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YHO, an Air-Stable Ionic Hydride

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Supporting Information

ABSTRACT: Metal hydride oxides are an emerging field in solid-state research. While some lanthanide hydride oxides (*Ln*HO) were known, YHO has only been found in thin films so far. Yttrium hydride oxide, YHO, can be synthesized as bulk samples by a reaction of Y_2O_3 with hydrides (YH₃, CaH₂), by a reaction of YH₃ with CaO, or by a metathesis of YOF with LiH or NaH. X-ray and neutron powder diffraction reveal an anti-LiMgN type structure for YHO (*Pnma*, a = 7.5367(3) Å, b =3.7578(2) Å, and c = 5.3249(3) Å) and YDO (Pnma, a =7.5309(3) Å, b = 3.75349(13) Å, and c = 5.3192(2) Å); in other words, a distorted fluorite type with ordered hydride and oxide anions was observed. Bond lengths (average 2.267 Å (Y-O),



2.352 Å (Y-H), 2.363 Å (Y-D), >2.4 Å (H-H and D-D), >2.6 Å (H-O and D-O), and >2.8 Å (O-O)) and quantummechanical calculations on density functional theory level (band gap 2.8 eV) suggest yttrium hydride oxide to be a semiconductor and to have considerable ionic bonding character. Nonetheless, YHO exhibits a surprising stability in air. An in situ X-ray diffraction experiment shows that decomposition of YHO to Y2O3 starts at only above 500 K and is still not complete after 14 h of heating to a final temperature of 1000 K. YHO hydrolyzes in water very slowly. The inertness of YHO in air is very beneficial for its potential use as a functional material.

INTRODUCTION

Hydrogen-containing functional materials are usually contextualized with hydrogen storage concepts. Apart from this, the employment of hydrides in catalysts,^{1,2} battery materi als_{1}^{3-5} and phosphors⁶ is becoming more important. LiLa₂HO₃ is a prominent example, as it was the first material to show pure hydride ion H^- conduction.⁷ It is a hydride oxide (sometimes also called oxyhydride and not to be confused with hydroxides), a term generalizing substances whose anionic sublattices are composed of both hydrogen and oxygen. This class of compounds is the least developed in comparison to the group of mixed anionic oxides, which are an emerging field for the development of new materials.⁸ Other recent examples for hydride oxides are LaSrCoH_{0.7}O₃,⁹ SrVO₂H,¹⁰ $Sr_3Co_2H_{0.84}O_{4.33}$,¹¹ and $BaTiH_xO_{3-x9}$ ¹² which are promising candidates in the design of hydrogen-containing functional materials, as some of them are usually inert to air. This is an outstanding behavior, as ionic hydrides such as lithium hydride (LiH) and calcium hydride (CaH_2) decompose quickly in air.

Hydride oxides with the general formula REHO (RE: rare earth element) were first reported in the 1960s¹³ and studied more intensively during recent years. They crystallize in two different structure types. The fluorite structure type with space group $Fm\overline{3}m$ is known for La-Pr and Sm-Er.^{2,13-17} It exhibits a face centered cubic lattice of RE atoms, whose tetrahedral voids are occupied by H and O in a disordered fashion. For SmHO, GdHO, and HoHO, long-term stability in air at room temperature was shown.^{16,17} Variable H/O ratios were reported for the large lanthanides (La-Pr), whereas the ratios

of the smaller ones seem to be fixed at 1:1. YHO was observed only in thin films,¹⁸ and its crystal structure was discussed on the basis of quantum-mechanical calculations.¹⁹ The large lanthanide ions (La-Nd) crystallize in a fluorite type superstructure with a space group of P4/nmm, in which the anions are ordered (LaHO structure type).^{14,20-22} The lanthanum, cerium, and praseodymium compounds are hygroscopic and react quickly with humid air. While LaHO and PrHO can be stored in dry air, CeHO reacts pyrophorically to form CeO₂. No report is given on the air stability of NdHO.

