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NdHO, a novel oxyhydride

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ABSTRACT

A new metal oxyhydride; neodymium oxyhydride, NdHO, has been synthesized from a reactant mixture of metal hydride (CaH_2 or NdH_3) and neodymium oxide (Nd_2O_3). The unit cell dimensions decrease smoothly in the series from LaHO, CeHO, PrHO to NdHO, in line with the lanthanide contraction. The crystal structure of NdHO is described on the basis of Rietveld refinement on neutron powder diffraction data:

Space group: $P4/nmm$ (no. 129, D_{4h}^7).Axis lengths: $a = 7.8480(5) \text{ \AA}$, $c = 5.5601(8) \text{ \AA}$.Volume: $V = 342.46(6) \text{ \AA}^3$.

The tetragonal structure is derived from the fluorite structure, showing complete ordering of hydride and oxide ions over the anion sublattice. The formation of NdHO was further substantiated by Raman spectroscopy.

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1. Introduction

Electropositive metals, among these the rare earth metals, play important roles in hydrogen storage and in La_5Ni type battery electrodes. It has been demonstrated that Ce-metal surfaces that have been exposed to oxygen, achieve faster hydrogen adsorption kinetics than the pure metal surface [1]. This may suggest the presence of a hydride-oxide phase at the interface.

Relatively few *stoichiometric* oxyhydrides are known in the literature, examples being LaHO, CeHO and PrHO described by Brice and Moreau [2] and Malaman and Brice [3] and Ln_2LiHO_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ and Nd) investigated by Schwarz [4]. PuHO has been suggested as a transient phase during wet oxidation of Pu-metal [5].

Several *non-stoichiometric* oxyhydrides are known; for instance $\text{LaSrCoO}_3\text{H}_{0.7}$ synthesized by Hayward et al. [6] (Ref. [7] may be consulted for further examples). The current objective is to enhance the knowledge of oxyhydrides – and we report here on the new compound NdHO. The interest in these compounds stems from their possible importance for understanding electrical properties of complex rare earth materials. Furthermore this aspect is important for detailed characterization of perovskite type oxides under reducing conditions. For some of these an

apparent hydride ion conductivity has earlier been measured in investigations by Widerøe et al. [8,9]. A useful recent paper on similar reduced compounds may be found in Ref. [10].

2. Experimental

2.1. Synthesis

All samples were synthesized in an argon filled glove box (dew point -40°C), with a Kanthal tube furnace attached. The appropriate precursor compounds for reaction types (1) and (2) were mixed in an agate mortar and the powders were pressed uniaxially into pellets and loaded into a high grade alumina boat with lid. Firing took place for 12 h in a mixture of 7% H_2 gas in Ar. The hydrogen was added to assist a low partial pressure of oxygen to create reducing conditions. The furnace holding the reaction mixtures was a dedicated high pressure oven, evacuated at room temperature and then filled to about 1/3 of atmospheric pressure before heating. *One should be aware of the hazards of working with hydrogen, even though high pressures were not needed here.* During solid state reaction at a temperature of about 650°C the total pressure was approximately 1 bar and the hydrogen partial pressure roughly 0.07 bar. The total amount of hydrogen in the furnace tube was about 3 liters. After the heating the samples

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were reground and pressed to pellets and finally subjected to X-ray diffraction analysis, see below.

Neodymium oxyhydride, NdHO, was synthesized using a metal hydride (CaH_2 or NdH_3) and neodymium oxide (Nd_2O_3) as precursors. CaO for reference was made by calcination of CaCO_3 (Aldrich) at 1000°C for 3–4 h at which stage approximately 98.5% of the CO_2 has been removed. The purity of CaH_2 was 95% (Merck). In order to get reactive Nd metal samples, lumps of solid Nd weighing typically 2–5 g were melted in a melt-spinner, where the metal was sprayed onto a fast rotating wheel in an inert atmosphere at cooling rates of approximately 1 million Kelvin per second. The result was long and thin Nd metal strips, being approximately 0.1 mm thick, 3 mm wide and a few meters long. For the synthesis of neodymium hydrides, the metal strings were cut into small pieces that were placed in a high pressure balance (Sartorius type 7012). This balance could reach 450°C and 50 bars of H_2 pressure. Metal hydrides with compositions varying from $\text{NdH}_{2.27}$ to NdH_3 were made by hydrogenating the metal pieces, and these hydrides were used in the further synthesis. $\text{Nd}(\text{OH})_3$ was made by hydrating Nd_2O_3 in water at 50°C for 15 h. The hydroxide was gently dried and identified by its X-ray pattern. The characterization of the obtained NdHO was done under best obtainable inert conditions.

