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Mechanochemical Synthesis of $LnCoO_3$ (Ln: La, Pr, Dy)

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Synthesis of lanthanoid cobaltates, $LnCoO_3$ (Ln: La, Pr, Dy), *via* the mechanochemically prepared complex (oxy-)hydroxides has been studied. The hydroxides are prepared by grinding $Co(OH)_2$ or Co_3O_4 with Ln_2O_3 (Ln: La, Dy) or Pr_6O_{11} in acetone containing a very small amount of H_2O in $LnCoO_3 \cdot 4H_2O$ composition. The starting hydroxides act as the reactive grinding aids to each other. La_2O_3 and $Co(OH)_2$ form the complex hydroxide, $LaCo(OH)_5$, that is a sort of inorganic polymers having La-O-Co bond. The hydration affinity of trivalent Co^{3+} ions is not high enough to form complex hydroxide $LaCo(OH)_6$. Then, the addition of H_2O_2 to the grinding liquid results in the formation of oxyhydroxide, $LaCoO(OH)_4$. These (oxy-)hydroxides are directly converted to pseudo-tetragonal $LaCoO_3$ at 600°C and rhombohedral $LaCoO_3$ above 800°C without forming any by-product. The redox interaction between $Co(OH)_2$ and Pr_6O_{11}, which shows the poor reactivity with Fe_2O_3, enables the formation of $PrCoO(OH)_4$. Contrary, the reaction with Dy_2O_3 becomes poor.

Key words: $LaCoO_3$, $PrCoO_3$, $DyCoO_3$, synthesis, mechanochemistry, crystallization

1. INTRODUCTION

Perovskite lanthanoid transition-metal oxides are candidate as redox catalysts and gas sensors, electrode materials for fuel cells, and so on [1,2]. These materials are synthesized by solid-state reactions and recently by build-up processes such as sol-gel methods. The authors have demonstrated the synthesis of perovskite-$LnFeO_3$ (Ln: La, Pr, Sm, Gd, Dy, and Yb) by a mechanochemical route in previous papers [3,4]. In this synthesis process, the starting Ln_2O_3 and Fe_2O_3 powders have been ground in organic liquids containing a small amount of H_2O, where Ln_2O_3 provides a $Ln(OH)_3$ colloids acting as a reactive grinding aid. The other starting material, Fe_2O_3, is kneaded into the colloid to form complex oxyhydroxides. Slightly hydrated $LnFeO_3 \cdot xH_2O$ (x=0.9-1.4) has been obtained by the dehydration-condensation of the intermediate oxyhydroxide under the grinding stress.

In the present paper, this mechanochemical process has been applied to the synthesis of $LnCoO_3$ (Ln: La, Pr, Dy). The reactivity is discussed in relation to the potential of the starting materials to redox and hydration reactions in the combination of $Co^{II}Co^{III}{}_2O_4$ or $Co^{II}(OH)_2$ and La_2O_3, Pr_6O_{11} or Dy_2O_3. The effect of H_2O_2 as an oxidant in the grinding liquid has also been studied.

2. EXPERIMENATL

High-purity lanthanoid oxide powders (purity: >99.9%) supplied from Hokko Chem. Ind. were used after the heat-treatment at 500°C for 3h. The specific surface area (*SSA*) was 6.5 (La_2O_3), 2.2 (Pr_6O_{11}), and 1.6 $m^2 \cdot g^{-1}$ (Dy_2O_3). The cobalt source used, Co_3O_4 and $Co(OH)_2$, was the reagent-grade powders (Kanto-Kagaku). Mechanical grinding was conducted by the use of a planetary mill (Kurimoto-Tekko-Sho). Weighed mixture of the starting powders (20g as $LnCoO_3$) was encapsulated into the grinding vessel (capacity: 410cm^3) made of stainless-steel with acetone (76cm^3), a small portion of H_2O (equivalent amount to $LnCoO_3 \cdot 4H_2O$ composition including H_2O for $Co(OH)_2$), and grinding media (ϕ2, YTZ balls, fractional filling: 0.40). Grinding was performed for 3h with 15min cooling interval in every 1h to maintain the temperature below 50°C. The ground products were filtered with 0.2μm Teflon membrane, washed with acetone, and dried at 85°C under vacuum. The ground products were calcined at 300-1000°C for 1h in air for crystallization.