In our study, we aimed to expand the known REHO series toward yttrium and investigate its thermal resistivity toward air at elevated temperatures by in situ powder X-ray diffraction (PXRD). Furthermore, YHO can form from yttria Y₂O₃ and has a similar diffraction pattern. As yttria is an important material for luminophors,²³ spectral filtering,²⁴ and quantum information processing, for example,²⁵ this study provides an important insight into its chemistry under reducing conditions.

EXPERIMENTAL SECTION

Four different methods were employed for the synthesis of yttrium hydride oxide YHO (Table 1) using (a) yttria Y2O3 and yttrium hydride YH₃, (b) yttria and calcium hydride CaH₂, (c) yttrium hydride and calcium oxide CaO, and (d) yttrium oxide fluoride YOF and alkaline hydride AH (A = Li or Na). Unless otherwise stated, all

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Table 1. Overview of the Different Synthesis Strategies for YHO^a

label	reaction scheme	yield/wt %
a	$Y_2O_3 + YH_3 \rightarrow 3YHO$	83
b	$Y_2O_3 + CaH_2 \rightarrow 2YHO + CaO$	85
с	$YH_3 + CaO \rightarrow YHO + CaH_2$	95
d	$YOF + NaH \rightarrow YHO + NaF$	81
	$YOF + LiH \rightarrow YHO + LiF$	72

^{*a*}Experiments were conducted in fused silica ampules under an argon atmosphere at 975 K < T < 1175 K (a, b, and c) or in aluminum crucibles under a hydrogen atmosphere and 725 K (d). The yield refers to the weight ratio of yttrium-containing phases, which were determined by a Rietveld analysis.

samples were handled in an argon filled glovebox, in which the oxygen and water content were kept below 1 ppm. Yttria (Aldrich, 99.99%) was dried prior to use at 1373 K for $6 h^{26}$ and transferred while hot into the glovebox. Yttrium hydride or yttrium deuteride was obtained from metallic yttrium (Smart Elements, 99.99%, stored under argon) and hydrogen (Air Liquide, 99.9%) or deuterium (Air Liquide, 99.8%) at 2-5 MPa and 573 K in Inconel (Böhler L718V) autoclaves. Yttrium oxide fluoride was obtained from yttria and a slight excess (1.1 equiv) of powdered polytetrafluoroethylene (Alfa Aesar) at 823 K in air.²⁷ Calcium hydride was obtained from calcium (Alfa Aesar, 99.5%) and hydrogen at 6 MPa and 675 K; calcium oxide was prepared from calcium carbonate at 1275 K and transferred while hot into the glovebox. Syntheses (a), (b), and (c) were conducted in fused silica glass ampules, and synthesis (d) was conducted in sealed aluminum crucibles. For synthesis (a), 1-2 g of 1:2 molar mixtures of yttria:yttrium hydride or deuteride, respectively, was annealed at 1173 K for 48 h with a heating rate of 50 K h^{-1} . For synthesis (b), 0.4 g of a 1:4 molar mixture of yttria:calcium hydride was annealed at 1173 K for 48 h with a heating rate of 50 K h^{-1} .¹⁶ For synthesis (c), 0.1 g of a 1:1 molar mixture of yttrium hydride:calcium oxide was heated at a rate of 25 K h⁻¹ to 973 K and annealed for 48 h. For synthesis (d), 35 mg (NaH) and 30 mg (LiH) of 1:1.3 molar mixtures of yttrium oxide fluoride:sodium hydride (Aldrich, 95%) and 1:1 molar mixtures of yttrium oxide fluoride:lithium hydride were transferred into a differential scanning calorimeter (DSC, Q1000, TA Instruments) with an attached pressure chamber and heated to 723 K at 1 MPa hydrogen gas with a rate of 1 K min⁻¹; then, the mixture was annealed for 2 h and cooled at the same rate to 300 K. After 0.5 h, the procedure was repeated. To investigate the air stability of YHO at room temperature, a sample was prepared via synthesis (a) for powder X-ray diffraction (PXRD) in Guinier geometry (for details, see below) with exposure to air while collecting PXRD patterns in regular intervals. The stability toward liquid water was investigated by grinding a sample of (a) under deionized water for 1 min before preparing a Guinier PXRD sample.