2.2. X-ray powder diffraction

The samples were studied under inert conditions using an air- and humidity tight container with an X-ray transparent Al-foil window. Powder diffraction was done in a STOE θ – θ diffractometer with Bragg–Brentano geometry. Unfiltered X-ray radiation from a Siemens 2.2 kW Cu tube illuminated the samples and the diffracted beams were analyzed by an energy dispersive Kevex detector tuned to 8.04 keV within an energy window of 300 eV. Both $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ are within this energy range, and splitting of diffraction peaks into doublets was visible at high 2θ angles.

2.3. Neutron powder diffraction

High resolution powder neutron diffraction (PND) data were collected at 293 K with the PUS two-axis diffractometer [$\lambda = 1.5554 \text{ \AA}$ obtained with a (5 1 1) focusing Ge monochromator] accommodated at the JEEP II reactor at IFE (Institute for Energy Technology, Kjeller, Norway). The sample was contained in a cylindrical vanadium container with 5 mm inner diameter, carefully sealed with an indium washer in a glove box, in order to prevent sample degradation during transport and measurement. The diffraction pattern was registered by means of two detector banks, each covering 20° in 2θ and containing a stack of seven position-sensitive ^3He detectors. 2400 data points were subsequently used in Rietveld refinements carried out by means of the GSAS suite of programs [11].

2.4. Raman spectroscopy

Raman spectra were measured with a DILOR-XY 800 mm focal length multichannel spectrometer with beam splitter coupled microscope entrance, horizontal green laser light excitation (300 mW of Ar^+ 514.5 nm or frequency doubled Nd:YVO₄ at 533 nm) and liquid N_2 -cooled CCD light detection. Rayleigh scattered light was filtered off with a double pre-monochromator (slits 300 μm). The Raman spectral resolution was about 4 cm^{-1} and the precision about $1\text{--}2 \text{ cm}^{-1}$, obtained by calibration with Raman lines from crystalline S_8 and *cyclo*-hexane. Experimental procedures are detailed in [12]. The spectra were recorded at room temperature (25°C) directly from powders in capillary glass ampoules sealed under Ar.

3. Synthesis routes

Hydroxides and oxyhydroxides of rare earth metals, taking La as example, are described as $\text{La}(\text{OH})_3$ and LaOOH , respectively. These compounds contain protons with the formal oxidation state +1. Hydrides such as CaH_2 and NdH_3 , on the other hand, contain hydride ions with the formal oxidation state –1. Oxyhydrides of the rare earth elements are thus expected to be stable only under (strongly) reducing conditions. To produce NdHO several different starting materials are possible. Fig. 1 depicts the ternary diagram between the elements neodymium, oxygen and hydrogen and indicates that several reaction paths may possibly lead to NdHO formation.

We currently hypothesize that such mixed oxide-hydrides, written as MH_2O_y , can be made by exchange of hydride and oxide ions, symbolised by the metathetic reaction (1).



