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# Solvothermal treatment of rare earth chloride hydrates

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## Abstract

The reaction of rare earth (RE) chloride hydrates in 1,4-butanediol (1,4-BG) at 300 °C in the presence of small amounts of *n*-hexylamine and 1,6-hexanediamine yielded phase-pure $RE(OH)_2Cl$ for La–Dy, but $RE(OH)_2Cl$ obtained from Ho to Yb and Y was contaminated with an unknown compound. The space group of $RE(OH)_2Cl$ formed by this reaction was $P2_1/m$ [No. 11]. Thermal analysis of the products in an air flow indicated that the $RE(OH)_2Cl$ phases for the RE elements other than Ce were dehydrated into REOCl, while $Ce(OH)_2Cl$ was decomposed at 350 °C yielding $CeO_2$ without formation of CeOCl. For the RE elements with smaller ionic size, REOCl was further decomposed into $RE_2O_3$ but REOCl with larger ionic size was not decomposed even after calcination at 1000 °C. The morphology of $RECl_3$ was altered by the solvothermal reaction, indicating that $RE(OH)_2Cl$ were formed via a dissolution–crystallization mechanism.

*Keywords:* Solvothermal reaction; Rare earth chloride hydrate; Rare earth chloride dihydroxide; 1,4-Butanediol; Glycothermal reaction

## 1. Introduction

Solvothermal methods have been widely studied for the synthesis of a variety of inorganic materials [1]. We found that various mixed oxides were directly crystallized when two suitable starting materials such as alkoxide, acetylacetonate, or acetate were allowed to react in 1,4-butanediol (1,4-BG) at 200–300 °C [2–4]. The use of 1,4-BG is, in the most cases, essential for formation of crystalline products under the glycothermal conditions [5].

In the solvothermal methods, use of chlorides as starting materials has been scarcely examined, because hydrochloric acid, generated during the reaction, is corrosive to metals. To avoid this phenomenon, the following methods are considered: (1) hydrolysis of the starting chloride, followed by solvothermal reaction of the thus-obtained hydroxide and (2) the solvothermal reaction in the presence of amines to neutralize the liberated acid. In the former method, the precursor hydroxide is gelatinous and it is difficult to control the water content in the gel. When hydroxide gel containing a large amount of water is allowed to react under the solvothemal conditions, essential nature of the reaction can be that of hydrothermal one.

In this paper, we examined the solvothermal reaction of rare earth (RE) chloride hydrates in the presence of an appropriate quantity of amine bases to neutralize the liberated acid. We clarified the crystalline structure of the products obtained by the reaction and the relationship between the crystalline structure and ionic size of RE element.

## 2. Experimental

RE chloride hydrates were purchased from Wako Pure Chemical Industry. Guaranteed 1,4-BG (nacalai tesque) was used without further purification.

Yttrium chloride hexahydrate (7.58 g, 25 mmol) was suspended in 100 ml of 1,4-BG in a test tube serving as autoclave liner and hexylamine (20 ml) and 1,6-hexanediamine (16 ml) were added to the tube (N/Cl ≈ 5). Hexylamine was added to neutralize the liberated acid in the gas phase and 1,6-hexanediamine, in the liquid phase. The tube was placed in a 300 ml autoclave. Additional 1,4-BG (30 ml)

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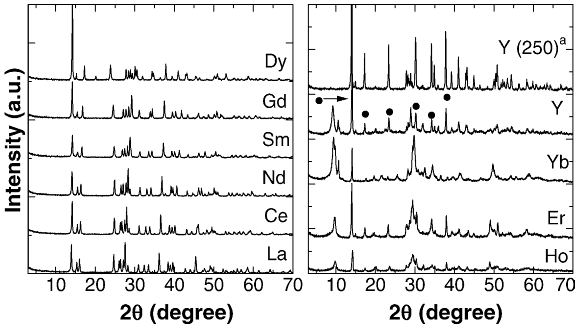

Fig. 1. XRD patterns of the products obtained by the reactions of rare earth chloride hydrates in 1,4-BG at 300 °C for 2 h: (a) product obtained at 250 °C for 2 h, (●) $Y(OH)_2Cl$.

and hexylamine (10 ml) were placed in the gap between the autoclave wall and the test tube. The autoclave was completely purged with nitrogen, heated to 300 °C at a rate of 2.3 °C/min, and kept at that temperature for 2 h. After the assembly was cooled to room temperature, the resulting product was collected by centrifuging. The product was washed with methanol and distilled water repeatedly by vigorous mixing and centrifuging, and then air-dried.

