Synthesis of Needle-shaped Rare Earth Oxide by Solvothermal Treatment of Rare Earth Chloride

Saburo Hosokawa, Shinji Iwamoto, Masashi Inoue*
Graduate School of Engineering, Kyoto University, Kyoto, 615-8510, JAPAN,
inoue@scl.kyoto-u.ac.jp

Summary

The reaction of rare earth (RE) chloride hydrates (Y, Er and Yb) in 1,4-butanediol (1,4-BG) at 300 °C for 2 h gave mixtures of RE(OH)₂Cl and RE₂O₃\(\cdot\)xH₂O, and the products were composed of irregularly-shaped particles. The prolonged reaction (10 h) also yielded a mixture of RE(OH)₂Cl and RE₂O₃\(\cdot\)xH₂O for Er or Y, but phase-pure RE₂O₃\(\cdot\)xH₂O was obtained for Yb. The latter product was comprised of needle-shaped single crystals with 0.2–0.6 µm width and 5–15 µm length. The reaction in toluene at 300 °C for 2 h yielded phase-pure Yb₂O₃\(\cdot\)xH₂O and SEM image of the product showed the formation of irregularly-shaped particles. By the prolonged reaction time (6 h), the morphology of Yb₂O₃\(\cdot\)xH₂O changed, and needle-shaped single crystals with 80–190 nm width and 0.5–1.0 µm length were obtained, which were much smaller than those obtained in 1,4-BG. The Yb₂O₃\(\cdot\)xH₂O phase decomposed to Yb₂O₃ at 350–500 °C, preserving the needle-shaped morphology, which was maintained even after calcination at 800 °C. Single crystals of Yb₂O₃ obtained by calcination of Yb₂O₃\(\cdot\)xH₂O at 500 °C had very small voids and the voids were enlarged to 35 Å in diameter by calcination at 800 °C.

1. Introduction

One dimensional crystals such as carbon nanotubes have unique physical and chemical properties and have been proposed for a wide range of application (Liu et al., 1999). Rare earth compounds have been used in high performance luminescent devices, magnets, catalysts and so on (Adachi et al., 1998; Hosokawa et al., 2003). It have been reported that rare earth oxides with one dimensional crystals are prepared by the means of template, sol-gel and hydrothermal methods, etc (Fang et al., 2003; Cao, 2004; Murata et al., 2004; Yada et al., 2002; Wu et al., 2004).

We have been exploring the synthesis of inorganic materials in organic media at elevated temperatures and have found that various mixed oxides are 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 (Inoue et al., 1989–2004). The use of 1,4-BG is, in the most cases, essential for formation of crystalline products under the glycothermal conditions (Inoue, 2004).

In the solvothermal methods, the use of chlorides as the 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. (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 solvothermal conditions, essential nature of the reaction can be that of hydrothermal one. Recently, we found that the reaction of rare earth (RE) chloride hydrates in 1,4-butanediol (1,4-BG) at 300 °C for 2 h in the presence of small amounts of n-hexylamine and 1,6-hexanediamine yielded phase-pure RE(OH)₂Cl for La–Dy, but the product obtained from Ho–Yb and Y was a mixture of RE₂O₃\(\cdot\)xH₂O and RE(OH)₂Cl (Hosokawa et al., 2005).

In this work, the morphology of the products obtained by the solvothermal reaction of RE chlorides in the presence of amines was investigated.
2. Experimental Method

2.1 Solvothermal treatment

RE chloride hydrates were purchased from Wako Pure Chemical Industry. Yttrium chloride hexahydrate (9.45 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-hexanediame (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-hexanadiamine, in the liquid phase. The tube was placed in a 300-ml autoclave. Additional 30 ml of 1,4-BG and 10 ml of hexylamine 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 the prescribed time. After the assembly was cooled to room temperature, the resulting product was collected by centrifugation. The product was washed with methanol and distilled water repeatedly by vigorous mixing and centrifuging, and then air-dried.