The thermodynamics of reactions such as (1) have not been measured nor predicted for any metal. The high stability of the produced CaO will, however, assist in driving the reaction towards the desired $\text{MH}_{2q}\text{O}_{x-q}$ products. For $M = \text{Ca, Sr, Ti, Y, Gd}$ and Sm using the synthetic conditions mentioned under 2.1, we did not observe formation of any mixed oxyhydride phases. For instance, we observed that $\text{CaTiO}_3 + \text{CaH}_2$ reacted to give $\text{CaO} + \text{TiH}_{1.924}$. Exclusively for $M = \text{La, Ce, and Nd}$, however, we observed formation of oxyhydrides, exemplified by reaction (2)



Two alternative routes were thereafter tested:



Since NdH_3 and $\text{Nd}(\text{OH})_3$ easily give off, respectively, H_2 and H_2O upon heating, we carried out reactions (3) and (4) in sealed evacuated quartz ampoules. Both reactions (3) and (4) were found to lead to NdHO formation. A further possibility is that a reaction between Nd-metal and hydroxides and/or water-containing compounds will liberate hydrogen gas, which may react back with unconsumed Nd-metal to form Nd-hydrides as a transient

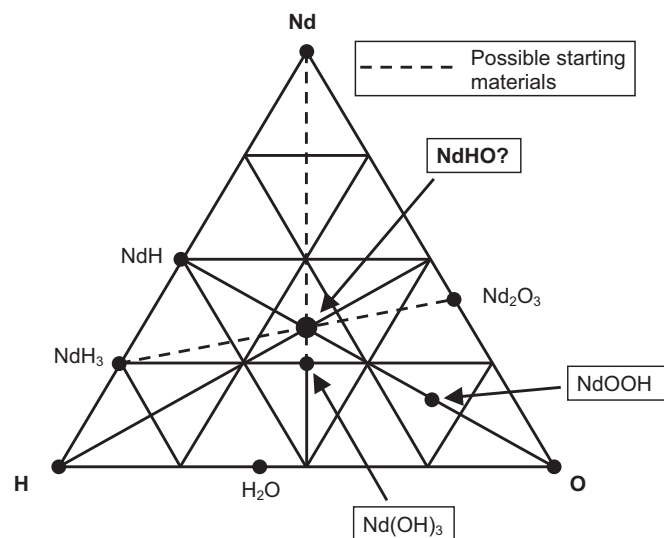


Fig. 1. Ternary diagram between neodymium, oxygen and hydrogen. Dotted lines connect some of the possible starting materials that have been investigated.

phase, assuming that the hydrogen gas cannot escape from the reaction ampoule.

4. Results

4.1. X-ray diffraction

Fig. 2 shows the obtained X-ray diffraction (XRD) pattern for a sample made from a mixture of Nd_2O_3 and CaH_2 with a ratio of 1:1.5 after being treated in a gas mixture of 7% of H_2 in Ar at a temperature of 650 °C for 20 h. The XRD pattern shows reflections from CaO while no CaH_2 is observed. In general the peaks from Nd-containing phases are much stronger than the CaO peaks, due to the higher scattering power and also the higher concentrations. A new phase, described below as NdHO, is the major Nd-containing phase in the sample. However, the sample also contains some NdH_{2+x} and unreacted Nd_2O_3 . All the remaining 30 observed XRD

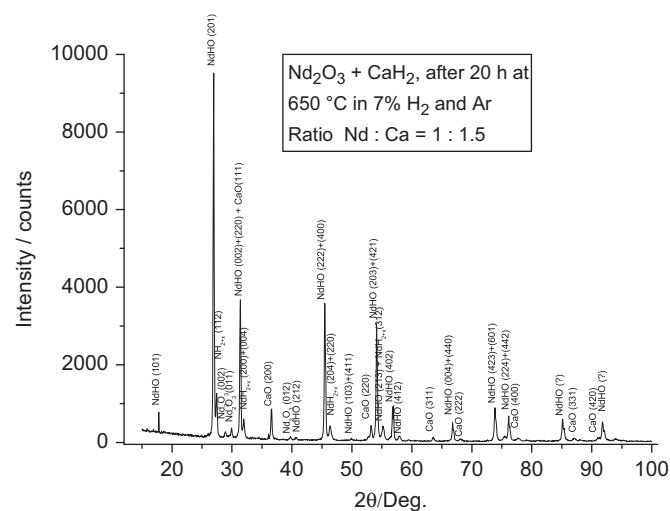


Fig. 2. X-ray diffraction pattern obtained for a sample of Nd_2O_3 + CaH_2 mixed in a 1:1.5 mole ratio heated at 650 °C for 20 h in a 93% Ar:7% H_2 gas mixture.

