Synthesis of $\beta$-Co(OH)$_2$ Plate-like Crystallites and Their Hydrothermal Growth

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Well-faceted hexagonal plate-like particles of $\beta$-Co(OH)$_2$ have been prepared by a precipitation method. $\alpha$-Co(OH)$_2$ was formed first, and then transformed to $\beta$-Co(OH)$_2$ with a typical size of 0.5 $\times$ 0.1 $\mu$m. Growth of $\beta$-Co(OH)$_2$ micro-crystals up to 9 $\times$ 0.5 $\mu$m was carried out in NaOH aqueous solutions under hydrothermal conditions. The basal plane of the synthesized $\beta$-Co(OH)$_2$ platelets was [001], as revealed by oriented particulate monolayer X-ray diffraction (OPML-XRD), which was kept after hydrothermal growth. The obtained platelets are considered to be suitable templates for the fabrication of textured layered-cobaltite thermoelectric ceramics by the reactive-templated grain growth (RTGG) method.

[Received August 7, 2003; Accepted December 24, 2003]

Key-words: $\beta$-Co(OH)$_2$, Platelet, Template, Precipitation, Hydrothermal, Textured ceramic

1. Introduction

Transition metal layered hydroxide materials, such as cobalt hydroxide and nickel hydroxide, have received increasing attention in recent years due to their many important technological applications.$^{1,2}$ Hydroxides and oxide-hydroxides of cobalt are of importance on account of their applications in alkaline secondary batteries.$^{3,4}$ A further interesting application of these materials is as precursors of heterogeneous catalysts.$^{5,6}$ The hydroxides of cobalt have a hexagonal layered structure and exist in two polymorphic forms, $\alpha$ and $\beta$.$^{7,8}$ The first form is isostructural with hydroxocarbonate-like compounds, while the second is brucite [M(OH)$_2$]-like and consists of hexagonally packed hydroxyl ions with Co(II) ions occupying alternate rows of octahedral sites.

Recently, during the searching of thermoelectric materials for power generation, misfit layered cobaltites were reported to exhibit metallic conductivity and large thermpower.$^{9-11}$ The crystal structures of the misfit layered cobaltites consist of CdI$_2$-type CoO$_2$ layers and rocksalt-type [M$_2$O$_3$]$^{n+}$ layers stacking alternately along the c-axis.$^{10-13}$ Due to the anisotropic transport properties of these materials, textured polycrystals are needed for thermoelectric power generation applications. We noted the crystallographic similarity between CdI$_2$-type $\beta$-Co(OH)$_2$ and the CoO$_2$ layers in terms of the edge-sharing CoO$_6$ octahedra, and have reported$^{14,15}$ in-situ topotactic syntheses of highly-textured [Ca$_{0.5}$Co$_{0.5}$O$_{2.62}$ and other misfit layered cobaltites by the reactive-templated grain growth (RTGG) method using $\beta$-Co(OH)$_2$ as a reactive template. We already reported the small-scale synthesis of $\beta$-Co(OH)$_2$ platelets by a precipitation method.$^{16}$ However, a large-scale synthesis process of high-aspect ratio particles must be established for the fabrication of thermoelectric materials. In this study, we report the synthesis of $\beta$-Co(OH)$_2$ platelets in a large scale by precipitation and their hydrothermal growth.

2. Experimental procedures

Figure 1 gives the flow chart of the large-scale synthesis for $\beta$-Co(OH)$_2$ platelets. CoCl$_2$·6H$_2$O and NaOH were used as the starting materials and the synthesis of $\beta$-Co(OH)$_2$ platelets was carried out in a 50 dm$^3$ plastic container with nitrogen bubbling. The amount of NaOH introduced was 8% excess to the equivalent ratio for CoCl$_2$. As-prepared $\beta$-Co(OH)$_2$ was employed for the further growth under hydrothermal conditions in NaOH aqueous solution at 120°C for 24 h. The concentrations of NaOH and $\beta$-Co(OH)$_2$ were varied and the crystalline phases and morphologies of the grown particles were investigated.

The crystal structures were determined by powder X-ray diffraction (XRD) with a Cu target (Rigaku Rint2200). In particular, for determination of the face index of the basal planes of the particles, the orientation of the desired monolayer (OPML)-XRD$^{37}$ was employed. For this measurement, a few drops of 3 wt% gelatin aqueous solution containing 1 wt% sample powder were evenly spread over a glass plate and dried at room temperature. Morphology of the obtained powders was examined by scanning electron microscopy (SEM, Akashi Sigma-V) observation. The particle size analysis was performed using a laser scattering particle size distribution analyzer (Horiba, LA-910). Elemental analysis was conducted by inductively coupled plasma atomic emission spectrometry (ICP-AES; Shimadzu ICPS-2000).

