged by the value of ΔH (metal–O).

3.2. Crystallographic properties of $LnCoO_3$ perovskite

Some perovskite oxides AMO_{3-x}(A = calcium, strontium, barium; M = 3d element) exhibit non-stoichiometry in a wide range, $0 < x < 0.5$ [9]. In these non-stoichiometric oxides, the defects are arranged along particular directions or in parallel planes. Especially, it has been established in $CaFeO_{2.5}$ (the mineral brownmillerite) that the defective structure is made up of separate sheets of corner-linked (MO_4) tetrahedra and corner-linked (MO_6) octahedra [10, 11]. Since the lattice oxygen for $LnCoO_3$ was consumed by low temperature reduction, the change of structure of $LnCoO_3$ perovskite oxides could be expected to occur under a reducing atmosphere.

When $LnCoO_3$ was reduced under a hydrogen atmosphere at some temperatures, the change of the diffraction pattern was observed. Diffraction patterns for $NdCoO_3$ are shown in Fig. 2. When the variation of a main line was rapid the 2θ range 30–35° was scanned as shown in Fig. 3. $NdCoO_3$ has a perovskite structure with pseudo cubic symmetry (a_c = 0.755 nm). Hagenmuller *et al.* [12] have reported that $NdCoO_3$ is pseudo-tetragonal with the orthorhombic symmetry (a = 0.5345 nm, b = 0.5345 nm, c = 0.756 nm. The relationship between the orthorhombic cell and the cubic perovskite cell for our sample was $a_0 \simeq 2^{-1/2}a_c$, $b_0 \simeq 2^{-1/2}a_c$, $c_0 \simeq a_c$. Therefore, actual symmetry for $NdCoO_3$ used was probably orthorhombic. When the isothermal reduction was carried out at 400° C, the X-ray intensity of (2 2 0) line of the original cubic symmetry decreased with the time and the (1 1 0) line of the tetragonal structure appeared, and then the X-ray intensity of (1 1 0) line increased with the time. Moreover, when the reduction temperature was raised to 435° C, the cubic and the orthorhombic symmetry appeared with the decrease of the tetragonal symmetry. The final X-ray powder diffraction pattern of $NdCoO_{3-x}(x = 1.1)$ could be indexed on a cubic cell (a_c = 0.39 nm) and an orthorhombic cell (a_0 = 0.522 nm, b_0 = 0.559 nm, c_0 = 0.795 nm. The relationship between the cubic cell and the orthorhombic cell was $a_0 \simeq 2^{1/2}a_c$, $b_0 \simeq 2^{1/2}a_c$, $c_0 \simeq 2a_c$. When $LnCoO_3$ was treated under a helium atmosphere, the diffraction pattern of an original cubic symmetry did not change. Also, when the hydrogen gas was pumped out in the course

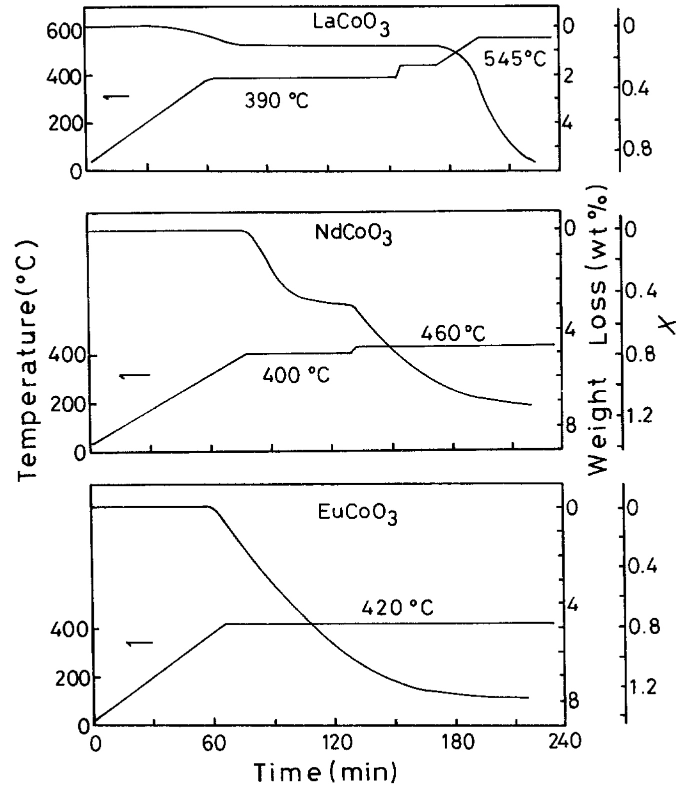

Figure 1 Weight-loss curves for $LnCoO_{3-x}$ heated in a hydrogen atmosphere. $P_{H_2} = 2 \times 10^6$ Pa.