X-ray powder diffraction (XRD: Model XD-D1 Shimadzu, Kyoto, Japan) was recorded using Cu Kα radiation and a carbon monochromator. For Rietveld analysis, the XRD pattern was measured on another diffractometer (Model Rint 2500, Rigaku, Tokyo, Japan) and analysed by RIETAN-2000 program [6].

Diffuse reflectance FT-IR spectra of the products were recorded in the range 4000–700 $cm^{-1}$ on a Nicolet spectrophotometer (Model Magna-IR 560, Madison, USA) and the background spectrum employed was that of KBr.

Simultaneous thermogravimetric and differential thermal analyses were performed on a thermal analyser (Model DTG-50, Shimadzu, Kyoto, Japan) at a rate of 5 °C/min in a 40 ml/min flow of dried air.

The morphology of the products was observed with a scanning electron microscope (SEM), Hitachi S-2500CX.

## 3. Results and discussion

### 3.1. XRD patterns and IR spectra of the products

The XRD patterns of the products obtained by the reaction in 1,4-BG at 300 °C are shown in Fig. 1. Two types of products were detected, one for La–Dy (Group A) and the other for Ho–Yb and Y (Group B). The XRD pattern of the product obtained from lanthanum chloride hydrate essentially agreed with that reported for $La(OH)_2Cl$ (JCPDS: No. 85-0839) [7] albeit with large difference in the relative intensities. In the XRD pattern of the product from yttrium chloride hydrate (Fig. 1), the peaks specified by closed circles are attributed to $Y(OH)_2Cl$ (JCPDS: No. 19-1445) [8] but the other peaks could not be identified from JCPDS cards. However, when the reaction of yttrium chloride hydrate was carried out at 250 °C, only $Y(OH)_2Cl$ was formed without the contamination of the unknown phase. Therefore, the reaction of $RECl_3$ with smaller ionic size yielded a mixture of $RE(OH)_2Cl$ and an unknown compound, and the latter compound seems to be derived from $RE(OH)_2Cl$.

Rietveld refinement was carried out to identify the crystal structure of $La(OH)_2Cl$. $La(OH)_2Cl$ could not be refined with the space group, $P2/m$ [No. 10], as the JCPDS card noted, but had a space group of $P2_1/m$ [No. 11] (Fig. 2). The products from Nd, Gd, Sm and Dy chloride hydrates could also be refined with the same space group.

IR spectra of the products are shown in Fig. 3. Both the spectra of the products did not show characteristic bands due to the organic residue, but showed two sharp bands around 3600 $cm^{-1}$ due to the stretching vibration modes of structural OH groups. Klevstov et al. reported that the interaction between OH group and Cl in hydroxychloride contributed to these peaks [9]. A broad band at around 3400 $cm^{-1}$ observed

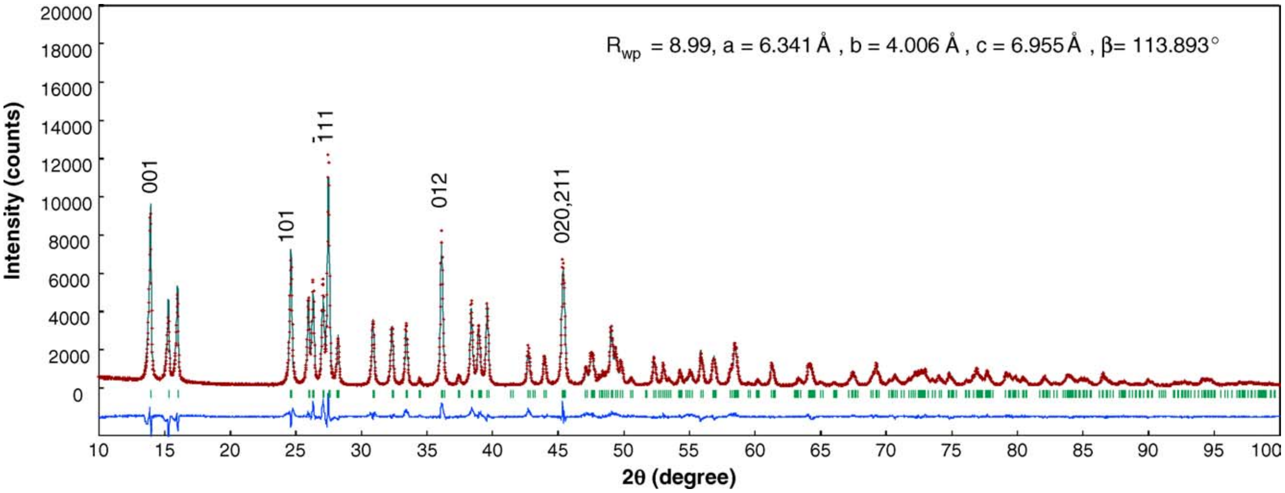

Fig. 2. Examined and simulated XRD patterns of $La(OH)_2Cl$.

