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CRYSTALLOGRAPHIC PROPERTIES OF $LnCoO_3$(Ln = La-Eu) PEROVSKITE IN A HYDROGEN ATMOSPHERE

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The crystallographic properties of $LnCoO_3$ under a hydrogen atmosphere were determined by X-ray diffraction and the thermogravimetric analysis which were carried out to pursue *in situ* the reaction of reduction of $LnCoO_3$. It was shown that the reduction process proceeded through the formation of a series of oxygen-deficient structures in keeping the perovskite structure.

The perovskite oxide is very commonly found in compounds of general formula ABO_3 and is very important because many of these compounds are widely used for the functional materials, such as electrode materials for fuel cells or batteries, catalysts and gas sensors.[1-3] We are interested in the stability of the perovskite phase in the reducing atmosphere at high temperature with respect to the use of these compounds in the technical process. Nakamura *et al.*[4] studied the stability of $LaBO_3$(B = V, Cr, Mn, Fe, Co, Ni) type perovskite 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 $LaNiO_2$.[5] $LnCoO_3$(Ln = La-Eu) is the active catalyst for the oxidation of CO and the highly sensitive gas sensor for alcohol.[6-8] It was reported that the trivalent cobalt ion on the surface of $LaCoO_3$ reduced to Co^0 under the atmosphere of H_2 at 350 °C.[9] However, the change of the crystal structure of $LnCoO_3$ perovskite in reducing atmosphere has been rarely observed. In this paper, the crystallographic properties examined by X-ray diffraction method at different degrees of reduction are presented.

The samples were prepared by the solid-state reaction of dried Ln_2O_3(Ln = La-Eu) and CoO. The well ground mixtures of the constituents 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 cobalt oxide were detected. In order to avoid reoxidation after reduction, the measurement 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 an chamber with a beryllium 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 reaction temperature of this X-ray apparatus did not raise. Weight-loss curves were

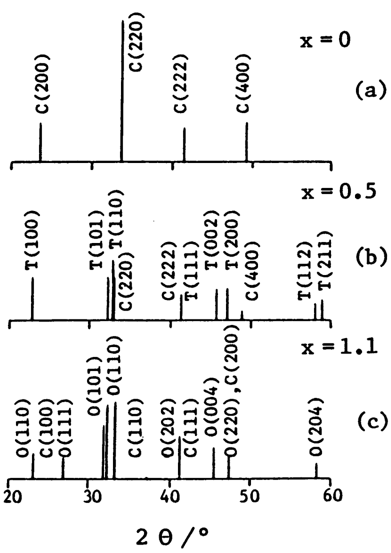


Fig. 1. X-Ray diffraction pattern of $NdCoO_{3-x}$. (a) fresh sample at 400 °C, (b) after reducing for 80 min at 400 °C, (c) after reducing for 80 min at 435 °C. C : cubic, T : tetragonal, O : orthorhombic

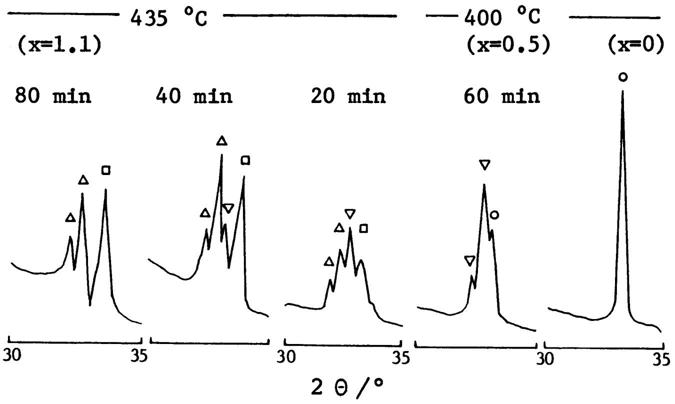


Fig. 2. Variation of X-ray(Cu Kα) diffractogram for $NdCoO_{3-x}$ at 400 °C and 435 °C in a hydrogen atmosphere(P_{H_2} = 2 x 10^6 Pa). O : cubic(I), ▽ : tetragonal, □ : cubic(II), △ : orthorhombic

taken on High Pressure Thermal Gravimetric Meter(SINKU-RIKO Co.).