peaks can be indexed on the assumption of a tetragonal unit cell. This assignment was subsequently fully supported by the neutron diffraction, see below. As the molar ratio between the moles of (Nd_2O_3) to the moles of (CaH_2) is varied from 1:1 to 1:2, less and less Nd_2O_3 remains after the reaction with CaH_2 in the heat, cf. reaction (5).

4.2. Neutron diffraction and Rietveld refinement

In order to verify the presence of NdHO and to describe its crystal structure, powder neutron diffraction data were collected for a sample derived from a reaction of Nd_2O_3 and CaH_2 in a 1:1 mole ratio. The incoherent scattering from the hydrogen atoms give rise to a rather high level of background scattering, see Fig. 3. Rietveld analysis of the data in Fig. 3 proved presence of impurities of CaO (space group $Fm\bar{3}m$; 12 wt%) and Nd_2O_3 (space group $P\bar{3}m1$; 21 wt%). With no other significant impurities present, the remaining 67 wt % was identified as NdHO. The fit between the observed and the calculated intensities is included in Fig. 3. Final R-indicators for the $N_{\text{obs}}=2720$ data points were $R_{\text{wp}}=0.0411$, $R_p=0.0320$, and $R(F^2)=0.145$.

Crystal structure data for NdHO derived from the Rietveld refinements of the high resolution powder neutron diffraction data are shown in Table 1. The space group that gave the best fit was $P4/nmm$ and the unit cell dimensions were $a=7.8480(5)$ Å,

Table 1

Crystal structure data for NdHO derived from Rietveld refinements of high resolution powder neutron diffraction data. Calculated standard deviations given in parentheses. For symmetry the international symbols are given with the Schönflies symbols in parentheses.

Atom	x/a	y/b	z/c	B_{iso} (Å ²)	Wyckoff site	Symmetry
Nd1	0.75	0.25	0.00	0.98(7)	2a	$m2 (D_{2d})$
Nd2	0.25	0.25	0.9440(17)	0.98(7)	2c	$4mm (C_{4v})$
Nd3	0.00	0.00	0.50	0.98(7)	4e	$2/m (C_{2h})$
O	0.25	0.5064(23)	0.7432(29)	1.52(10)	8i	$m (C_s)$
H	0.25	0.515(4)	0.261(5)	3.4(3)	8i	$m (C_s)$

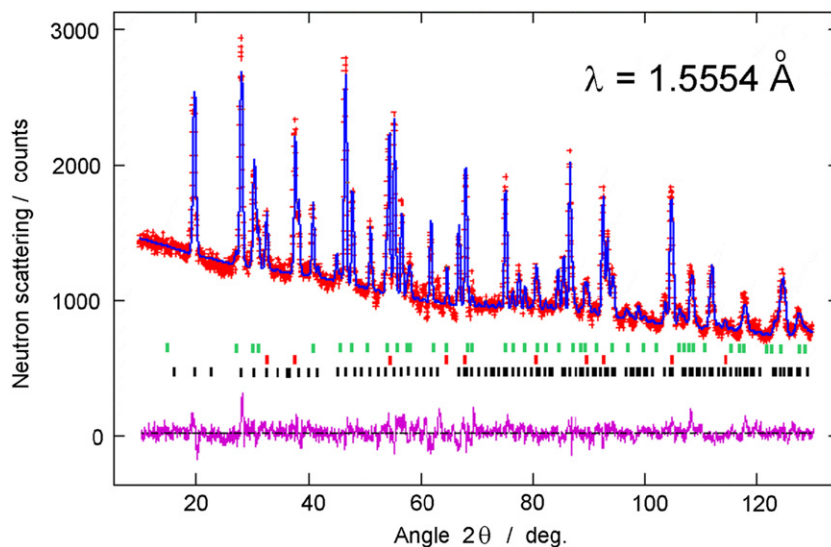


Fig. 3. Neutron diffraction from a powder sample derived from the reaction of Nd_2O_3 with CaH_2 in a 1:1 mole ratio. The fit between the Rietveld calculated intensities (blue curve) and the observed data points (red crosses) is obvious (difference curve between observed and calculated intensities shown at the bottom). Bragg peak positions are shown as bars for Nd_2O_3 (upper green), CaO (middle red) and NdHO (lower black ones). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