Crystalline phases were identified by X-ray diffractometry (XRD, Cu$K\alpha_1$, 40kV, 20mA) and X-ray photoelectron spectroscopy (XPS, Mg$K\alpha$, 8kV, 30mA). Dehydration behavior of the ground products was examined by TG-DTA (10 $K \cdot min^{-1}$). Morphology was observed by scanning electron microscopy (SEM, Hitachi, S4300). *SSA* was determined by a N_2-adsorption BET method.

3. RESULTS AND DISCUSSION

3.1 TG-DTA of the starting $Co(OH)_2$

Figure 1 shows the thermal decomposition behavior of $Co(OH)_2$. The thermogravimetric curve indicated the mass loss at 200°C, 210-430°C and 930°C. The initial decomposition process at 200°C was the dehydration associated with the oxidation of Co^{II}. An exothermic peak was observed at 204°C

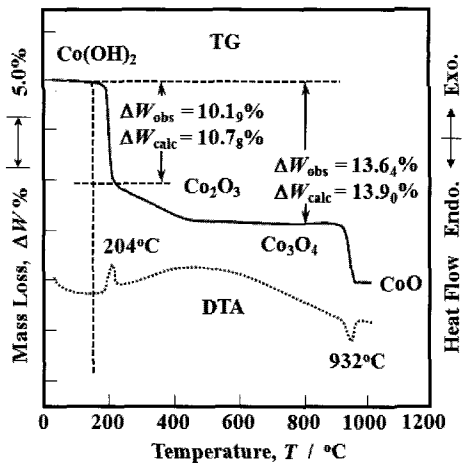

Fig. 1 TG-DTA curves of $Co(OH)_2$.

and the determined mass loss (ΔW_{obs} = 10.1$_9$%) agreed with the calculation, 10.78% on reaction (1).

$$2Co^{II}(OH)_2 + 1/2O_2 \rightarrow Co^{III}{}_2O_3 + 2H_2O \quad (1)$$

The Co_2O_3 formed was instable and decomposed to Co_3O_4 at 210-430°C. The ΔW_{obs}, 13.64%, was almost equal to 13.90% for reaction (2).

$$3Co^{II}(OH)_2 + 1/2O_2 \rightarrow Co^{II}Co^{III}{}_2O_4 + 3H_2O \quad (2)$$

Co_3O_4 further decomposed to CoO above 930°C. This observation was referred to estimate the composition of the ground products.

3.2 Bond characteristics of the ground products

The XPS spectra of the ground products are shown in **Fig. 2**. For LC1 using Co_3O_4, the La3d peaks (844.2 and 848.1eV) and O1s peak (534.2eV) were very close to those of $La(OH)_3$, and the Co2P peak was negligibly weak. This indicated the less interaction of Co_3O_4 and $La(OH)_3$ and the surface of Co_3O_4 covered by $La(OH)_3$. It was estimated that the pulverized Co_3O_4 was knead with the adhesive $La(OH)_3$. The La3d peak for LC2 and LC3 appeared at 845.2 and 842.0eV, which were a little higher energy than those for $LaCoO_3$. The Co3d peak for LC2 and LC3 (782.1 eV) was close to that of $LaCoO_3$ rather than $Co(OH)_2$. The O1s spectra also showed the E_B (531.7e for LC2, 532.2eV for LC3) close to $LaCoO_3$, $Co(OH)_3$ and $La(OH)_2$ However, the shoulder of O1s spectrum for $LaCoO_3$ was not observed. Then, the hydrated $LaCoO_3$, La,Co-hydroxide, or La,Co-oxyhydroxide were proposed as the structure of the ground products LC2 and LC3. The progress in reactions was suggested for LC3 because of the closer E_B of O1s peak to $LaCoO_3$.