TABLE II Crystallographic data of $LnCoO_{3-x}$. Unit cell dimensions (nm).

$LaCoO_{3-x}$:	rhombohedral $(x = 0)$ $a = 0.542$ $c = 0.130$	→	cubic (I)* $(x = 0.2)$ $a = 0.393$	→	cubic (II) $(x = 0.9)$ $a = 0.390$	+	orthorhombic* $(x = 0.9)$ $a = 0.781$ $b = 0.891$ $c = 0.824$
$NdCoO_{3-x}$:	cubic $(x = 0)$ $a = 0.755$	→	tetragonal* $(x = 0.5)$ $a = 0.383$ $c = 0.391$	→	cubic $(x = 1.1)$ $a = 0.390$	+	orthorhombic* $(x = 1.1)$ $a = 0.522$ $b = 0.559$ $c = 0.795$
$SmCoO_{3-x}$:	orthorhombic $(x = 0)$ $a = 0.528$ $b = 0.535$ $c = 0.749$	→			cubic† $(x = 1.3)$ $a = 0.380$		
$EuCoO_{3-x}$:	orthorhombic $(x = 0)$ $a = 0.525$ $b = 0.537$ $c = 0.747$	→			cubic* $(x = 1.3)$ $a = 0.378$		

*the experimental conditions are the same as Fig. 1.
†after reducing for 3 h at 440° C.

of the reduction, no diffraction diagram varied between before and after the degassing.

Since the measurement of the X-ray diffraction was carried out in the same condition as the thermogravimetric analysis, the reduction of $NdCoO_3$ took place in the same extent of weight-loss. The overall reaction scheme can be written as follows:

$$NdCoO_3 + xH_2 \rightarrow NdCoO_{3-x} + xH_2O. \quad (2)$$

x is ~ 0.5 at 400° C and ~ 1.1 at 435° C as shown in Fig. 1. At $x = 0.5$ or 1.0, it was expected that $NdCoO_3$ gave rise to Nd_2CoO_4, $Nd_2Co_2O_5$, CoO, Nd_2O_3 or Co by the reduction, as judged by Equation 2. However, the diffraction lines of these compounds did not show. Thus, it is shown that the variation of the crystal symmetry proceeded through the formation of a series of oxygen-deficient structures in keeping with the perovskite structure.

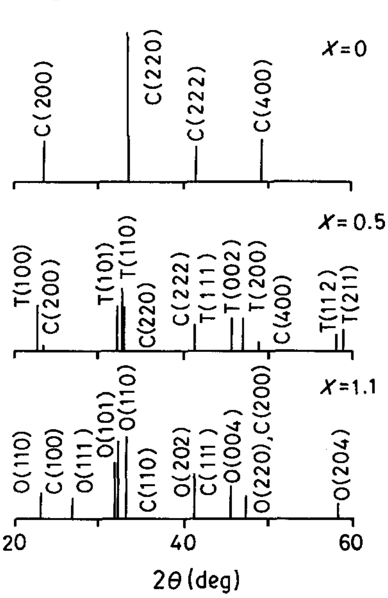

Figure 2 X-Ray diffraction pattern of $NdCoO_{3-x}$. (a) fresh sample at 400° C, (b) after reducing for 80 min at 400° C, (c) after reducing for 80 min at 435° C. C; cubic, T; tetragonal, O; orthorhombic.

The variations of the crystal symmetry are summarized in Table II. In the 0–1 wt % weight-loss region, at first the crystal symmetry of $LaCoO_3$ changed from rhombohedral to cubic (I) and then the phase of cubic (II) and orthorhombic symmetry were maintained in the 1–6 wt % weight-loss region. Rao *et al.* [13] have reported that $La_2Co_2O_5$ being prepared by the reduction of $LaCoO_3$ in dilute hydrogen at 670 K indexed on an orthorhombic unit cell (a = 0.546 nm, b = 1.5908 nm, c = 0.57 nm) with a brown millerite structure. The X-ray powder diffraction pattern of $LaCoO_{3-x}$ was quite different from that of brown millerite and could be indexed on a cubic cell (a_c = 0.39 nm) and an orthorhombic cell (a_0 = 0.781 nm, b_0 = 0.891 nm, c_0 = 0.824 nm), the relationship with the cubic cell being $a_0 \simeq 2a_c$, $b_0 \simeq 5^{1/2}a_c$, $c_0 \simeq 5^{1/2}a_c$. For the reduction of $LaCoO_3$ in the mixture gas of H_2–N_2 at 1 bar, Sis *et al.* [14] pointed out that in the 0–3.25 wt % weight-loss region, the structure is monoclinic and at the loss of the weight of 3.25 wt % the crystal structure apparently reverted to the original rhombohedral symmetry