Powder neutron diffraction (PND) data of YDO and YHO obtained from route (a) were collected on the E9 high resolution diffractometer at Helmholtz Zentrum Berlin (HZB) at 298(2) K using a vanadium sample holder of 6 mm diameter.²⁸ All powder Xray diffraction experiments were conducted with Cu Ka1 radiation from curved Ge(111) monochromators at T = 296(2) K. Most specimens were measured in Debye-Scherrer geometry on a Stoe STADI-P diffractometer. Samples were mixed with powdered diamond and filled into 0.3 mm glass capillaries (WJM Glas/Müller GmbH, Berlin) prior to fusing. Experiments in Guinier geometry were conducted on a Huber G670 diffractometer. The powders were dispersed in Apiezon grease and placed either on top of one or between two Kapton sheets (for noninert or inert measurements, respectively). In situ data were collected on a Rigaku Smart Lab diffractometer using an Anton Paar HTK1200 reaction chamber and Bragg-Brentano geometry. The sample (YHO, obtained from route (a)) was heated in 25 K steps from 300 to 1075 K with a rate of 5 K min⁻¹ in air. At each step, the temperature was equilibrated for 10 min

before starting the measurement that lasted 15 min. In total, each temperature step lasted 30 min.

PXRD data were analyzed by the Rietveld technique using the software Topas version 5 (Bruker AXS) and full profile analysis. The background was fitted using a Chebychev fifth order polynomial. PND data were analyzed with FullProf using a pseudo-Voigt reflection profile. A polynomial of third (YDO) and fifth (YHO) order described the background. In both PXRD and PND, zero-point error, scaling factor, lattice, profile and atomic parameters, and isotropic displacement factors B_{iso} were refined if the phase ratio exceeded 10 wt %; otherwise only the former four parameters were refined. The B_{iso} values from PXRD data were corrected by an offset value (overall *B*). It was refined from the diamond reflections using a literature value for diamond ($B_{iso}(C) = 0.142 \text{ Å}^{2}$)²⁹ and fixed afterward. The H content of YHO obtained from Y₂O₃ and YH₃ was determined by the carrier gas hot extraction method on four specimens using a VARIO EL microanalyzer (Elementar Analysensysteme GmbH).

The density functional theory (DFT) calculations were performed with the Vienna *ab initio* simulation package (VASP)^{30,31} version 5.4.4 using projector-augmented wave pseudopotentials (PAWs)³² from the VASP database. In case of the rare earth elements, PAWs simulating trivalent ions were employed for RE = Ce-Lu (RE 3), and for yttrium, the s- and p-levels of the fourth principal quantum number were treated as semicore states (Y sv). For lanthanum, hydrogen, and oxygen, the standard PAWs were used (La, H, O). The exchange correlation potential was approximated with the GGA-PBE method,³³ and the Brillouin zone was integrated using the tetrahedron method with Blöchl corrections.³⁴ The k-grid was generated automatically and Γ -centered, ensuring a k-point density of 0.03 Å⁻¹. The cutoff energy was set to 800 eV. Structure optimizations were conducted with full degrees of freedom (cell volume, cell shape, and atomic positions) using a conjugate gradient algorithm, converging forces to 10 μ eV Å⁻¹ and electronic energies to 1 μ eV. Thus, obtained energies were used to calculate free reaction enthalpies $\Delta_r G$. The energies of RE_2O_3 and REH_3 stem from structures with space groups $Ia\overline{3}$ (bixbyite structure type) and $P\overline{3}c1$ (YD₃ structure type), respectively, which exhibited smaller values than other modifications. The optimized structures were used as input for density of states (DOS) calculations. Here, the k-grid was enhanced to a k-point density of 0.01 $Å^{-1}$, and the DOS were calculated with a resolution in energy of 1 meV.