2.2 Characterization

X-ray powder diffraction (XRD: Model XD-D1, Shimadzu, Japan) was recorded using CuKα radiation and a carbon monochromator. Simultaneous thermogravimetric and differential thermal analyses were performed on a thermal analyser (Model DTG-50, Shimadzu, 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, or a transmission electron microscope (TEM), Hitachi H-800, operated at 200 kV. Nitrogen adsorption isotherm was measured using a volumetric gas-sorption system (Model Autosorb-1, Quantachrome, USA).

3. Results and discussion

3.1 The structure and morphology of the as-synthesized products

The XRD patterns of the as-synthesized products obtained by the reaction of RE chloride hydrates (Y, Er and Yb) in 1,4-BG at 300 °C for 2 or 10 h are shown in Fig. 1. The phases of RE(OH)₂Cl and RE₂O₃·xH₂O were detected in the products obtained by the reaction for 2 h (Hosokawa et al., 2005). For Er and Y, mixtures of RE(OH)₂Cl and RE₂O₃·xH₂O were obtained by the prolonged reaction (10 h), but phase-pure RE₂O₃·xH₂O was obtained for Yb. The XRD patterns of the products obtained by the reaction in toluene are shown in Fig. 2. Irrespective of reaction time, Y(OH)₂Cl, the mixture of Er(OH)₂Cl and Er₂O₃·xH₂O, and Yb₂O₃·xH₂O were obtained from the corresponding RE chloride hydrates and the ratio of the two phases was not changed by the reaction time.

![Fig. 1 XRD patterns of the as-synthesized products obtained by the reaction of RE (Y, Er and Yb) chloride hydrates in 1,4-BG at 300 °C for 2 or 10 h.](image-url)
Fig. 2 XRD patterns of the as-synthesized products obtained by the reaction of RE (Y, Er and Yb) chloride hydrates in toluene at 300 °C for 2 or 6 h.

The SEM images of the products obtained by the reaction in 1,4-BG for 2 h showed the formation of irregularly-shaped particles (Fig. 3). By the prolonged reaction time, morphology of the products for Y or Er was partly changed and needle-shaped crystals were formed; however, major products were irregularly-shaped. On the other hand, the Yb₂O₃•xH₂O product obtained with prolonged reaction time (10 h) was composed of needle-shaped crystals with 0.2–0.6 µm width and 5–15 µm length.

The SEM images of the Y and Er products obtained in toluene showed irregularly-shaped crystals irrespective of the reaction time (Fig. 4). Although the Yb₂O₃•xH₂O phase obtained in toluene for 2 h consisted of irregularly-shaped crystals, prolonged reaction time (6 h) changed the morphology; needles with 80–190 nm width and 0.5–1.0 µm length were obtained, which were much smaller than those obtained in 1,4-BG.

Fig. 3 SEM images of the as-synthesized products obtained by the reaction of hydrated chlorides of: a and d, Y; b and e, Er; c and f, Yb; in 1,4-BG at 300 °C for: a, b, and c, 2 h; d, e, and f, 10 h.
Fig. 4 SEM images of the as-synthesized products obtained by the reaction of hydrated chlorides of: a and c, Er; b and d Yb; in toluene at 300 °C for: a and b, 2 h; b and d, 6 h.

These results indicate that RE(OH)₂Cl formed by the solvothermal reaction is composed of irregularly-shaped large crystals, while prolonged reaction yielded needle-shaped crystals of Yb₂O₃•xH₂O.

Forced hydrolysis (180 °C, 120 h) of RE chloride hydrate (6 mmol) in water (25 ml) was also examined using an autoclave made of teflon. No precipitates were formed, nor was pH of the solution varied by the reaction, indicating that hydrolysis of rare earth chloride scarcely occurred at low temperatures.

