Experimental report

13/09/2024

Proposal: 5-24-722 **Council:** 4/2023

Title: In situ investigation of H/O exchange in rare-earth hydride oxides YHO and HoHO

Research area: Chemistry

This proposal is a new proposal

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Samples: HoHO
YHO

Instrument	Requested days	Allocated days	From	To
D20	2	2	15/09/2023	18/09/2023

Abstract:

Hydride oxides (also called oxyhydrides) show fascinating properties, e. g. hydride ion conductivity, catalytic activity in the ammonia production or as luminescence hosts. Rare-earth metal hydride oxides REHO crystallize either in the cubic fluorite-type structure with disordered hydrogen and oxygen atom distribution or in pseudo-cubic derivatives thereof with ordered anion distribution. Controlling the composition of these hydride oxides is of utmost importance to tune the above mentioned properties and a more detailed understanding of H/O exchange during the reaction with air is thus highly desirable. In situ X-ray data show that YHO and HoHO react in air at about 600 K to an intermediate, presumably a hydrogen-poor hydride oxide, before forming cubic bixbyite-type Y2O3 or Ho2O3. We will follow the reaction of YHO and HOHo in air by in situ neutron powder diffraction during slow heating. Rietveld refinements will provide full crystal structures with positions of hydrogen atoms and hydrogen content for all phases including reaction intermediates. This will complete the knowledge of rare-earth hydride oxides (oxyhydrides) as bulk phases.

In situ Investigations on H/O exchange in rare-earth hydride oxides YHO and HoHO (experiment 5-24-722)

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Rare-earth hydride oxides *RE*HO crystallize in structures related to the fluorite-type structure [1]. Especially YHO has received much attention for showing a color-neutral, reversible photochromic effect in thin films, which's detailed mechanism however remains incompletely understood, but likely is governed by oxygen excess in the anionic partial structure [2]. During the oxidation of YHO (anti-LiMgN type, *Pnma*) and HoHO (Half-Heusler phase, LiAlSi type, $F\bar{4}3m$), in air, intermediate phases, assumed to be oxygen-rich hydride oxides $REH_{1-2x}O_{1+x}$ (*RE* = Y, Ho), occur (**Figures 1, 2**).

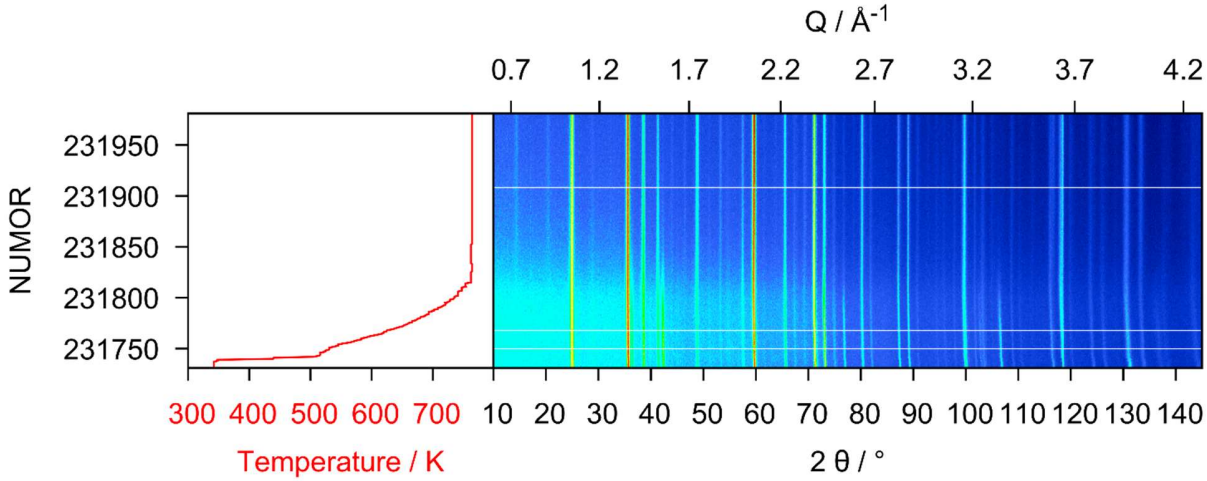

Figure 1: *In situ* neutron powder diffraction data of the reaction of YHO in air taken on diffractometer D20 at λ = 1.86684(2) Å in a single crystal sapphire cell [3] under various temperature conditions. Intensities are in false colors, each measurement (NUMOR) with two minutes data collection time. White lines indicate measurement interruptions.