RESULTS AND DISCUSSION

The reaction of yttrium oxide and yttrium hydride produced a gray powder. As the latter decomposes at elevated temperatures,³⁵ an excess of it ensured high yield. However, small amounts of yttrium hydride (5-20 wt %) remained in the sample. The sample's color is thus a mixture of the dark colored yttrium hydride and the reaction products. PXRD analysis showed a new phase with a reflection pattern similar to Y_2O_3 or LaHO as well as reflections belonging to fluorite type YHO (Figure S1 in the Supporting Information). The latter has only been reported in thin films.¹⁸ Indexing the remaining reflections yielded a primitive orthorhombic cell with a = 7.537Å, b = 7.516 Å, and c = 5.325 Å. A model in $P2_1mn$, derived from LaHO in P4/nmm via Pmmn, explained all the reflections of the PXRD pattern. The hydrogen content of the sample, determined by CHN elemental analysis, suggested the composition of YHO (exp.: 1.220(5) wt %, calc.: 1.14 wt %). The other synthesis approaches (Table 1, b-d) yielded orthorhombic YHO, whose lattice parameters are not significantly different (Figures S3-S6). Thus, YHO seems to exhibit a fixed composition. The DSC experiments of the reaction of YOF with LiH and NaH show broad exothermic signals at mild conditions (ca. 600 K; Figures S9 and S10). To determine the atomic positions of hydrogen in YHO, neutron diffraction data were collected on a deuterated sample of YDO

(D = ²H, Figure 1). D has a significantly smaller incoherent scattering length compared to ¹H (b_i (¹H) = 25.3 fm, b_i (D) =



Figure 1. Rietveld refinement of the crystal structure of YDO (top) and YHO (bottom) obtained from synthesis route (a) (Table 1) on the basis of PND data at 298(2) K (E9, HZB, Germany, $\lambda = 1.79820(2)$ Å). Top: $R_{wp} = 7.7\%$, GooF = 1.6. Bragg markers denote from top to bottom YDO *Pnma* (68.2(7) wt %, $R_{Bragg} = 4.2\%$, a = 7.5309(3) Å, b = 3.75349(13) Å, c = 5.3192(2) Å), YDO *Fm* $\overline{3}m$ (12.3(3) wt %, a = 5.28501(14) Å), and YD₂ *Fm* $\overline{3}m$ (19.4(4) wt %, a = 5.19688(8) Å). Bottom: $R_{wp} = 1.6\%$, GooF = 2.1. Bragg markers denote from top to bottom YHO *Pnma* (71(1) wt %, $R_{Bragg} = 11.4\%$, a = 7.5367(3) Å, b = 3.7578(2) Å, c = 5.3249(3) Å), YHO *Fm* $\overline{3}m$ (10.7(6) wt %, a = 5.30227 Å), and YH₂ *Fm* $\overline{3}m$ (18.2(8) wt %, a = 5.2081(2) Å). Red: measurement. Black: calculated. Blue: difference. An offset of 10⁴ counts was added to the difference curve of YHO. Rietveld refinements of PXRD data of both structures are provided in Figures S1 and S2 in the Supporting Information.

4.0 fm),³⁶ which results in a lower background. Starting from the anion positions derived from LaHO, O and D sites were successfully allocated and positions refined. Furthermore, the 1:1:1 composition was confirmed by the refinement. A subsequent symmetry search resulted in a smaller cell (b' = b/2) with space group *Pnma* and an isotypical structure to LiMgN³⁷ (Table 2). YDO is thus the first representative of the LiMgN antitype. There is no direct crystallographic group–

Table 2. Crystal Structure Parameters of YDO and YHO on the Basis of Powder Neutron Diffraction Data at 298(2) K^a

atom	Wyckoff	label	x	у	z	$B_{\rm iso}/{\rm \AA}^2$
Y	4c	•	0.3756(7)	1/4	0.2806(5)	0.20(3)
		*	0.3734(5)	1/4	0.2782(5)	0.52(4)
0	4 <i>c</i>	•	0.6434(5)	1/4	0.4852(7)	0.24(6)
		*	0.6442(4)	1/4	0.4828(8)	0.51(6)
D	4 <i>c</i>	•	0.0996(5)	1/4	0.5156(8)	1.67(9)
Н		*	0.1031(6)	1/4	0.508(2)	2.29(9)