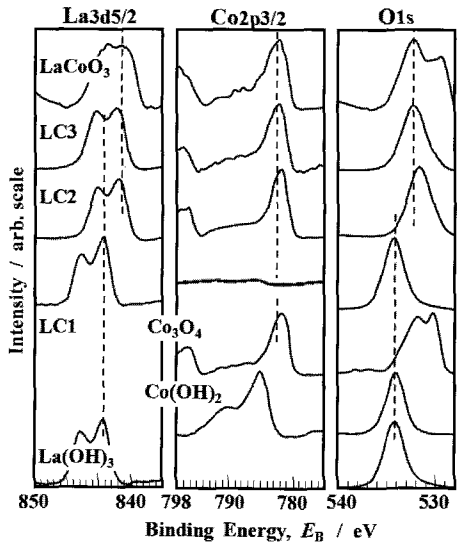

Fig. 2 XPS spectra of ground products.

The La3d and O1s XPS spectra for LC1 calcined at 400 and 700°C unchanged from those of the ground product, and the Co2p peak started to appeare at 400°C and increased at 700°C (**Fig. 3**). The La3d and Co2p spectra for LC2 and LC3 at 300°C unchanged from those of their ground products, but the O1s spectrum for LC3 showed the shoulder similar to $LaCoO_3$ at E_B = 530eV. $LaCoO_3$ should form at the quite low-temperature of 300°C. At 1000°C, all the ground products showed the XPS spectra for $LaCoO_3$.

3.3 Crystallization of the ground products

The estimation from XPS was ascertained by XRD. **Figure 4** shows the XRD patterns of the ground and calcined LC1. As estimated from the XPS results, the ground product was the mixture of $La(OH)_3$ and Co_3O_4. $La(OH)_3$ was dehydrated and crystallized to La_2O_3 at 600-700°C. The reflections of Co_3O_4 remained upto 700°C. However, the reflections for Co_3O_4 were evidently small against those of the mortar-mixed $La(OH)_3$-1/3 Co_3O_4, meaning the formation of the mixed hydroxide in part. The yield (Ψ) of the ground product was evaluated to be 43% by comparing the peak intensity of $La(OH)_3$ in LC1 to that of the mortar-mixed one. The ground products LC2 and

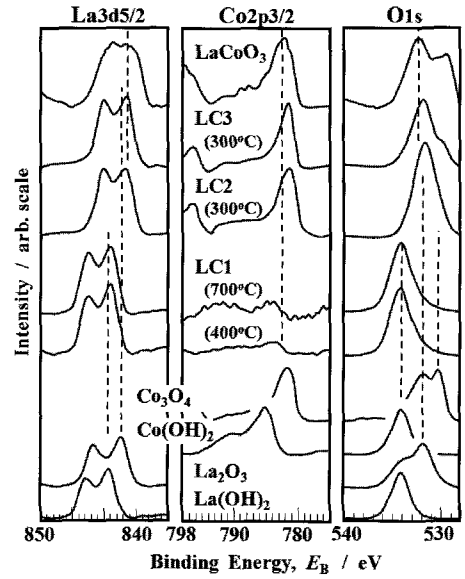

Fig. 3 Dependence of XPS spectra on calcination temp.