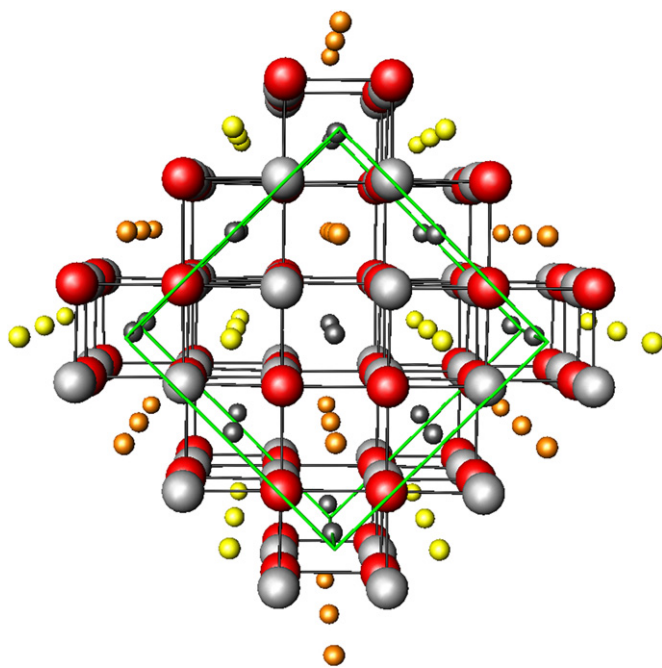


Fig. 4. View of the NdHO structure. Small orange (or dark gray) spheres represent Nd1, yellow (or light gray) ones Nd2, and black ones Nd3. Larger red (or dark) spheres represent oxygen and gray-white ones hydrogen atoms.

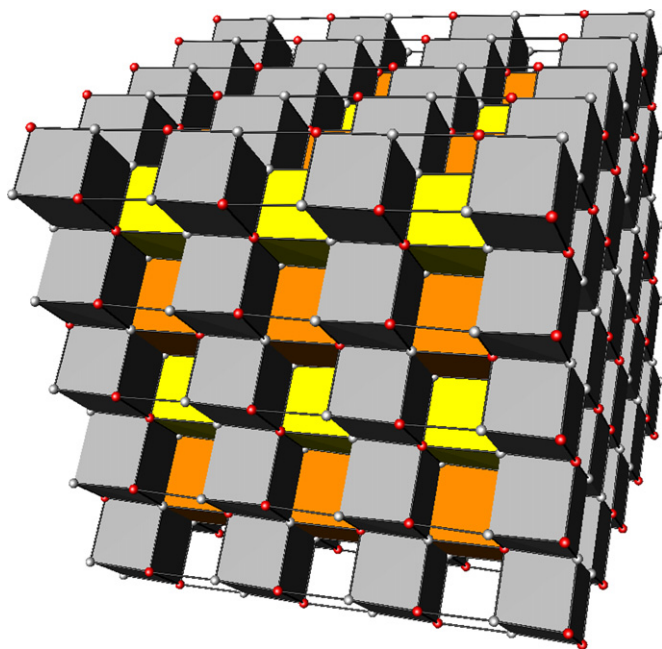


Fig. 5. Alternative sketch of the NdHO structure. Orange (or darker gray) cubes contain Nd1, yellow (or light) ones Nd2, while grey ones contain Nd3. Small red (or dark) spheres represent oxygen and white ones hydrogen atoms.