^aYDO: •, *Pnma*, *a* = 7.5309(3) Å, *b* = 3.75349(13) Å, *c* = 5.3192(2) Å. YHO: *, *Pnma*, *a* = 7.5367(3) Å, *b* = 3.7578(2) Å, *c* = 5.3249(3) Å.

subgroup relationship between the YDO and LaHO structures, but of said crystallographic relationship, there is an indirect one via the aristotype CaF_2 in $Fm\overline{3}m$ (cf. Bärnighausen tree in Figure S12). Similar structures (i.e., bixbyite type Y_2O_3 ($Ia\overline{3}$), YOF type ($R\overline{3}m$), and LaOF type (P4/nmm)) are also found in different branches of the fluorite type symmetry tree.³⁸ The most related structure is that of LaOF, which is obtained from a *klassengleiche* transformation of the Pt₂Si type, which is in turn an aristotype of YDO.

The coordination polyhedron of yttrium atoms in YDO is a distorted tetragonal prism; deuterium and oxygen atoms are both coordinated in a distorted tetrahedral fashion (Figure 2).



Figure 2. Coordination polyhedra in the crystal structure of YDO.

Table 3. Atomic Distances in YDO (Pnma) an	d YHO
(Pnma) up to 3 Å on the Basis of Powder New	atron
Diffraction Data at 298(2) K	

			distance/Å	
atom 1	atom 2	quantity	YDO	ҮНО
Y	D/H	1	2.308(6)	2.307(8)
		2	2.355(3)	2.372(6)
		1	2.425(6)	2.377(7)
			2.363 ^a	2.352 ^a
Y	0	1	2.249(6)	2.217(5)
		2	2.257(3)	2.273(3)
		1	2.292(6)	2.314(5)
			2.266 ^a	2.268 ^a
D/H	D/H	2	2.408(3)	2.440(4)
D/H	0	1	2.676(6)	2.633(11)
		1	2.684(6)	2.727(11)
		2	2.696(4)	2.676(4)
			2.685 ^a	2.679 ^a
0	0	2	2.866(4)	2.879(3)
^{<i>a</i>} Mean valu	es are given	in italics.		

The Y–D and Y–O bond lengths (Table 3) agree with those in trigonal YD₃ (Y–D: 2.13–2.52 Å)³⁹ and bixbyite type Y₂O₃ (Y–O: 2.24–2.33 Å).⁴⁰ The large D–O bond distances illustrate the anionic nature of D and prove that YDO is a hydride oxide and not a hydroxide (D–O distance in YOOD: 0.959 Å).⁴¹ The D–D bond distance is slightly smaller than that of O–O due to the higher Coulomb repulsion of O^{2–} compared to D[–]. In comparison with LaHO, the yttrium polyhedra show a significant tilt toward a (5.0(1)°, *cf.* Figure 3; LaHO: 2.803(3)°,²⁰ NdHO: 4.049(2)°).²² This results from the smaller size of yttrium compared to lanthanum ions ($r(Y^{3+})$ = 1.159 Å, $r(La^{3+}) = 1.300$ Å),⁴² as the tilt enables the anions to better shield the cationic charges. It furthermore demands



Figure 3. Crystal structures of YDO (left) and LaHO (right).²⁰

the cations to shift from another in the *c* direction, which is incompatible with the symmetry in P4/nmm. Here, half of the lanthanum atoms, La3, are situated on a mirror plane.