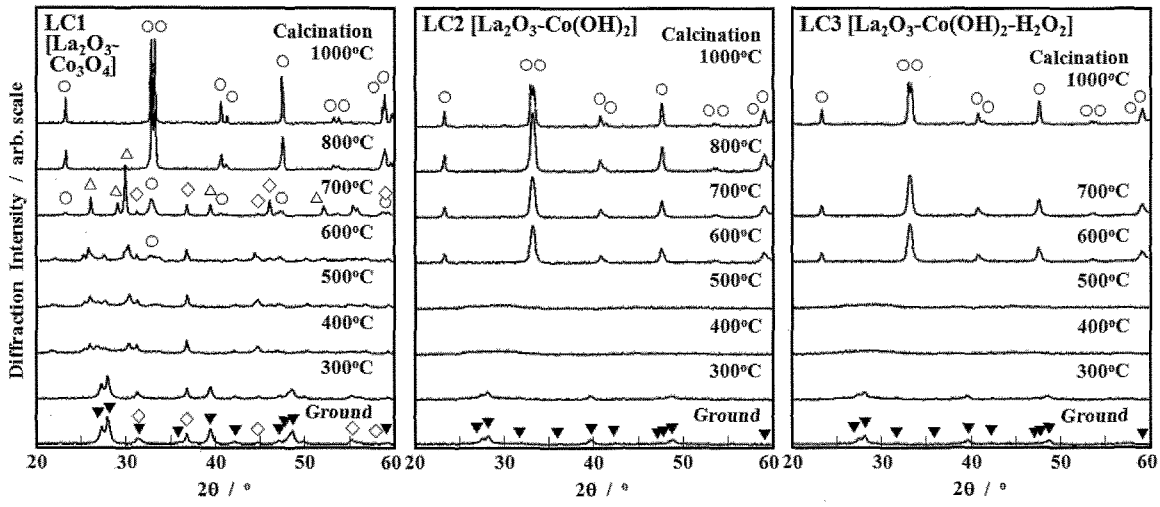

Fig. 4 XRD profiles of the ground products and calcined powders; ○: $LaCoO_3$, ◇: Co_3O_4, ▼: $La(OH)_3$, △: La_2O_3.

LC3 contains small amounts of $La(OH)_3$. The yield (Ψ) for LC2 and LC3 increased to 87% and 88%, respectively. The ground products were amorphous at 300-500°C, crystallized to pseudo-tetragonal $LaCoO_3$ at 600°C, and converted to rhombohedral phase above 800°C without forming any by-product. These observations were consistent with the discussion on XPS spectra.

3.4 TG-DTA of the ground products

Figure 5 shows the TG-DTA curves of LC1, LC2 and LC3. The ground product LC1 showed the mass loss at 400 and 700°C. The observed mass loss (ΔW_{obs}) at 100-1000°C was 10.3$_6$%, which agreed with 9.01% for the following reaction (3) when considering a little hydration of Co_3O_4. The ground product LC2 and LC3 indicated ΔW_{obs} of 13.3$_4$% and 12.8$_6$% at 1000°C, respectively. These values agreed with ΔW_{calc}, 13.09% and 12.78%, for the reactions (4) and (5).

$$La(OH)_3 + 1/3Co_3O_4 + 1/12O_2 \rightarrow LaCoO_3 + 3/2H_2O \quad (3)$$

$$LaCo(OH)_5 + 1/4O_2 \rightarrow LaCoO_3 + 5/2H_2O \quad (4)$$

$$LaCoO(OH)_4 \rightarrow LaCoO_3 + 2H_2O \quad (5)$$

The DTA curve for LC2 indicated the exothermic peak for the oxidation of Co^{II} to Co^{III} at 170°C. However it was not observed for LC3. The hydrogen peroxide doped into the grinding liquid oxidized Co^{2+} to Co^{3+} with low hydration affinity, then, leads the formation of oxyhydroxide (ΔW_{calc} =12.78%) rather than hydroxide. The $LaCo(OH)_5$ (LC2) and $LaCoO(OH)_4$ (LC3) formed amorphous $LaCoO_3$ at 400-600°C and crystallized at 641°C (LC2) and 609 °C (LC3) with about 2% mass loss.