$c=5.5601(8)$ Å and unit cell volume $V=342.46(6)$ Å³. Other space groups with similar X-ray diffraction absences like $P4/n$ (no. 85) gave inferior fits.

Fig. 4 shows the NdHO structure, calculated with the program ATOMS by means of the crystal structure parameters from Table 1 and the tetragonal space group $P4/nmm$ (no. 129) axes choice 2, D_{4h}^2 . Similarly, the packing of the polyhedra is depicted in Fig. 5.

Table 2

Calculated interatomic distances for NdHO. Calculated standard deviations in parentheses.

Central atom	Distance to atom (Å)	Distance to atom (Å)	Distance to atom (Å)
Nd1	O ($\times 4$) 2.386(19)	H ($\times 4$) 2.346(32)	
Nd2	O ($\times 4$) 2.301(17)	H ($\times 4$) 2.728(29)	
Nd3	O ($\times 4$) 2.384(9)	H ($\times 4$) 2.372(17)	
O	Nd1 2.386(19)	Nd2 2.301(17)	Nd3 ($\times 2$) 2.384(9)
H	Nd1 2.346(32)	Nd2 2.728(29)	Nd3 ($\times 2$) 2.372(17)

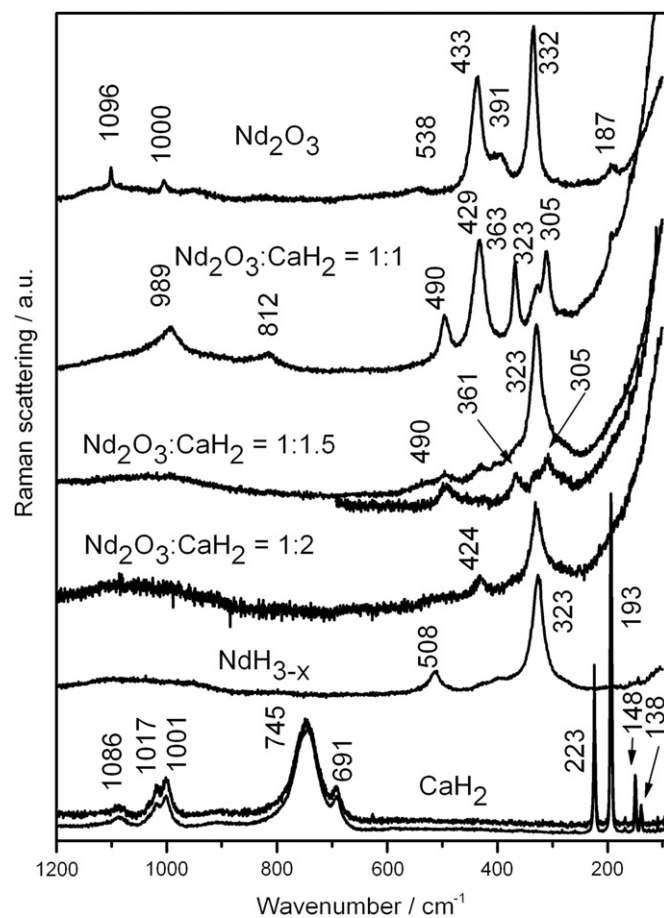


Fig. 6. Raman spectra of powder samples in sealed ampoules at room temperature: from top Nd_2O_3 , $\text{Nd}_2\text{O}_3:\text{CaH}_2=1:1$, $\text{Nd}_2\text{O}_3:\text{CaH}_2=1:1.5$ (two curves), $\text{Nd}_2\text{O}_3:\text{CaH}_2=1:2$, NdH_{3-x} , and CaH_2 (two curves). Calibrated wavenumber shifts given. Excitation was done with Ar^+ laser light (514.5 nm) except for CaH_2 , which was excited with frequency-doubled Nd:YVO₄ laser light (533 nm). The bands were also seen in anti-Stokes spectra.

