Synthesis of β -Co(OH)₂ Platelets by Precipitation and Hydrothermal Methods

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沈殿法及び水熱法による板状 β -Co(OH)₂ 結晶の合成

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Hexagonal β -Co(OH)₂ platelets with high crystallinity (0.3–10 μ m in average diameter and $\sim$ 5 in aspect ratio) have been synthesized. The platelets of 0.3–0.5 μ m in diameter were prepared by a precipitation method, and their sizes were affected by the cobalt ion concentration in the suspensions. Adding rate of precipitant, stirring rate of solution, and aging temperature gave little effect on their morphologies. The platelets with well developed facets were synthesized with high reproducibility, when chloride salt was used as a Co-source and the suspension was aged at room temperature for 86.4 ks. The platelets have been enlarged up to 5–10 μ m with maintaining morphology (hexagonal shape, $\sim$ 5 in aspect ratio) by hydrothermal treatment (at 393 K for 86.4 ks in 12 mol/dm³ NaOH aqueous solution).

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1. Introduction

Texture control of functional ceramics by the templated grain growth (TGG) and reactive TGG (RTGG) methods has received increasing attention for their capability to enhance bulk-material properties without using large single crystals.^{1)–5)} The preparation of anisometric template particles is one of the key technologies for the application of the processing methods to the fabrication of devices. Molten salt synthesis has been employed for the preparation of template materials or their precursors (eg. Bi₄Ti₃O₁₂, Sr₃Ti₂O₇, Ba₆Ti₁₇O₄₀, et al.) for the textured piezoelectric and dielectric oxide polycrystals.^{6)–10)} The precipitation method and the hydrothermal treatment would be less expensive techniques than the molten salt synthesis for the system because of the lower temperatures for crystal growth. Hirota et al. used α -Fe₂O₃ platelets, which had been prepared by the hydrothermal synthesis, for the fabrication of highly textured Mn–Zn ferrite ceramics for a magnetic head.¹¹⁾

Recently, authors have reported¹²⁾ that highly grain-oriented NaCo₂O₄ polycrystalline ceramic was prepared by the RTGG process using Co₃O₄ platelets as templates. Cobalt hydroxides (Co(OH)₂ and CoO(OH)) would also be useful materials as reactive templates (precursors) for the recently reported thermoelectric cobaltites such as NaCo₂O₄^{13),14)} and Ca₂Co₂O₅¹⁵⁾ because these hydroxides have hexagonal layered structures having lattice matching with cobaltite materials. The layered crystal structures of the complex cobalt oxides contribute to anisotropic thermoelectric properties,¹⁴⁾ so that the fabrication method of highly-textured ceramics would be a key technology in the mass-production of these materials for thermoelectric device applications.

Co(OH)₂ has been used for important applications, such as additives for alkaline batteries¹⁶⁾ and precursors for heterogeneous catalysts.¹⁷⁾ Most of the past works were limited in the prevention of oxidation of cobalt hydroxides for the improvement of battery performance.¹⁶⁾ Anisometric morphology and high crystallinity are both required for the template to be used in the RTGG process, because the process includes good alignment of template particles and *in-situ* topotaxial and/or epitaxial formation and growth of the product material. The control of both morphology and cry-

stallinity of Co(OH)₂ during the synthesis and growth, however, has not been fully established yet, especially in the point of use for a reactive template. In this study, Co(OH)₂ platelets were synthesized by precipitation and hydrothermal methods, and the morphology and crystallinity were examined.

2. Experimental

2.1 Effect of Co-source materials

Reagent-grade CoCl₂·6H₂O (99.99%, Kojundo Chemical Lab. Co., Ltd.), Co(NO₃)₂·6H₂O (99.99%, Kojundo Chemical Lab. Co., Ltd.), and NaOH (99.9%, Wako Pure Chemical Industries Ltd.) were used without further purification. Distilled water was used after outgassing by N₂ bubbling in order to prevent undesirable oxidation of precipitates due to dissolved oxygen.

An aqueous solution of NaOH (the precipitant, 0.20 mol/dm³) was added dropwise to aqueous solutions of CoCl₂·6H₂O and Co(NO₃)₂·6H₂O (0.10 mol/dm³). The suspensions (total amount: 0.90 dm³) were aged in a glass flask (1.00 dm³) at room temperature for 86.4 ks with N₂ bubbling. The precipitates were separated, washed with distilled water, and dried in N₂ flow.

The precipitates were characterized by powder X-ray diffraction (XRD, Model RINT2100, Rigaku Co.) and scanning electron microscopy (SEM, Model Sigma-V, Akashi Ltd.).