The second major difference between YDO and LaHO is the ordering scheme of the anions in the polyhedra surrounding the yttrium and lanthanum atoms, respectively. From the seven ways to distribute two atomic species on the vertices of a cube (Figure 4), the one with m symmetry is



Figure 4. The ordering scheme for anions *X* and *Y* in fluorite type related compounds *MXY* has seven possible rotationally distinct two-coloring of the eight vertices of a cube. The respective point symmetries given below are often lowered in compounds *MXY* by the distortion of the cubes. Ordering schemes for different anionic ratios are provided in Figure S15.

found in YDO, and those with 43m, 4mm, and mmm symmetries are found in LaHO. They result from the ordering of hydrogen (deuterium) and oxygen atoms and the tendency of similar ions to occupy symmetrically equivalent positions; the latter is equivalent to Pauling's rule of parsimony.⁴³ Only specific Wyckoff positions are compatible with these requirements (i.e., 4c in YDO and 8i in LaHO), causing different coordination environments. In comparison with oxide fluorides *REOF*, which show ordering schemes with symmetry 3m (YOF type R3m) and 4mm (LaOF type P4/nmm),⁴⁴ the tendency of hydrogen (deuterium) atoms to occupy neighboring positions to oxygen atoms is prominent; this is in contrast to fluorine atoms, which tend to segregate. Due to the different charges of

 F^- and O^{2-} , this segregation results in an inhomogeneous shielding of the cationic charges. As fluorine is highly electronegative, it can compensate this, contrasting hydrogen, which has only a medium electronegativity. Therefore, the anions in hydride oxides *RE*HO will surround the cations more homogeneously, which is why they adopt different structure types than oxide fluorides *RE*OF. A similar anionic ordering scheme to *RE*HO is found in lithium hydride nitride Li₄NH.⁴⁵

The driving force for the formation of anionically ordered or disordered *RE*HO compounds was attributed in the literature to the bonding behavior of oxygen: as the *RE*–O bond length increases with the *RE* radius, an ordered modification is preferred for larger *RE* cations because they enable shorter *RE*–O bond distances.² In YDO, a similar driving force might be present, as the ordering also enables a shorter *RE*–O distance (Figure S14). Thus, the anti-LiMgN structure type might be suitable for other small rare earth elements as well.

The crystal structure of YHO, as refined with PND data (Figure 1, Table 2), is very similar to that of YDO. The major differences are the lattice parameters and the thermal displacement factors (Table 2), which are caused by the isotopic effect of deuterium with a doubled mass as compared to protium. The high R_{Bragg} value results from the inferior signal-to-noise ratio, which is due to the high incoherent scattering length of ¹H. Further details of the crystal structure investigations may be obtained from FIZ Karlsruhe, Eggenstein-Leopoldshafen 76344, Germany (Fax: + 49-7247-808-666. E-mail: crysdata@fiz-karlsruhe.de) on quoting the deposition number CSD-1903936 (YDO) and CSD-1903938 (YHO).

DFT calculations of the anti-LiMgN and the LaHO structure type for REHO (RE = Y, La-Lu) show a structure directing effect of the cation radius. The free reaction enthalpy of the reaction as a function of the ionic radii r (Figure S16) shows a stabilization of the anti-LiMgN over the LaHO structure type with decreasing r. The offset of yttrium and lanthanum in the plot is due to the different pseudopotentials, which did not contain f states. The difference in the value of YHO to a previous publication of ours¹⁷ stems from an updated pseudopotential of yttrium. A calculation of the DOS confirmed the ionic character of YHO (Figure S17). In comparison with that of Y_2O_3 (Figure S18), the smaller band gap ($E_{gap}(YHO) = 2.8 \text{ eV}, E_{gap}(Y_2O_3) = 4.1 \text{ eV}$), which results from the hydrogen states near the Fermi level, and the higher dispersion is evident. Therefore, YHO seems to be a semiconductor. It should be noted that DFT calculations are known to underestimate band gaps.⁴⁶ The experimental E_{gap} of Y_2O_3 , for example, is about 5 eV.⁴⁷