The morphology of the RE(OH)₂Cl and RE₂O₃•xH₂O particles obtained by solvothermal reaction was completely altered from that of the starting material, indicating that RE(OH)₂Cl and RE₂O₃•xH₂O are formed via a dissolution-crystallization mechanism, RE chloride dissolving into a mixture of the organic solvents (1,4-BG or toluene) and water originated from the crystallization water of the starting materials.

\[
\text{RECl}_3 + 2\text{H}_2\text{O} \rightarrow \text{RE(OH)}_2\text{Cl} + 2\text{HCl}
\]

\[
2\text{RECl}_3 + a\text{H}_2\text{O} \rightarrow \text{RE}_2\text{O}_3•(a-3)\text{H}_2\text{O} + 6\text{HCl}\ (a \geq 3)
\]

3.2 Thermal decomposition of needle-shaped crystals of Yb₂O₃•xH₂O

The thermal decomposition behaviour was investigated by TG-DTA and XRD measurement of the samples calcined at various temperatures. The TG-DTA of needle-shaped crystals of Yb₂O₃•xH₂O obtained in 1,4-BG exhibited a weight loss at 350–500 °C associated with an endothermic peak, and another weight loss was also observed at around 700 °C (Fig. 5). The XRD patterns of the sample calcined at 500 °C indicated the formation of Yb₂O₃ (Fig. 6), suggesting that the weight loss observed at 350–500 °C is due to dehydration of crystallization water in Yb₂O₃•xH₂O. Since the weight decrease at around 700 °C was not accompanied by the change in the XRD pattern, the exhaust gas generated during calcination was analyzed as follows; Yb₂O₃•xH₂O was heated in a 20 % O₂/He flow at a rate of 10 °C/min and the exhaust gas was bubbled in a 0.1N-AgNO₃ solution. The clear solution of AgNO₃ was turned turbid at 800 °C. Therefore, the weight loss at around 700 °C is attributed to the desorption of chloride species from Yb₂O₃ surface.

Fig. 5 TG-DTA of needle-shaped crystals of Yb₂O₃•xH₂O obtained in 1,4-BG or toluene.
The TG-DTA behaviour of Yb₂O₃•xH₂O obtained in toluene was essentially identical with that of the sample obtained in 1,4-BG. However, the endothermic peak was sharper than that observed in the 1,4-BG product (Fig. 5). In addition, the XRD pattern of the sample calcined at 500 °C showed that a small amount of YbOCl was also formed besides predominantly formed Yb₂O₃ (Fig. 6). This result indicates that the product obtained by the reaction in toluene for 6 h was also contaminated with Yb(OH)₂Cl, although the XRD pattern did not show the peak due to this phase. The XRD pattern of the sample calcined at 800 °C showed that the byproduct (Yb(OH)₂Cl) was decomposed to Yb₂O₃.

Fig. 6. XRD patterns of needle-shaped crystals of Yb₂O₃•xH₂O and samples obtained by calcination thereof at the temperature specified in the figure for 30 min. a) Crystallite size (nm) calculated from the peak width is given in parenthesis.

Fig. 7. SEM (a, b, c) and TEM (d, e, f) images of: a and d, the as-synthesized Yb₂O₃•xH₂O crystals obtained by the reaction of YbCl₃•6H₂O in 1,4-BG at 300 °C for 10 h; and samples obtained by calcination thereof at: b and e, 500 °C; c and f, 800 °C.
Fig. 8. SEM (a, b, c) and TEM (d, e, f) images of: a and d, the as-synthesized Yb$_2$O$_3$•xH$_2$O crystals obtained by the reaction of YbCl$_3$•6H$_2$O in toluene at 300 ºC for 6 h; and samples obtained by calcination thereof at: b and e, 500 ºC; c and f, 800 ºC.