2.2 Observation of crystal growth during aging

An aqueous solution of NaOH (the precipitant, 0.20 mol/dm³) was added dropwise to an aqueous solution of CoCl₂·6H₂O (0.10 mol/dm³). The addition of the NaOH solution was completed in about 180 s. Then, the suspension (initial amount: 2.70 dm³) was aged in a glass flask (3.00 dm³) at room temperature with stirring at 160 rpm and N₂ bubbling. During aging, a part of the suspension (about 20 × 10^{−3} dm³) was sampled after given aging time (0.36, 1.8, 3.6, 10.8, 21.6 and 86.4 ks) and the precipitates in each suspension were separated.

Particle size distribution (PSD) was determined by a laser scattering particle size analyzer (Model LA910, Horiba Ltd.). The precipitates (about 100 mg) were dispersed into an aqueous solution (about 30 × 10^{−3} dm³) of so-

dium hexametaphosphate (0.1 mass%) for the measurement of size distribution.

2.3 Examination of precipitation conditions

An aqueous solution of NaOH (the precipitant, 0.20 or 0.05 mol/dm³) was added dropwise to an aqueous solution of CoCl₂·6H₂O (0.10 or 0.025 mol/dm³). Adding rate of NaOH solution and stirring rate of the suspension were varied from 0.083 to 0.25 × 10⁻³ dm³/s and from 40 to 320 rpm, respectively. The suspensions (total amount: 2.70 dm³) were aged in a glass flask (3.00 dm³) for 86.4 ks at room temperature or 323 K with N₂ bubbling. The precipitates were separated, washed with distilled water, and dried in N₂ flow.

2.4 Hydrothermal treatment

The powder specimen of Co(OH)₂ of 0.3 μm in diameter (about 0.5 g) prepared by the precipitation (starting solutions: 0.20 mol/dm³ NaOH and 0.10 mol/dm³ CoCl₂·6H₂O, aging conditions: room temperature, 160 rpm, 86.4 ks, N₂ bubbling) was dispersed into an aqueous solution of NaOH (12 mol/dm³, 50 × 10⁻³ dm³). The suspension was confined in a Teflon-lined autoclave (capacity 100 × 10⁻³ dm³) and heat-treated at 393 K for 86.4 ks. The autoclave was not equipped with a vent valve and thus a small amount of air was remained in the autoclave. The heat-treated specimen was separated, washed with distilled water, and dried in N₂ flow.

3. Results and discussion

3.1 Effect of Co-source materials

β-Co(OH)₂ platelets were obtained with high reproducibility by using CoCl₂·6H₂O as Co-source. Figure 1 gives an SEM micrograph of the prepared platelets having a hexagonal shape, an average diameter of ~0.3 μm, and an aspect ratio of ~5. The insufficient N₂ bubbling gave β-Co(OH)₂ with distorted facets and a small amount of Co₃O₄ phase detected. Sufficient N₂ bubbling was required for high crystallinity because β-Co(OH)₂ is readily oxidized by dissolved oxygen.

The use of Co(NO₃)₂·6H₂O as Co-source gave a low reproducibility of β-Co(OH)₂ and platelets of CoO(OH) and Co₃O₄ tended to form instead. The use of nitrate is considered to promote oxidation reaction in the suspension, so that it would lead to crystals composed of Co with a higher valence number, such as in CoO(OH) and Co₃O₄, rather than in β-Co(OH)₂. The precipitation environment (starting materials, species of existing ions, pH, atmosphere, existence of oxidizing agents) can affect the crystalline phase of resultant precipitates. Figure 2 gives SEM micrographs of CoO(OH) and Co₃O₄ platelets prepared typically from the

Fig. 1. SEM micrograph of β-Co(OH)₂ prepared by the precipitation method with the use of CoCl₂·6H₂O (0.10 mol/dm³) and NaOH (0.20 mol/dm³) as starting solutions.

suspensions using Co(NO₃)₂·6H₂O as Co-source, where the suspensions were aged for 259.2 ks at room temperature, stirred vigorously, without N₂ bubbling. CoO(OH) and Co₃O₄ are also candidate templates for highly textured thermoelectric cobaltite ceramics, however, crystallinity was low for the particles prepared in this study. Preparation conditions of β-Co(OH)₂ by using CoCl₂·6H₂O were examined in detail as described in the following sections.

3.2 Crystal growth in precipitation method

Table 1 summarizes the characteristics of the precipitates sampled after various aging time, which were prepared by using CoCl₂·6H₂O and NaOH solutions. Precipitates were formed right after the addition of the precipitant. Because of the extremely low solubility of Co(OH)₂ (solubility product: 3.16 × 10⁻¹⁵ mol³/dm⁹), it is considered that Co(OH)₂ was immediately and completely deposited by the addition of precipitant.