When $LnCoO_3$ was reduced under a hydrogen atmosphere at some temperatures, the diffraction pattern changed with time is shown in Fig. 1. When the variation of a main line was fast, the 2θ range 30-35° was scanned as shown in Fig. 2. $NdCoO_3$ has a perovskite structure with the cubic structure. However, when the isothermal reduction was carried out at 400 °C, the X-ray intensity of (220) line of the original cubic structure decreased with time and the (110) line of the tetragonal structure appeared and then the X-ray intensity of (11 0) line increased with time. Moreover, when the reduction temperature raised, the crystal structure of $NdCoO_{3-x}$ changed from tetragonal to cubic and orthorhombic. When $LnCoO_3$ was treated under a helium atmosphere, the diffraction pattern of a original cubic structure did not change. Also, when the hydrogen gas was pumped out in the course of the reduction, no diffraction diagram varied between before and after the degassing.

The reduction of samples was carried out in the same condition as the measurement of the X-ray diffraction. The isothermal reductions were carried out at 400 °C and 435 °C as shown in Fig. 3. If the overall reaction scheme can be written as follows :

$$NdCoO_3 + x\,H_2 \longrightarrow NdCoO_{3-x} + x\,H_2O \qquad (1)$$

where x is about 0.5 at 400 °C and about 1.1 at 435 °C. At x = 0.5, it is considered that the stoichiometry can follow from either,

$$2\,NdCoO_3 + H_2 \longrightarrow Nd_2CoO_4 + CoO + H_2O \qquad (2)$$

or

$$2\,NdCoO_3 + H_2 \longrightarrow Nd_2Co_2O_5 + H_2O \qquad (3)$$

If Nd_2CoO_4 and $Nd_2Co_2O_5$ are appeared, Nd_2CoO_4 will be the K_2NiF_4 structure, and

Table 1. Crystallographic data of $LnCoO_{3-x}$

$LaCoO_{3-x}$:	rhombohedral (x=0) a = 5.42 c = 13.0	$\longrightarrow$ cubic(I) (x=0.2) a = 3.93	$\xrightarrow{a)}$ cubic(II) a = 3.90	+ orthorhombic [b)] (x=0.9) a = 7.81, b = 8.91 c = 8.24
$NdCoO_{3-x}$:	cubic (x=0) a = 7.55	$\longrightarrow$ tetragonal (x=0.5) a = 3.83 c = 3.91	$\xrightarrow{c)}$ cubic a = 3.90	+ orthorhombic [d)] (x=1.1) a = 5.22, b = 5.59 c = 7.95
$SmCoO_{3-x}$:	orthorhombic (x=0) a = 5.28, b = 5.35 c = 7.49	$\longrightarrow$	cubic [e)] (x=1.3) a = 3.80	
$EuCoO_{3-x}$:	orthorhombic (x=0) a = 5.25, b = 5.37 c = 7.47	$\longrightarrow$	cubic [f)] (x=1.3) a = 3.78	

unit : Å

a) after reducing for 2 h at 400 °C. b) after reducing for 1 h at 545 °C. c, d) the experimental conditions are referred to the text. e) after reducing for 3 h at 440 °C. f) after reducing for 3 h at 420 °C.

