Experimental report

22/02/2021

Proposal: **5-22-775** **Council:** 4/2019

Title: Crystal structures of the hydride oxides LiLaEuH2O2, SmHO and their deuterides

Research area: Chemistry

This proposal is a resubmission of 5-22-768

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Samples:
LiLaEuH2O2
SmHO
SmDO
LiLaEuD2O2

Instrument	Requested days	Allocated days	From	To
D4	2	3	30/08/2020	03/09/2020

Abstract:

Mixed anionic metal hydrides, especially hydride oxides, have attracted attention recently as functional materials. For example, LiEu2HOCl2 and terbium doped GdHO were found to exhibit photoluminescence. The crystal structure of two further hydride oxide, LiLaEuH2O2 and SmHO will be determined by neutron powder diffraction, which is needed in order to unambiguously locate lithium and hydrogen atoms. The metal atom substructures were determined by X-ray diffraction and show similarities to those of LiLaSrH2O2 and SmH2. While for metal hydrides usually only deuterides are investigated with neutron diffraction in order to avoid the strong incoherent scattering of 1H, in this case both hydrides and deuterides will be measured. This is because for both compounds H/O disorder is possible and the scattering lengths of D and O atoms are very similar. Because of the strong neutron absorption of Sm and Eu the wavelengths will be chosen carefully (70 pm for Eu and 50 pm for Sm samples). The location of hydrogen atoms will complete the crystal structures and allow to explain the properties of these compounds, e. g. photoluminescence, ionic conductivity and chemical reactivity.

Crystal structures of the hydride oxides SmHO, SmDO, and $LiLaEuD_2O_2$ (5-22-775)

Hydride oxides are an emerging class of compounds with representatives showing interesting properties like hydride ion conduction or photochromism. For the design of functional materials based on them, a thorough knowledge about the anion ordering is fundamental. Previously, the anion disordered CaF_2 type was assigned to several compounds *RE*HO (*RE* = Sm, Gd – Er) and indications of a significant phase width with respect to the H/O ratio reported [1]. The latter has a great influence on the anion substructure, as in H-rich compounds $REH_{1+2x}O_{1-x}$ additional crystallographic sites must be occupied, and in O-rich compounds $REH_{1-2x}O_{1+x}$, voids are formed. We therefore conducted a combined powder neutron diffraction experiment on the two Sm representatives SmHO and SmDO. The isotopical sensitivity of neutrons and the greatly differing coherent scattering lengths of H and D enable a sophisticated analysis of the anion substructure (b_c(H) = -3.7 fm, b_c(D) = 6.7 fm, b_c(O) = 5.8 fm) [2]. To avoid the high neutron absorption of Sm, the experiments were performed with neutrons of small wavelength (λ = 0.4957 Å), which also alters the coherent scattering length of Sm (b_c = 5.41 fm) [3].

In contrast to our observations for HoHO [4], the anion disordered substructure could be confirmed by our measurements for SmHO (Figure 1, Table 1). Additionally, the octahedral interstice (Wyckoff site 4*b*) is significantly occupied by oxide anions. The independent refinement of the anion's occupancy factors produced a significantly charge-balanced structure model, and the substances composition has to be re-written to $SmH(D)_{1.040(18)}O_{0.936(17)}$, *ergo*, an H-rich variety. Additional undescribed reflections (e.g. at 18.3 and 23.9° 2Θ) indicate a different anion ordering than described here with increased unit cell volume. However, further experiments need to verify this, e.g. electron and high temperature X-ray diffraction measurements.

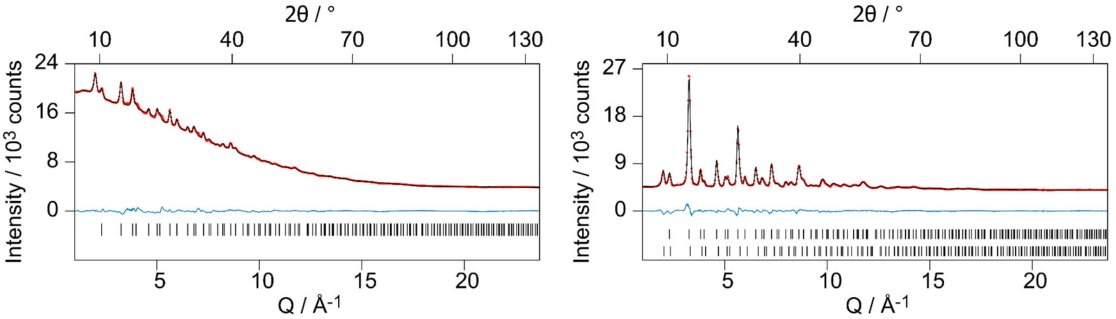

Figure 1. Rietveld refinements of the crystal structures of SmHO (left) and SmDO (right). SmHO: R_{wp} = 1.0%, *GoF* = 12.7, R_{Bragg}(SmHO) = 13.8%. SmDO: R_{wp} = 2.5%, *GoF* = 10.4, R_{Bragg}(SmDO) = 6.0%; Bragg markers denote SmDO (top) and SmD_2 (bottom). Red: observed, black: calculated, blue: difference.