3. Results and discussion

3.1 Synthesis of $\beta$-Co(OH)$_2$ plate-like crystallites

Upon the addition of NaOH solution, blue suspension was formed first, and then the suspension color changed from blue to bluish green, whitish blue and finally rose pink. XRD measurements (Fig. 2) revealed that after 2 h aging the precipitates contained both $\alpha$- and $\beta$-Co(OH)$_2$. Only $\beta$ phase remained after 8 h aging (Fig. 2b and Fig. 2c). SEM micrograph of the product after 2 h aging (Fig. 3A) displays roughly spherical particles, with a mean diameter of about 50 nm, gathered with
platelets with a size of about 500 nm in agglomerates, which with a size of about 2 μm. After 8 h aging, small amount of α-Co(OH)$_2$ remained (Fig. 3B), which was not detected by XRD. No significant change in particle size and thickness has been observed with further aging (Figs. 3C and 3D). The platelets obtained after 24 h aging show clean surface with a typical size of 0.5 × 0.1 μm (Fig. 3D).

We found only β-Co(OH)$_2$ phase, however, even only after 6 min aging for a small scale synthesis in the previous report. The detection of a phase in the present work is attributable to the slower α→β transformation in a large scale synthesis due to the possible non-uniformity in the solution. After 24 h aging, the precipitates became well-faceted hexagonal platelets. OPML-XRD (Fig. 4) measurement revealed that the basal plane is {001}, which implies the particles can be used as reactive templates for layered coaltalites with a CoO$_2$ sublattice layer. It should be noted that the large scale synthesis of β-Co(OH)$_2$ particles with a similar morphology to the small scale would be significantly important for the industrial fabrication of the textured coaltalite ceramics.

### 3.2 Hydrothermal Growth of β-Co(OH)$_2$

The β-Co(OH)$_2$ obtained after 24 h aging was employed for the growth studies. Experiments were firstly carried out by varying the concentration of β-Co(OH)$_2$ in 12 M NaOH at 120°C for 24 h. It has been found that for low β-Co(OH)$_2$ concentrations (0.1, 0.5, 1 M), impurity phases [Co$_2$O$_3$ and amorphous CoO(OH)$_2$] were presented in the product as shown by XRD, while for a β-Co(OH)$_2$ concentration of 2 M the product is pure phase. The second serial experiments were carried out by varying the concentration of NaOH from 2 to 12 M while the concentration of β-Co(OH)$_2$ was kept at 2 M. The products were pure phase β-Co(OH)$_2$, and in 12 M NaOH the obtained particles include the largest with the highest aspect ratio typically in ca. 9 × 0.5 μm. Therefore, the optimum condition for hydrothermal growth of β-Co(OH)$_2$
was determined as 2 M $\beta$-Co(OH)$_2$ in 12 M NaOH at 120°C for 24 h since single phase particles with a high aspect ratio are considered to be suitable as reactive templates.

**Figure 5** gives the SEM photos of the product grown under the optimum conditions. **Figure 6** shows the normal and OPN XRD patterns of the product. It can be seen that the basal plane of the grown $\beta$-Co(OH)$_2$ remains to be $\{001\}$. **Figure 7** shows the particle size distribution of the $\beta$-Co(OH)$_2$ platelets before and after hydrothermal growth measured by a laser scattering particle size distribution analyzer. The measured median radiuses were 0.49 μm and 8.96 μm, respectively; the crystals have been grown ca. 18 times larger. On the other hand, the aspect ratio increased ca. 4 times from 5 to nearly 20. The elemental analysis by ICP-AES showed that the product of 2 M $\beta$-Co(OH)$_2$ in 12 M NaOH contained only 0.026 wt% Na, and the Co content was 62.6 wt%, which means the purity of the grown $\beta$-Co(OH)$_2$ was ca. 99%.

4. Conclusions

Well-faceted hexagonal plate-like $\beta$-Co(OH)$_2$ was precipitated, through the transformation from $\alpha$-Co(OH)$_2$, by adding NaOH solution to CoCl$_2$ solution. The basal plane of the synthesized $\beta$-Co(OH)$_2$ platelets was $\{001\}$ as revealed by OPN–XRD. Hydrothermal growth of 2 M $\beta$-Co(OH)$_2$ in 12 M NaOH at 120°C for 24 h increased the size of platelets from 0.5 μm to 9 μm and the aspect ratio increased from 5 to nearly 20, while the basal plane remained the $\{001\}$. The high aspect ratio of the hydrothermally grown $\beta$-Co(OH)$_2$ must be suitable reactive template for layered cobaltite polycrystals with highly preferred $\{001\}$ orientation by RTGG method.

Acknowledgements

Authors would like to thank Mr. Naoyoshi Watanabe and Mr. Yuzo Kawai of Toyota CRDL for observation and chemical analysis of the powder specimens, respectively.

References