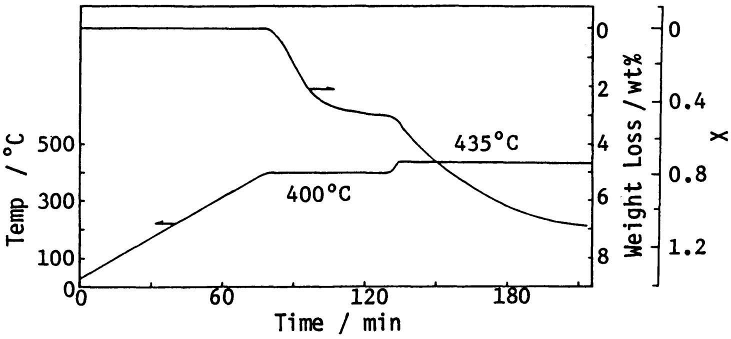


Fig. 3. Weight-loss curve for $NdCoO_{3-x}$ heated in a hydrogen atmosphere. $P_{H_2} = 2 \times 10^6$ Pa.

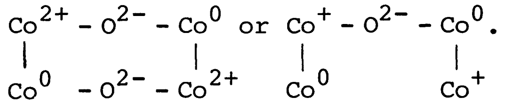
$Nd_2Co_2O_5$ will have a monoclinic lattice. However, Nd_2CoO_4, $Nd_2Co_2O_5$, and then CoO diffraction lines did not appear. Therefore it seems that the reaction in Eqs. 2 and 3 does not take place under our experimental conditions. At x = 1.0, the overall reaction can be written as follows:

$$2\,NdCoO_3 + 2\,H_2 \longrightarrow Nd_2CoO_4 + Co + 2\,H_2O \qquad (4)$$

$$4\,NdCoO_3 + 2\,H_2 \longrightarrow Nd_2Co_2O_5 + 2\,CoO + Nd_2O_3 + 2\,H_2O \qquad (5)$$

$$NdCoO_3 + H_2 \longrightarrow NdCoO_2 + H_2O \qquad (6)$$

Since metallic Co, Nd_2O_3, Nd_2CoO_4, and $Nd_2Co_2O_5$ were not observed, the reaction of Eq. 6 may occur under our experimental conditions in a similar manner as described elsewhere.[5)] Thus, it is shown that the variation of the crystal symmetry proceeded through the formation of a series of oxygen-deficient structures in keeping the perovskite structure.

The variation of the crystal structure are summarized in Table 1. In the 0-1 wt% weight-loss region, at first the crystal structure of $LaCoO_3$ changed from rhombohedral to cubic(I) and then the phase of cubic(II) and orthorhombic structure appeared with decreasing the cubic(I) phase. Moreover, the cubic(II) and orthorhombic structure were stable in the 1-6 wt% weight-loss region. On the other hand, when $SmCoO_3$ and $EuCoO_3$ were reduced, a cubic $SmCoO_{3-x}$ and a cubic $EuCoO_{3-x}$ only appeared. In the region $x = 1.0-1.3$, the cubic phase held and metallic Co or CoO diffraction lines did not appear. Since Ln^{3+} ions were not reduced to the divalent state under the experimental conditions, it is considered that the low valence state of cobalt ion, Co^+ or Co^0, exists in the reduced form corresponding to the formula range $LnCoO_{2.0} - LnCoO_{1.7}$. Under the experimental conditions, since the perovskite structure kept and no metallic Co diffraction lines showed, we may considered the existence of cluster as follows; $Co^0 - O^{2-} - Co^{2+} - Co^0 - O^{2-} - Co^{2+}$, $Co^0 - Co^+ - O^{2-} - Co^0 - Co^+$,  $\begin{array}{ccccc} Co^{2+} & - & O^{2-} & - & Co^0 \\ | & & & & | \\ Co^0 & - & O^{2-} & - & Co^{2+} \end{array}$ or $\begin{array}{ccccc} Co^+ & - & O^{2-} & - & Co^0 \\ | & & & & | \\ Co^0 & & & & Co^+ \end{array}$. It would seem that these clusters are incorporated in the reduced perovskite. Further, physicochemical evidence should be corrected to support the valence state of cobalt ion in the reduced form. Thus, the crystallographic properties of $LnCoO_3$ in a hydrogen atmosphere change with the rare earth ion contained in the perovskite oxide. It appears that these properties will be largely affected by the radius of rare earth ion and the binding energy of oxygen which coordinates to the metal ions.[7]

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