The suspension colored blue in the beginning (samples 1-1 and 1-2, aged for 0.36 and 1.8 ks), and then gradually changed its color to pink with aging time (1-3 to 1-6, aged

Fig. 2. SEM micrographs of (a) CoO(OH), and (b) Co₃O₄ prepared by using Co(NO₃)₂·6H₂O (0.10 mol/dm³) and NaOH (0.20 mol/dm³) as starting solutions.

Table 1. Characteristics of Precipitates Sampled after Different Aging Time

Sample name	Aging time /ks	Color of suspension	Characteristics of precipitates	
			Crystalline phase	Ave. particle size /μm
1-1	0.36	Vivid blue	β-Co(OH) ₂	32.1 *
1-2	1.8	Bluish purple	β-Co(OH) ₂	30.7 *
1-3	3.6	Purple	β-Co(OH) ₂	35.2 *
1-4	10.8	Pinkish purple	β-Co(OH) ₂	0.31
1-5	21.6	Pink	β-Co(OH) ₂	0.32
1-6	86.4	Pink	β-Co(OH) ₂	0.29

* Average size of agglomerated particles

Fig. 3. XRD patterns of precipitates sampled after different aging time: (a) 1-1 (0.36 ks), (b) 1-2 (1.8 ks), (c) 1-4 (10.8 ks), (d) 1-6 (86.4 ks). Starting solutions: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.10 mol/dm^3) and NaOH (0.20 mol/dm^3).

for 3.6 to 86.4 ks). All the precipitates, including sample 1-1 (aged for 3.6 ks), were identified as β -Co(OH)₂ (JCPDS No. 30-0443) by XRD (Fig. 3). Crystallinity of sample 1-1 was relatively low, which indicates the existence of small crystallites and/or amorphous phase. Diffraction peaks were sharpened with aging time up to 10.8 ks. However, the XRD patterns were similar for the samples aged for 10.8 to 86.4 ks. Figure 4 shows SEM micrographs of samples 1-1 and 1-2 (aged for 0.36 and 1.8 ks). The large-size samples were agglomerates of small crystals with undeveloped facets. On the other hand, sufficiently aged sample (1-6, aged for 86.4 ks), gave discrete hexagonal platelets with developed facets as shown in Fig. 1. Figure 5 gives PSD measurements of samples aged for 0.36, 1.8, 10.8, and 86.4 ks. Rather large agglomerates (10–100 μm in diameter) were detected for the samples of 1-1 and 1-2 (aged for 0.36 and 1.8 ks). The average size and the size distribution of the particles were similar for samples 1-4 and 1-6 (aged for 10.8 and 86.4 ks). Thus, the aging time of 86.4 ks was considered to be sufficient for the preparation of discrete platelets with developed facets.

In general, the size and the morphology of crystals depend on both the number of nucleus and the growth mechanism. The suspension would give the primary nuclei of β -Co(OH)₂ formed immediately because of the low solubility of β -Co(OH)₂. The XRD patterns of the precipitates indicate, however, that the suspension contained numerous amorphous crystallites at the early stage of precipitation. Thus, the nuclei of β -Co(OH)₂ grew gradually by means of solution-reprecipitation, where the amorphous crystallites were incorporated into the nuclei, and thus the facets of the crystals were developed. Furthermore, the ultimate sizes of the crystals were determined by the number of primary nucleus dependent on the early stage of precipitation in this system.

3.3 Effects of the precipitation conditions on β -Co(OH)₂ prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Table 2 summarizes the characteristics of precipitates

Fig. 4. SEM micrographs of β -Co(OH)₂ sampled after different aging time: (a) 1-1 (aging time: 0.36 ks), (b) 1-2 (1.8 ks). Starting solutions: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.10 mol/dm^3) and NaOH (0.20 mol/dm^3).

Fig. 5. Particle size distributions of precipitates sampled after different aging time. Starting solutions: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.10 mol/dm^3) and NaOH (0.20 mol/dm^3).

synthesized by using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH under various precipitation conditions. All the precipitate samples were identified as β -Co(OH)₂ by XRD.

Platelets with ~ 0.3 (sample 2-1) and $\sim 0.5 \mu\text{m}$ (2-2) in average diameter were prepared with high reproducibility. Figure 6 gives an SEM micrograph of sample 2-2. The micrograph of sample 2-1 was quite similar to the precipitates as shown in Fig. 1. The β -Co(OH)₂ were larger

Table 2. Preparation Conditions and Characteristics of Crystals Obtained in the Precipitation Method

