

## HoF(OH)<sub>2</sub>: A fluoride-containing holmium(III) hydroxide with UCl<sub>3</sub>-type crystal structure

F. C. Goerigk and Th. Schleid

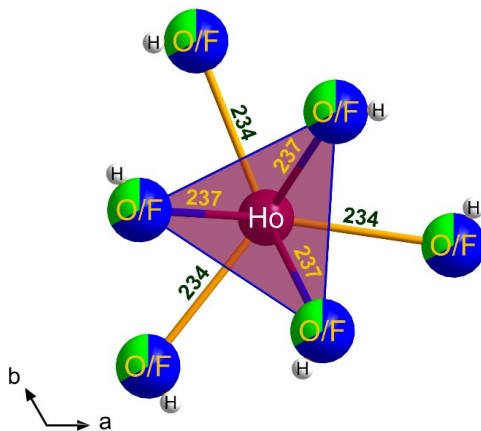
University of Stuttgart, Institute for Inorganic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

schleid@iac.uni-stuttgart.de

Rod-shaped single crystals of HoF(OH)<sub>2</sub> could be synthesized from Ho<sub>2</sub>O<sub>3</sub> and HoF<sub>3</sub> using a high-pressure hydrothermal synthesis route in order to obtain crystalline holmium fluoride oxide (HoFO). The reaction was performed in a gold capsule filled with the starting materials and about 15 vol-% of demineralized water to provide suitable conditions. The gold capsule was sealed by cold-welding and placed into a rock-salt pressure cell. Using an end-loaded piston-cylinder high-pressure apparatus deriving from the *Boyd* and *England* design, the cell pressure was dwelled on 500 °C at 10.5 kbar for five days [1]. After quenching to room temperature, small pale-yellow crystals were isolated and investigated using single-crystal X-ray diffractometry. The hexagonal unit cell of the measured crystals showed a noticeable deviation regarding the detected axes and density, when compared to UCl<sub>3</sub>-type Ho(OH)<sub>3</sub> ( $a \approx 626.6$  pm,  $c \approx 355.3$  pm,  $\rho_X = 5.94$  g/cm<sup>3</sup> [2]; our results for HoF(OH)<sub>2</sub>:  $a \approx 603.3$  pm,  $c \approx 356.8$  pm,  $\rho_X = 6.44$  g/cm<sup>3</sup>). Therefore, it was concluded that a mixed F<sup>-</sup>/OH<sup>-</sup> anion site is present, leading to the composition HoF(OH)<sub>2</sub>. The F<sup>-</sup>-to-OH<sup>-</sup> ratio of 1:2 is plausible, when the molar volumes of UCl<sub>3</sub>-type Ho(OH)<sub>3</sub> ( $V_m = 36.38$  cm<sup>3</sup>/mol) [2] and HoF(OH)<sub>2</sub> ( $V_m = 33.86$  cm<sup>3</sup>/mol) are compared with the one of YF<sub>3</sub>-type HoF<sub>3</sub> (29.03 cm<sup>3</sup>/mol;  $d(\text{Ho-F}) = 229 - 232$  pm plus 250 pm for C.N. = 8+1) [3].

The UCl<sub>3</sub>-type crystal structure of HoF(OH)<sub>2</sub> (space group:  $P6_3/m$ ) features one crystallographic position for each ion. Ho<sup>3+</sup> is surrounded by nine anions in the shape of a tricapped trigonal prism [HoF<sub>3</sub>(OH)<sub>6</sub>]<sup>6-</sup> (Figure 1) with interatomic distances of  $d(\text{Ho-F/OH}) = 237$  pm for the prism anions and  $d(\text{Ho-F/OH}) = 234$  pm for the capping ones. This finding contrasts with the crystal structure of Ho(OH)<sub>3</sub>, where the bond lengths to the prism corners are with 242 pm almost 3 pm shorter than those to the caps [2].

To investigate the mixed occupation of the anion site with OH<sup>-</sup> and F<sup>-</sup> anions, wavelength-dispersive X-ray spectrometry (WDXS) was performed for the measured crystal. The spectrum clearly showed the presence of both the O-K<sub>α</sub> and the F-K<sub>α</sub> emission line in relevant intensity with a F:O ratio of 35:65 and thus confirmed the structure model derived from the single-crystal X-ray diffraction data.



**Figure 1.** Mixed-anionic coordination sphere of the Ho<sup>3+</sup> cations in the UCl<sub>3</sub>-type crystal structure of HoF(OH)<sub>2</sub> as tricapped trigonal prism [HoF<sub>3</sub>(OH)<sub>6</sub>]<sup>6-</sup> with interatomic distances  $d(\text{Ho-F/OH})$  in pm.

[1] F. R. Boyd, J. L. England, (1960) *J. Geophys. Res.* **65**, 741.

[2] G. W. Beall, W. O. Milligan, H. A. Wolcott, (1977) *J. Inorg. Nucl. Chem.* **39**, 65.

[3] M. Piotrowski, H. Ptasiewicz-Bak, A. Murasik, (1979) *Phys. Status Solidi A* **55**, 163.

**Keywords:** crystal structure; rare-earth metals; holmium; fluorides, hydroxides