3.5 Synthesis of $PrCoO_3$ and $DyCoO_3$

This mechanochemical process was applied to the synthesis of $PrCoO_3$ and $DyCoO_3$. **Figure 6** shows the XRD patterns of the ground product and the calcined powders for Pr_6O_{11}-$Co(OH)_2$ system without doping H_2O_2. On the synthesis of praseodymium ferrite $PrFeO_3$, Pr_6O_{11}, shows poor reactivity with FeO(OH) under grinding, and the XRD reflections of Pr_6O_{11} remained even at 700°C [3]. It was considered that the high stability

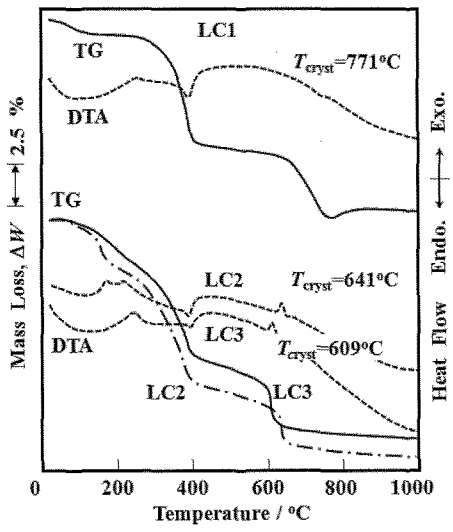

Fig. 5 TG-DTA curves of LC1, LC2 and LC3.

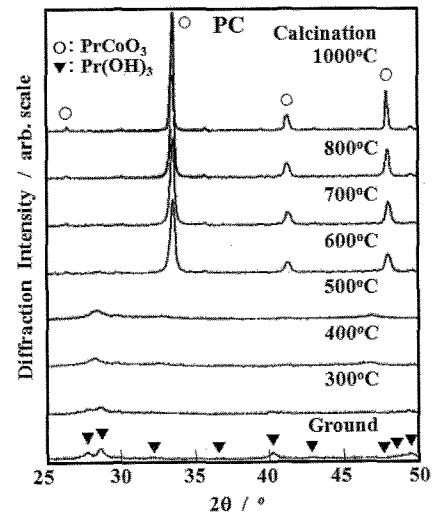

Fig. 6 XRD profiles for Pr_6O_{11}-$Co(OH)_2$ system.

as oxide, that is the low affinity to hydration, of Pr^{IV} was the reason for the poor reactivity. So, when the Co^{II} can reduce the Pr^{IV} to Pr^{III}, there is a possibility to progress the formation of hydroxide or oxyhydroxide. The XRD patters of the ground product PC indicated only the small reflections of $Pr(OH)_3$ and no reflections from Pr_6O_{11}. The mass loss value (ΔW_{obs}=12.17%) was comparable to the calculated value (ΔW_{calc}=12.69%) for the oxy-hydroxide, $PrCoO(OH)_4$. The yield of $PrCoO(OH)_4$ in the ground product (Ψ) was obtained to be 88% from the peak intensity of $Pr(OH)_3$. The overall reaction can be represented as the following equation.

$$1/6Pr^{III}{}_2Pr^{IV}{}_4O_{11} + Co^{II}(OH)_2 + H_2O + 1/12O_2 \rightarrow Pr^{III}Co^{III}O(OH)_4 \quad (6)$$

The small amount of O_2 required in (6) would be supplied from the ambient atmosphere under grinding or calcination. Tetragonal $PrCoO_3$ was successfully synthesized above 600°C.

Another example of the application was the synthesis of $DyCoO_3$. The dysprosium ferrite, $DyFeO_3$, is one of the most easily synthesized materials in the series of $LnFeO_3$. However, contrary to the Pr_6O_{11}-$Co(OH)_2$ system, the reactivity in Dy_2O_3-$Co(OH)_2$ system markedly degraded. The reflections for Dy_2O_3 were observed in the grinding product and their intensity increased with the raise in temperature. The reason for the poor reactivity of DC was unclear; however, the addition of the oxidant should be needed.