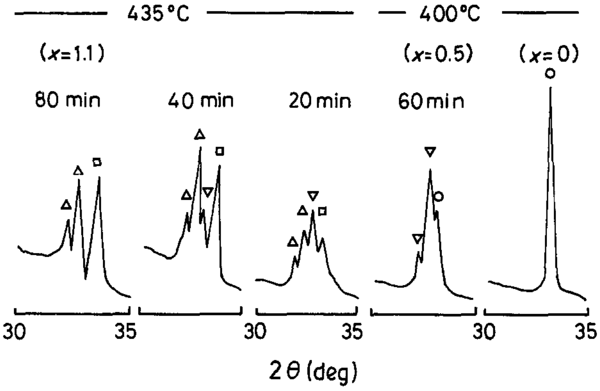

Figure 3 Variation of X-ray (Cu-*Kα*) diffractogram for $NdCoO_{3-x}$ at 400° C and 435° C in a hydrogen atmosphere ($P_{H_2} = 2 \times 10^6$ Pa). (○) cubic (I), (▽) tetragonal, (▣) cubic (II), (△) orthorhombic.

with one loss of lanthanum and cobalt. When $\mathrm{LaCoO_3}$ was reduced to a weight loss of 4.56 wt %, another change in the symmetry occurred and distinct lines from $\mathrm{La_2O_3}$ and oxides of cobalt were seen. However, under our experimental conditions, metallic cobalt, $\mathrm{La_2O_3}$ and CoO were not observed and the crystal symmetry change differed from that as reported by Sis *et al.* [14]. On the other hand, when $\mathrm{SmCoO_3}$ and $\mathrm{EuCoO_3}$ were reduced, the cubic symmetry only appeared. When in $\mathrm{ABO}_{3-x}x \leqslant 0.25$, ABO_{3-x} phase are known to crystallize in the cubic perovskite structure because the vacancies are not ordered in the long range [15]. For $\mathrm{SmCoO_3}$ and $\mathrm{EuCoO_3}$, when the consumption of lattice oxygen began, the cubic symmetry immediately appeared and there was finally the cubic symmetry. On the basis of X-ray diffraction, we were not able to detect any ordering of vacancies in this phase and the pattern could be indexed on a cubic perovskite cell with $a = 0.38\,\mathrm{nm}$ for SmCoO_{3-x} and $a = 0.378\,\mathrm{nm}$ for EuCoO_{3-x}, respectively. In the region $x = 1.0$–1.3, the cubic phase held and metallic Co or CoO diffraction lines did not show. Since $\mathrm{Ln^{3+}}$ ions were not reduced to the divalent state under the experimental conditions, it is considered that the low valent state of cobalt ion, $\mathrm{Co^+}$, or $\mathrm{Co^0}$, exists in the reduced form in corresponding to the formula range $\mathrm{LnCoO_{2.0}}$– $\mathrm{LnCoO_{1.7}}$. Under the experimental conditions, since the perovskite structure kept and no metallic cobalt diffraction lines showed, we may consider the existence of cluster as follows:

$$\mathrm{Co^0}\text{—}\mathrm{Co^{2+}}\text{—}\mathrm{Co^0}\text{—}\mathrm{Co^{2+}},\ \mathrm{Co^0}\text{—}\mathrm{Co^+}\text{—}\mathrm{Co^0}\text{—}\mathrm{Co^+},$$

$$\begin{array}{ccc} \mathrm{Co^{2+}}\text{—}\mathrm{Co^0} & & \mathrm{Co^+}\text{—}\mathrm{Co^0} \\ |\qquad\quad | & \text{or} & |\qquad\quad | \\ \mathrm{Co^0}\text{——}\mathrm{Co^{2+}} & & \mathrm{Co^0}\text{—}\mathrm{Co^+}. \end{array}$$

It would seem that these clusters are incorporated in the reduced perovskite. Further, physicochemical evidence should be collected to support the valence state of cobalt ion in the reduced form. Thus, the crystallographic properties of $\mathrm{LnCoO_3}$ in a hydrogen atmosphere change from $\mathrm{LaCoO_3}$ to $\mathrm{EuCoO_3}$. It appears that these properties will be largely affected by the binding energy of oxygen which coordinates to the metal ions as described above.

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