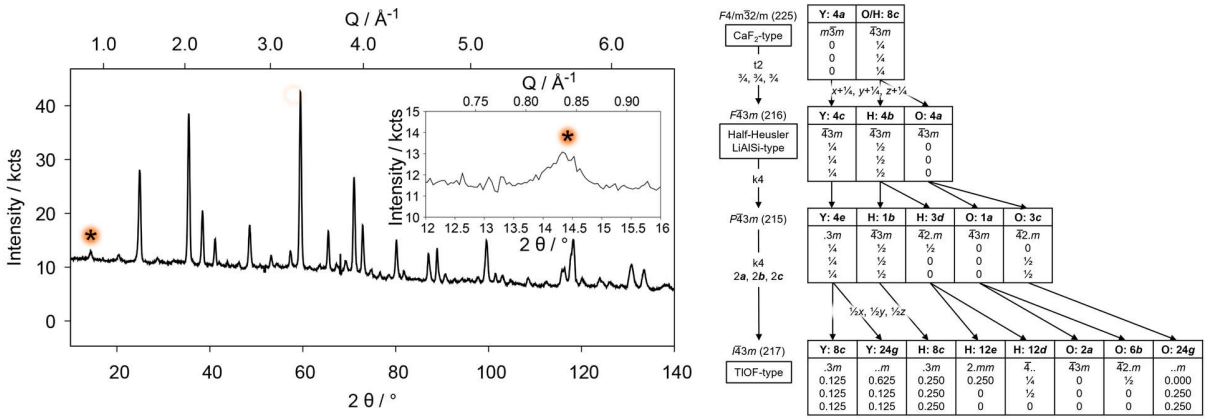

Figure 2: Left: Neutron powder diffraction data (summed over NUMOR 231950 – 231970) of the intermediate phase found during the oxidation of YHO in air taken on diffractometer D20 at λ = 1.86684(2) Å in a single crystal sapphire cell [3] at 764 K. The additional reflection discussed in the text is marked by an asterisk *. Right: Possible Bärnighausen tree used to explain the additional reflection by a two-fold superstructure of CaF_2-type YHO.

A similar experiment was conducted on a sample of HoHO (**Figure 3**). Similar to YHO, a decrease in incoherent scattering background, followed by the appearance of the additional, low-angle superstructure reflection could be observed, hinting towards a very similar behavior of this compound in air. Likewise, a complete structure refinement of this structure is currently in progress. This observation shows that it will be worthwhile to study more rare-earth metal hydride oxides on their behavior in air, to conclude trends depending on the respective metals.

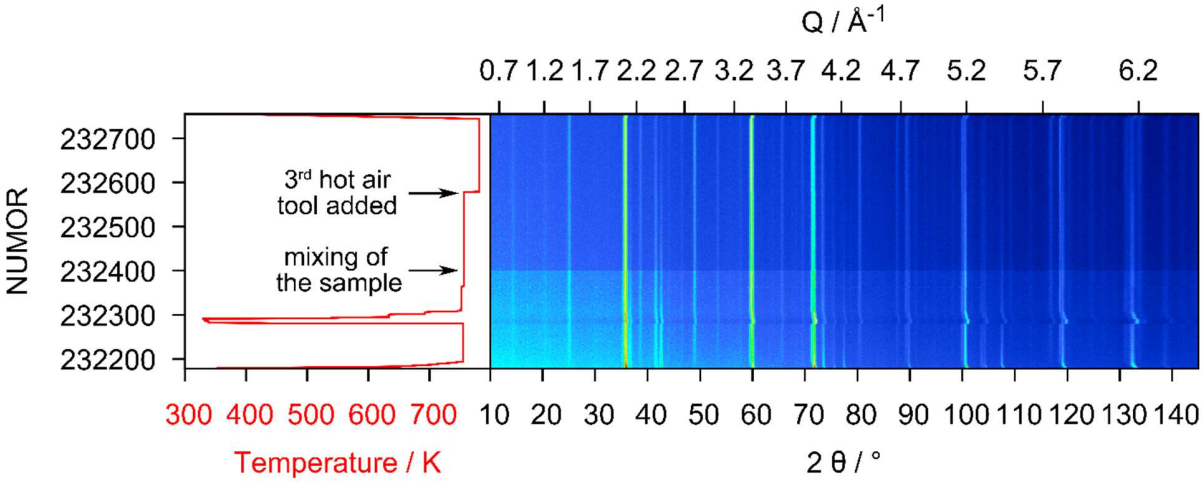

Figure 3: *In situ* neutron powder diffraction data of the reaction of HoHO in air taken on diffractometer D20 at λ = 1.86684(2) Å in a single crystal sapphire cell [3] under various temperature conditions. Intensities are in false colors, each measurement (NUMOR) with two minutes data collection time.

Literature

[1] N. Zapp, *Rare Earth Heteroanionic Hydrides with Secondary O^{2-}, F^- and N^{3-}-Ions Related to the CaF_2- and K_2NiF_4-Structure Types*, Dissertation, Leipzig University, **2021**.

[2] T. Mongstad, C. Platzer-Björkman, J. P. Maehlen, L. P. Mooij, Y. Pivak, B. Dam, E. S. Marstein, B. C. Hauback, S. Z. Karazhanov, *Sol. Energy Mater. Sol. Cells* **2011**, *95,* 12, 3596.

[3] A. Götze, H. Auer, R. Finger, T. C. Hansen, H. Kohlmann, *Phys. B (Amsterdam, Neth.)* **2018**, *551*, 395-400