To evaluate the air stability of YHO, an *in situ* PXRD experiment was conducted from 300 to 1075 K in air (Figure 5). Orthorhombic YHO starts to decompose only at above 500 K, and even at 1025 K, a significant amount is still present. Fluorite type YHO is observed up to 600 K, and YH₂ is observed until 725 K. Bixbyite type Y_2O_3 is the decomposition product of each phase (2YHO + $O_2 \rightarrow Y_2O_3 + H_2O$). The reaction mechanism of YHO to Y_2O_3 needs further evaluation, as at least one intermediate phase is observed with a reflection pattern similar to Y_2O_3 . This disturbed the refinement of Y_2O_3 , particularly at 800 \pm 50 K, which is why the phase ratios derived here show inconsistencies. The corresponding intensity maximum is a result of interfering reflections of all these phases. The total duration of the experiment, 16 h, further illustrates the remarkable stability of YHO in air. A



Figure 5. In situ X-ray diffraction data and phase analysis of the thermal decomposition of YHO in air (heating rate: 5 K min⁻¹). Top: part of diffraction data (λ : CuK_{α 1}; square root of intensity). Bottom: phase ratios from Rietveld refinement. Error bars are smaller than the displayed symbols. The full diffraction plot is shown in Figure S11.

similar thermal stability of an ionic hydride was only observed for the hydride silicate $\text{LiSr}_2(\text{SiO}_4)\text{H}^{.48}$ At room temperature, YHO did not react with air in 20 days. Only the YH₂ phase showed a decrease in intensity; the decomposition product is probably amorphous (Figure S7). Treatment of YHO with liquid water did not produce any gas bubbles or a change in color. The Rietveld refinement showed a decrease in the phase ratio of YHO toward YH₂ (85.8(1)% to 75.7(2)%), which indicates a slow hydrolysis to a probably amorphous product (*cf.* Figure S8).

For thin films, the hydrolysis of YH₂ led to the formation of isotypic YH_xO_y.¹⁸ After treatment with water, a group of reflections between those of YH₂ and YHO appears, indicating a variable composition of cubic YHO at mild conditions. Treatment with mineralic acids (pH <1) leads to a decomposition of YHO under formation of hydrogen gas.

CONCLUSION

We reported on the synthesis of orthorhombic yttrium hydride oxide, YHO, a new representative of the REHO compound class, and we analyzed its crystal structure by powder neutron and powder X-ray diffraction. It is the first example of the anti-LiMgN structure type with space group Pnma, and it is thus related to the LaHO, YOF, LaOF, and bixbyite structure types via the fluorite aristotype, in which most rare earth hydride oxides crystallize. Additionally, a second modification of YHO (fluorite type, $Fm\overline{3}m$) was observed in a bulk material for the first time. Orthorhombic YHO can be obtained by different synthesis routes, starting from Y2O3, YH3, or YOF, with varying yields. DFT calculations confirmed its ionic character. These calculations predicted a semiconducting behavior and the possibility of other small rare earth elements to crystallize in this structure type. The stability of YHO in air and moisture, as observed in situ at elevated temperatures and ex situ at room temperature, is outstanding for an ionic hydride, and this stability marks YHO's significance in the search for functional materials containing anionic hydrogen-like catalysts or phosphors, as it is stable toward oxygen up to 500 K and can still be observed at 1025 K after 14 h of heating. Furthermore, YHO hydrolyzes only slowly in liquid water.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02308.

PXRD analysis of YHO obtained from Y_2O_3 , YH₃, and YOF; PXRD data of YHO stored in air; PXRD data of YHO treated with liquid water; DSC curves of YOF + AH (A = Li, Na); full *in situ* diffraction plot; Bärnighausen tree; comparison of the unit cells of orthorhombic YDO, cubic *REHO*, and tetragonal LaHO; correlation of normalized cell volume and polyhedral volumes of O and H with cationic radius; ordering schemes for MX_xY_{2-x} (0 < x < 2) compounds; DFT results; and DOS plots of YHO and Y_2O_3 (PDF)

Accession Codes

CCDC 1903936 and 1903938 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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