3.6 Morphology of ground and calcined LC2, PC, DC

The *SSA* and morphology of the ground and calcined powders are sited in **Table 1** and **Fig. 8**. The *SSA* of the ground products decreased with the increase in reactivity except DC. The SEM photographs in Fig. 8 showed the agglomeration. This was strongly related to the mechanism expected, where the adhesive $Ln(OH)_3$ colloids were used as the reactive grinding aid.

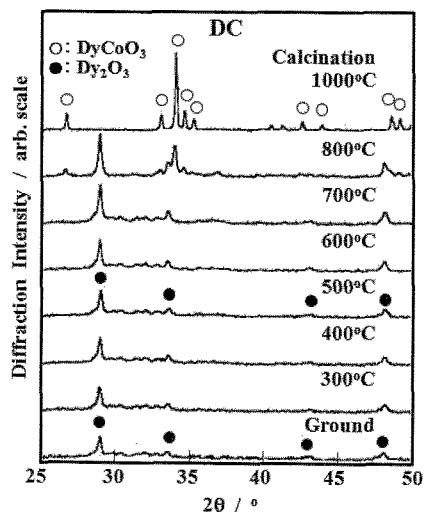

Fig. 7 XRD profiles for Dy_6O_3-$Co(OH)_2$ system.

Table 1. Specific surface area (*SSA*) of the ground and calcined powders

	Ground	Calcined powder			
		400°C	700°C	800°C	1000°C
LC1	47.5	42.8	6.9	5.3	—
LC2	23.9	13.2	3.9	—	1.4
LC3	17.9	11.4	6.9	5.1	—
PC	12.2	10.2	3.0	—	1.7
DC	11.7	8.7	5.2	—	1.3

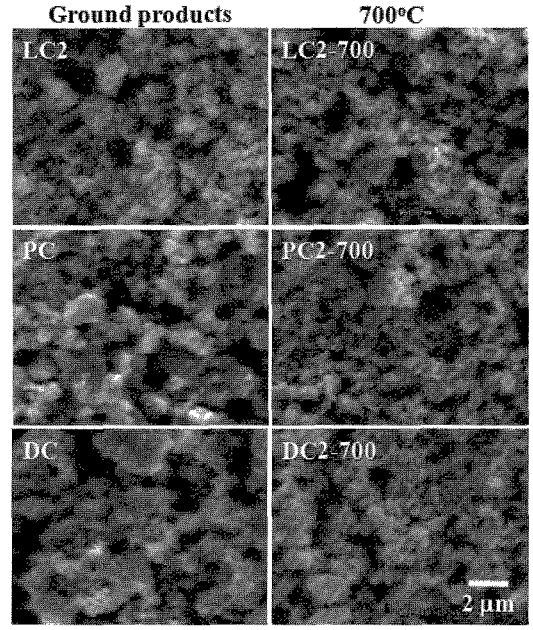

Fig. 8 Morphology of ground products.

4. CONCLUSION

The mechanochemical process is successfully applied to the synthesis of $LaCoO_3$. The ground products obtained from La_2O_3 and $Co(OH)_2$ are amorphous complex hydroxide and converted to prseudo-tetragonal $LaCoO_3$ at 600°C and rhombo-hedral one above 800°C. The addition of H_2O_2 to the grinding liquid results in the oxidation of Co^{II} to Co^{III} to contribute the formation of oxy-hydroxide, $LaCoO(OH)_4$, which can be dehydrated to amorphous $LaCoO_3$ at 300°C. The reduction activity of $Co^{II}(OH)_2$ enables the formation of $PrCoO_3$ from Pr_6O_{11}, but makes the synthesis of $DyCoO_3$ difficult.

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