Table 1. Crystal structure parameters of SmHO ($Fm\bar{3}m$, *a* = 5.462(3) Å) and SmDO ($Fm\bar{3}m$, *a* = 5.45816(11) Å).

Atom	Wyck.	*x*	*y*	*z*	*SOF*	B_{iso}(SmHO) / Å²	B_{iso}(SmDO) / Å²
Sm	4*a*	0	0	0	1	1.00(7)	0.17(4)
H / D	8*c*	¼	¼	¼	0.520(9)	0.21(3)	1.37(6)
O1	8*c*	¼	¼	¼	0.449(6)	B_{iso}(H)	B_{iso}(D)
O2	4*b*	½	½	½	0.038(5)	0	0

Recently, K_2NiF_4 type hydride oxides have attracted great attention [5, 6]. Mixed occupation of the two crystallographically independent anion sites by H^- and O^{2-} and of cationic sites by monovalent (alkali), divalent (alkaline earth) and trivalent (rare earth) allows for a rich variety of compounds with compositional degrees of freedom. This allows to influence important materials properties such as hydride ion conductivity or photoluminescence [5-8]. Single-crystal X-ray diffraction suggested the tetragonal K_2NiF_4 type with mixed occupation of La and Eu atoms. Neutron powder diffraction on D4 was performed at 0.7 Å because of the large absorption cross section of ^{nat}Eu for thermal neutrons [2]. Preliminary Rietveld refinement (Fig. 2) confirms the assignment of the structure type and the atomic arrangement as suggested by X-ray diffraction.

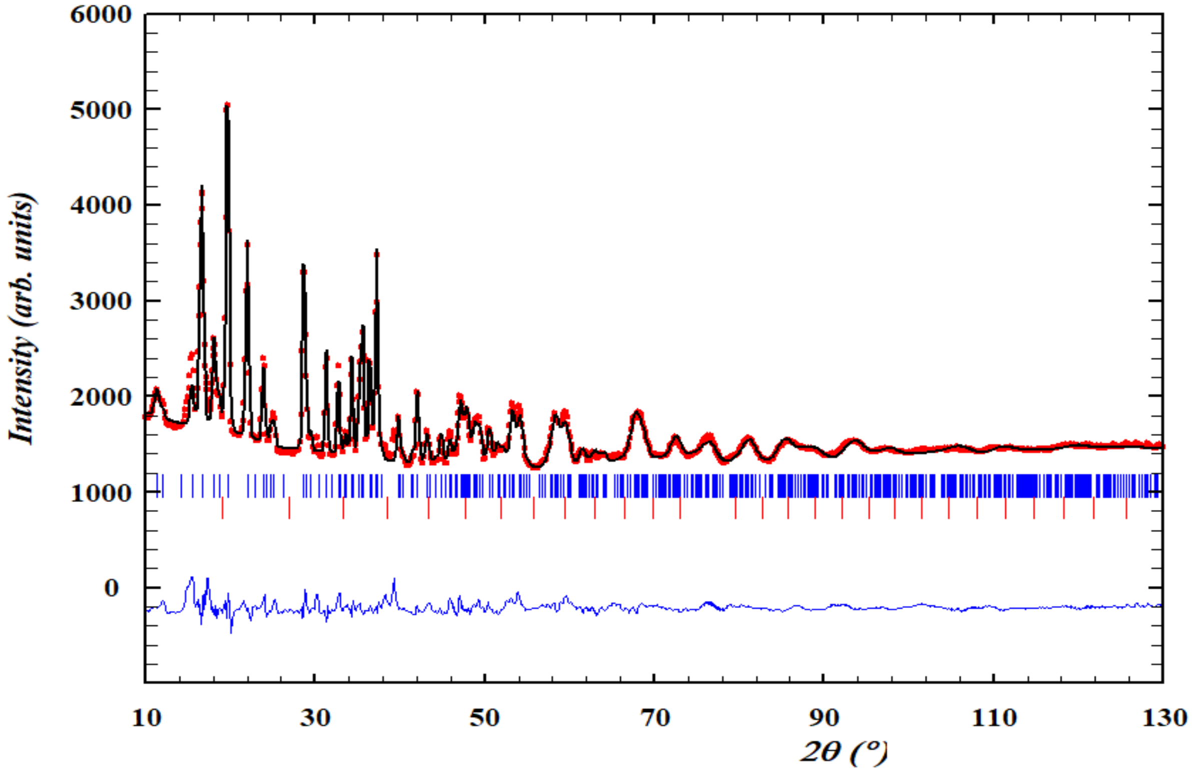

Figure 2. Preliminary Rietveld refinement of the crystal structure of $LiLaEuD_2O_2$ (K_2NiF_4 type, $I4/mmm$, a = 3.6927(7) Å, c = 13.428(3) Å). Red: observed, black: calculated, blue: difference.

References

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