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Hydrothermal Preparation of Some Rare Earth Trihydroxides and Some Rare Earth Oxide Hydroxides at Temperatures up to 900°C and Pressures up to 55 kb

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Hydrothermal methods have been used in the preparation of some rare earth trihydroxides and rare earth oxide hydroxides using pressure bombs, lined with pure silver or pure gold, at temperatures up to 500°C and pressures up to 700 atm.[1-6] It has, however, been reported, that compounds containing hydroxyl groups can be prepared at higher temperatures and pressures. In an investigation by Wilhelmi [7] of the system MoO_3–MoO_2 at 25 kb using a girdle high-pressure apparatus,[8] a partial transformation of MoO_3 to $Mo_4O_{10}(OH)_2$ was observed. It was assumed that the hydrogen necessary for the reduction of MoO_3 came from pyrophyllite, which can give off hydrogen in the temperature interval 600–1000°C.[7] In an investigation by Waintal [9] of the system Fe_2O_3–In_2O_3 at 110 kb and 1200°C using a high-pressure belt apparatus, indium oxide hydroxide was obtained. An investigation was undertaken to prepare rare earth hydroxide phases using temperatures over 500°C and pressures of 50–55 kb, in order to obtain hydroxide phases with densities greater than the densities of the known rare earth trihydroxides and rare earth oxide hydroxides.

Holmium oxide hydroxide, HoOOH, prepared according to Ref. 1, was treated in a belt high-pressure apparatus at 50 kb and 800°C for 1 h. The apparatus has been described by Waintal.[9] The X-ray powder pattern of the crystalline product, taken with a Guinier camera, using $FeK\alpha_1$ radiation, indicated a complete transformation of the monoclinic holmium oxide hydroxide to a new phase. All lines of the powder pattern were indexed on the basis of a tetragonal unit cell with the cell parameters given in Table 1. The new phase was assumed to be a tetragonal modification of holmium oxide hydroxide. The change in volume by the transformation from the monoclinic to the tetragonal modification is −6 %.

Table 1. Unit cell parameters for the tetragonal modification of some rare earth oxide hydroxides using $FeK\alpha_1 = 1.93597$ Å. Standard deviations in parantheses.

MOOH	*a* (Å)	*c* (Å)
Dy	5.57(3)	5.446(9)
Ho	5.541(6)	5.410(2)
Er	5.517(4)	5.383(1)
Tm	5.507(4)	5.364(1)
Yb	5.48(2)	5.326(4)

The high-pressure belt apparatus has been used in the hydrothermal preparation of some rare earth trihydroxides and the tetragonal modification of some rare earth oxide hydroxides at the experimental conditions given in Table 2. The starting materials were wetted with a 50 % solution of NaOH in water, and were kept in platinum ampoules, with a volume of 26 mm³. The crystalline products were in some

Table 2. Experimental conditions for hydrothermal preparations. Reaction time: 1 h.

Starting material	Pressure kb	Temp. °C	Product [a]
$Nd(OH)_3$	55	700	$Nd(OH)_3$
Sm_2O_3	55	700	$Sm(OH)_3$
Eu_2O_3	55	700	$Eu(OH)_3$
Gd_2O_3	55	700	$Gd(OH)_3$
Dy_2O_3	55	700	$Dy(OH)_3$ DyOOH
Ho_2O_3	55	900	$Ho(OH)_3$ HoOOH
Er_2O_3	55	700	ErOOH
Tm_2O_3	50	800	TmOOH
Yb_2O_3	55	700	YbOOH

[a] All trihydroxides are the usual known modification and all oxide hydroxides are the new tetragonal modification.

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