The SEM images of the samples calcined at various temperatures revealed that the needle shape of the crystals was maintained even after calcination at 800 ºC (Figs. 7 and 8). The TEM images of the samples (Figs. 7 and 8) showed that the as-synthesized products obtained in both 1,4-BG and toluene were rod-shaped. The selected area electron-diffraction (SAED) clearly revealed that each needle particle of Yb$_2$O$_3$•xH$_2$O is a single crystal. The contrast of the TEM image of the sample calcined at 500 ºC indicated that the needle-shaped crystals had the very small voids and that calcination at 800 ºC enlarged the voids. These voids seems to be formed by dehydration of Yb$_2$O$_3$•xH$_2$O and were enlarged by calcination at the higher temperatures. It is interesting to note that the SAED analysis clearly showed that the single-crystalline nature of the needle-shaped particle was preserved even after transformation into Yb$_2$O$_3$. This result can be explained by topotactic transformation from Yb$_2$O$_3$•xH$_2$O into Yb$_2$O$_3$ aligning the orientation of crystallites of Yb$_2$O$_3$ in exactly same direction.

The voids in the calcined samples were assessed by the N$_2$ adsorption technique (Fig. 9). Pore-size distribution calculated by the BJH method from the desorption branch of the N$_2$ adsorption isotherm indicated the presence of pores with a diameter of 35 Å in the sample calcined at 800 ºC. However, the voids in the sample calcined at 500 ºC were not detected. For the needle-shaped crystals obtained in 1,4-BG, the BET surface areas were 3 and 12 m$^2$/g for the samples calcined at 500 and 800 ºC, respectively. For the product obtained in toluene, the surface areas were 11 and 16 m$^2$/g after calcination at 500 and 800 ºC, respectively. Enlargement of BET surface area suggests that an intraparticle pore system was formed by the calcination at 800 ºC.

The pore volume at higher diameter (> 10$^2$ Å) can be attributed to the space between the needle-shaped particles, and the distribution curve was scarcely altered by the calcination at 800 ºC. This result accords with that obtained by SEM observation; that is, morphology of the particles was not altered by calcination. Since the dimension of the needle-shaped particles was not altered by calcination, the Yb$_2$O$_3$ particles obtained by calcination at 500 ºC must have voids. Since these voids were not detected by the N$_2$ adsorption method, they were closed voids or smaller than the molecular dimension of N$_2$. Therefore, calcination of the product at higher temperature enlarged the crystallite size of Yb$_2$O$_3$ (Fig. 6), which was accompanied by enlargement of intraparticle pores.
Fig. 9. Pore-size distribution calculated by the BJH method from the desorption branch of N₂ adsorption isotherm of the samples obtained by calcination of Yb₂O₃•xH₂O at: a and c, 500 °C; b and d, 800 °C; which was obtained by the reaction in 1,4-BG (a and b) or toluene (c and d) at 300 °C.

4. Conclusion

RE(OH)₂Cl formed by the solvothermal reaction was composed of irregularly-shaped large crystals, while prolonged reaction yielded needle-shaped crystals of Yb₂O₃•xH₂O. These products were formed via a dissolution-crystallization mechanism, RE chloride dissolving into a mixture of the organic solvents (1,4-BG or toluene) and water originated from the crystallization water of the starting materials. The particles of Yb₂O₃•xH₂O (80–190 nm width and 0.5–1.0 µm length) obtained by the reaction in toluene at 300 °C for 6 h were much smaller than those (0.2–0.6 µm width and 5–15 µm length) obtained by the reaction in 1,4-BG for 10 h. The needle-shaped Yb₂O₃•xH₂O was decomposed to Yb₂O₃ at 350–500 °C and the chloride species remaining on the Yb₂O₃ particles were desorbed at 700–800 °C. The needle shape of the Yb₂O₃•xH₂O crystals was maintained even after calcination at 800 °C. The SAED analysis clearly showed that the single-crystalline nature of the needle-shaped particle was preserved even after transformation into Yb₂O₃. The needle-shaped Yb₂O₃ obtained by calcination of Yb₂O₃•xH₂O at 500 °C had very small voids and they were closed voids or smaller than the molecular dimension of N₂. Calcination of the product at higher temperatures enlarged the crystallite size of Yb₂O₃, which was accompanied by enlargement of intraparticle pores.

References