Sample name	Precipitation conditions				Aging temperature ¹⁾ / K	Characteristics		
	CoCl ₂ ·6H ₂ O / mol·dm ⁻³	NaOH / mol·dm ⁻³	Adding rate of NaOH / 10 ⁻³ dm ³ ·s ⁻¹	Stirring rate / rpm		Crystalline phase	Ave. particle size / μm	Ave. aspect ratio
2-1	0.10	0.20	0.25	160	R.T.	β-Co(OH) ₂	0.3	5
2-2	0.025	0.025	0.25	160	R.T.	β-Co(OH) ₂	0.5	5
2-3	0.10	0.2	0.17	160	R.T.	β-Co(OH) ₂	0.3	5
2-4	0.10	0.2	0.083	160	R.T.	β-Co(OH) ₂	0.3	5
2-5	0.10	0.2	0.25	40	R.T.	β-Co(OH) ₂	0.3	5
2-6	0.10	0.2	0.25	320	R.T.	β-Co(OH) ₂	0.3	5
2-7	0.10	0.2	0.25	160	323	β-Co(OH) ₂	0.2	— ²⁾

1) Aging time: 86.4 ks, R.T.: room temperature

2) Not evaluated because the facets of the precipitates were rather obscure.

Fig. 6. SEM micrograph of β-Co(OH)₂ prepared by the precipitation method with the use of CoCl₂·6H₂O (0.025 mol/dm³) and NaOH (0.050 mol/dm³) as starting solutions. Fig. 7. SEM micrograph of β-Co(OH)₂ treated under hydrothermal conditions (at 393 K for 86.4 ks in 12 mol/dm³ NaOH aqueous solution).

(~0.5 μm) when prepared from the solution at lower cobalt ion concentration (0.025 mol/dm³). The increase in the particle size is attributable to the decreased number of β-Co(OH)₂ nucleus due to the low concentration of cobalt ion.

Adding rate of precipitant did not influence the appearance of crystals (samples 2-1, 2-3 and 2-4) although it is expected that the rate might control the primary nucleation and hence the crystal growth of β-Co(OH)₂. Stirring rate is well known to affect crystal growth in some cases, however, there appeared little influence on the size of β-Co(OH)₂ particles (samples 2-1, 2-5, and 2-6). Higher stirring rate and slower adding rate might improve uniformity of particle size, because one can expect that primary nucleation might occur more uniformly in these conditions. Higher aging temperature (sample 2-7, at 323 K) gave slightly diminished particles size and rather equiaxially shaped particles. Increasing temperature would be improper to prepare β-Co(OH)₂ platelets with developed facets.

All the precipitated platelets had similar aspect ratio, and {001} plane developed. In β-Co(OH)₂, the {001} plane is oxygen closed packed with the lowest surface energy, so that a crystal tends to grow with preferred {001} facets. The size and aspect ratio of the crystals were not varied in the range of precipitation conditions in this work.

3.4 Hydrothermal treatment of β-Co(OH)₂ platelets

Figure 7 gives an SEM micrograph of the particles (hexagonal shape, 5–10 μm in diameter, ~5 in aspect ratio) prepared by hydrothermal treatment (at 393 K for 86.4 ks in 12

mol/dm³ NaOH aqueous solution) of β-Co(OH)₂ (~0.3 μm in diameter, ~5 in aspect ratio). The XRD peaks of the prepared platelets were assigned for β-Co(OH)₂ as a dominant phase with a small amount of Co₃O₄. The latter phase was considered to be due to air contained in the autoclave. Since cobalt hydroxide partially dissolves into the dense basic solution, smaller crystals tend to dissolve and the growth of larger crystals is accelerated by solution-reprecipitation, which result in crystals (5–10 μm in diameter) were formed with maintained morphology (hexagonal shape, ~5 in aspect ratio).

Many small particles (less than ~0.3 μm) still remained under the conditions in this study. Optimized conditions (temperature, treating time, pH, and atmosphere, etc.) would produce β-Co(OH)₂ platelets with desired size and developed facets.

4. Conclusions

Hexagonal platelets of β-Co(OH)₂ were synthesized with high crystallinity by the precipitation and hydrothermal methods. In the precipitation method, the platelets with 0.3 and 0.5 μm in average diameter and ~5 in aspect ratio were prepared by changing the concentration of cobalt ion ranged from 0.10 to 0.025 mol/dm³. Adding rate of precipitant, stirring rate of the suspension, and aging temperature showed little influence. The platelets of β-Co(OH)₂ were synthesized with high reproducibility, when chloride salt was used as a Co-source, while the use of nitrate salt tended to give CoO(OH) and Co₃O₄ particles. Insufficient aging time gave

agglomerated precipitates with undeveloped facets, however, the aging time of 86.4 ks was sufficient for the preparation of discrete particles with developed facets. The sizes of β -Co(OH)₂ platelets were enlarged up to 5–10 μ m with maintained their morphology by hydrothermal treatment. The platelets obtained in this study are expected to be useful as reactive templates (precursors) for the fabricating of thermoelectric cobaltite materials, because of their high crystallinity and anisometry. The development of optimal templates for RTGG process is presently under investigations.

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