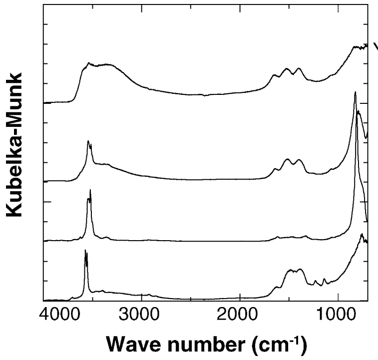

Fig. 3. IR spectra of the products obtained by the reactions of rare earth chloride hydrates in 1,4-BG at 300 °C for 2 h.

in Group B products seems to be due to the water molecules, suggesting that the unknown phase in Group B products contained a larger amount of structural water molecules. The IR spectra of Group B products also indicate the presence of the $RE(OH)_2Cl$ phase in the products.

### 3.2. Thermal decomposition behaviour

The TG-DTA data are summarized in Table 1 and typical profiles are shown in Fig. 4. For Group A products, a very sharp endothermic peak was observed at around 350 °C and the weight loss at this temperature range agreed with the theoretical weight loss from $RE(OH)_2Cl$ to REOCl. The XRD patterns of the products just after the weight loss were identified as REOCl (tetragonal). However, $Ce(OH)_2Cl$ was decomposed at 350 °C yielding $CeO_2$ without formation of CeOCl.

For Group B products, the weight loss was observed at <250 °C and XRD pattern of the product calcined at 200 °C was different from that of the as-synthesized product (Fig. 5), indicating that the water molecules are incorporated in the crystal structure of the unknown product. Therefore, it was tentatively assigned as $RE_2O_3{\cdot}xH_2O$ with an unidentified crystal structure. The weight loss at the temperature range from 250 to 450 °C was smaller than the theoretical weight

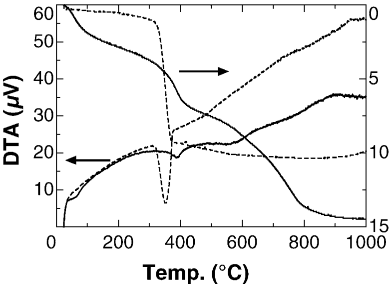

Fig. 4. TG-DTA profiles of the products: (· · ·) La and (—) Yb.

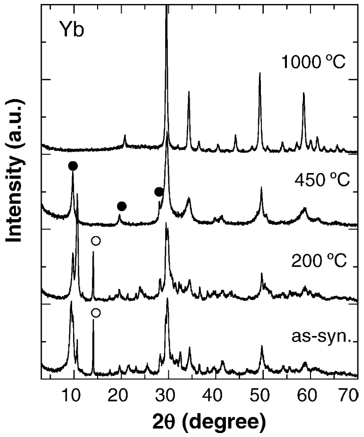

Fig. 5. XRD patterns of the product obtained from $YbCl_3{\cdot}6H_2O$ and samples obtained by calcination thereof at the temperature specified in the figure for 30 min: (●) h-YbOCl and (○) $Yb(OH)_2Cl$.

Table 1
Thermal analysis of the products

| Solvothermal product | Endotherm (°C) | Weight loss[a] (%) | $RE(OH)_2Cl$ content[b] (%) | Phase after calcination at 400–450 °C[c] | Weight loss[d] (%) | Phase after calcination at 1000 °C[c,e] |
|---|---|---|---|---|---|---|
| $La(OH)_2Cl$ | 370 | 8.4 (8.6)[f] | – | t-LaOCl | 0.3 | $LaOCl + La_2O_3$ (LaOCl) |
| $Ce(OH)_2Cl$ | – | 15 (8.6) | – | $CeO_2$ | 2.5 | $CeO_2$ |
| $Nd(OH)_2Cl$ | 346 | 8.5 (8.4) | – | t-NdOCl | 1.6 | $NdOCl + Nd_2O_3$ (NdOCl) |
| $Sm(OH)_2Cl$ | 356 | 8.1 (8.2) | – | t-SmOCl | 2.2 | $Sm_2O_3$ ($SmOCl + Sm_2O_3$) |
| $Gd(OH)_2Cl$ | 387 | 8.0 (7.9) | – | t-GdOCl | 6.2 | $Gd_2O_3$ ($GdOCl + Gd_2O_3$) |
| $Dy(OH)_2Cl$ | 378 | 8.1 (7.8) | – | t-DyOCl | 9.6 | $Dy_2O_3$ ($Dy_2O_3$) |
| $Ho(OH)_2Cl$ + UKW[g] | 387 | 6.1 (7.7) | 79 | $Ho_2O_3$ + h-HoOCl | 9.7 | $Ho_2O_3$ |
| $Er(OH)_2Cl$ + UKW | 380 | 6.6 (7.6) | 87 | $Er_2O_3$ + h-ErOCl | 10.1 | $Er_2O_3$ |
| $Yb(OH)_2Cl$ + UKW | 389 | 3.9 (7.4) | 53 | $Yb_2O_3$ + h-YbOCl | 7.4 | $Yb_2O_3$ |
| $Y(OH)_2Cl$ + UKW | 392 | 10.2 (11.4) | 89 | $Y_2O_3$ + h-YOCl | 15 | $Y_2O_3$ |

[a] Weight loss at the temperature range of 250–450 °C.
[b] Estimated from the weight loss between 250 and 450 °C.
[c] Phase identified by XRD pattern.
[d] Weight loss at the temperature range of 450–1000 °C.
[e] Phase identified after calcination of the product at 1000 °C for 30 min; the phases detected in the sample quenched just after the temperature reached 1000 °C are shown in parenthesis.
[f] Theoretical weight loss due to formation of REOCl from $RE(OH)_2Cl$.
[g] Unknown product, tentatively assigned as $RE_2O_3{\cdot}xH_2O$ having an unidentified crystal structure.

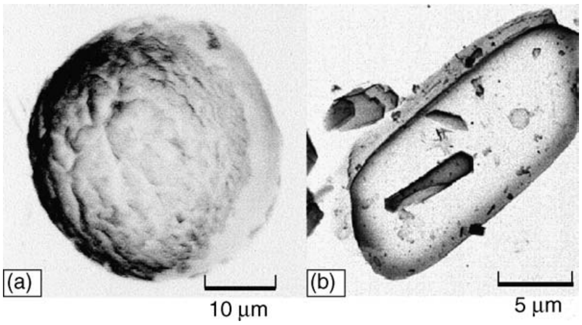

Fig. 6. SEM images of: (a) $YCl_3$ (dried at 250 °C) and (b) $Y(OH)_2Cl$ obtained in 1,4-BG at 250 °C.

loss due to dehydration of $RE(OH)_2Cl$ to REOCl because of the contamination of the unknown compound. The contents of $RE(OH)_2Cl$ in Group B products were estimated from the weight loss, and the results (Table 1) indicate that $RE(OH)_2Cl$ was the predominant phase in Group B products. The XRD pattern of the product just after the weight loss was identified as a mixture of REOCl (hexagonal) and $RE_2O_3$. This result is in accord with the previous assignment of the unknown product as $RE_2O_3{\cdot}xH_2O$, since all of the REOOH phases are known to be dehydrated into $RE_2O_3$ at the temperatures below 500 °C.

It was reported that REOCl with larger RE elements (La–Ho) exists in the tetragonal structure while REOCl with smaller RE elements (Tm–Lu) has the hexagonal structure, erbium being the crossover point [10,11]. In the present work, however, hexagonal HoOCl and YOCl were formed (Table 1), in spite of the fact that the hexagonal polymorph is thermodynamically unstable for Ho and Y.

Regardless of Groups A and B, moderate weight loss was observed at 450–1000 °C for the elements with smaller ionic size (<Gd), and REOCl was further decomposed into $RE_2O_3$. REOCl with larger ionic size was stable up to 1000 °C; however, it slowly decomposed at 1000 °C and small amounts of $RE_2O_3$ were detected when the products were calcined at 1000 °C for 30 min. Sokolova et al. [10] examined the thermal decomposition behavior of lanthanide chloride hydrates and reported that the temperature for the formation of REOCl had a tendency to decrease with the decrease in ionic size of RE element. They also reported that thermal stability of REOCl decreased in the same direction. These reported results suggest that chloride ions in the coordination sites of RE elements with smaller ionic size are more easily substituted with oxide anion. The present results are consistent with this tendency.

### 3.3. Reaction mechanism

Forced hydrolysis (180 °C, 120 h) of lanthanide chloride hydrate (6 mmol) in water (25 ml) was also examined using an autoclave made of Teflon. No precipitates were formed, and pH of the solution was not varied by the reaction, indicating that hydrolysis of lanthanide chloride scarcely occurred at low temperatures. The morphology of the $Y(OH)_2Cl$ particles obtained by solvothermal reaction at 250 °C was completely altered from that of the starting material (Fig. 6), indicating that $RE(OH)_2Cl$ were formed via a dissolution–crystallization mechanism; that is, rare earth chlorides were dissolved into the solvent and reacted with water originated from the crystallization water of the starting materials as depicted in the following equation:

$$RECl_3 + 2H_2O \rightarrow RE(OH)_2Cl + 2HCl.$$

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