The structure contains three different hydride-oxygen coordination environments around the Nd^{3+} cations, see Table 2. In all cases four hydride ions and four oxide ions form the cube coordination polyhedron around neodymium. Nd1 has an environment of distorted tetrahedral C_{4v} symmetry; Nd2 has four identical anions (C_{4v} symmetry) on corners of a “tetragonal cube”, whereas Nd3 has only a “face diagonal arrangement” and mirror plane (C_s) symmetry.

4.3. Lattice vibrations of NdHO observed by Raman spectroscopy

Raman spectroscopy was used as a supplementary tool for further probing existence and properties of the new NdHO

Table 3

Symmetry and unit cell dimensions for so far known rare earth oxyhydrides. Calculated standard deviations in parentheses.

Material	Space group	<i>a</i> (Å)	<i>c</i> (Å)
LaHO [2]	<i>P4/nmm</i>	8.074(1)	5.739(1)
CeHO [2]	Not verified	7.97	5.63
PrHO [3]	Not verified	7.88	5.57
NdHO, this work	<i>P4/nmm</i>	7.8480(5)	5.5601(8)

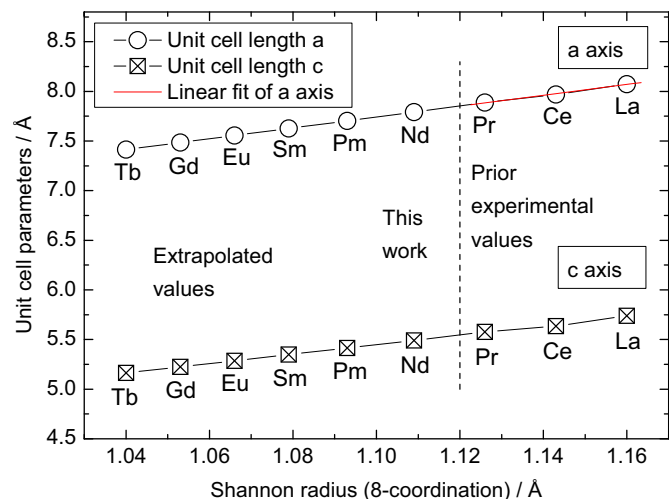
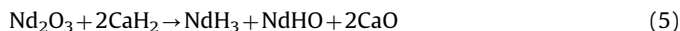


Fig. 7. Observed and estimated unit cell parameters of rare earth oxyhydrides as function of the 8-coordinated ionic radius from Shannon [13].

oxyhydride. The method has advantages, since it is possible to analyze hygroscopic or otherwise reactive samples in a sealed container, and because one of the possible reaction products, CaO, does not show up in Raman scattering processes and hence will not obscure the spectrum (in contrast to this, CaO is active in IR). The other starting materials Nd_2O_3 , CaH_2 and NdH_{3-x} have distinct Raman spectra. There are no data available in the literature for vibrational spectra of the already established oxyhydrides LaHO, CeHO and PrHO.

Fig. 6 shows our recorded spectra for the reaction mixtures. The spectra show that the strongest CaH_2 peaks at 745 and 193 cm^{-1} completely disappear and thus that all CaH_2 is consumed in the reaction with Nd_2O_3 as illustrated for the 1:2 reaction mixture



Peaks assigned to the NdHO phase are observed at 490, 361–363 and 305 cm^{-1} . The strong feature around 323 cm^{-1} possibly stems from fully hydrided NdH_3 .

5. Discussion

In Table 3 the present crystal structure data for NdHO is compared with previous results on LaHO, CeHO and PrHO as

obtained by Brice and Moreau [2] and Malaman and Brice [3]. It is likely that all these phases crystallize in the same *P4/nmm* space group. There is a small decrease in the unit cell dimensions for increased atomic number of the rare earth elements, consistent with the lanthanide contraction (La, Ce, Pr, and Nd have numbers 57, 58, 59 and 60, respectively).

Fig. 7 shows experimental and predicted unit cell parameters of the rare earth oxyhydrides as a function of the eight-coordinated ionic radius, as given by Shannon [13]. Experimental values for the *a* and *c* axes for La, Ce and Pr are taken from [2,3]. For the elements Nd to Tb the unit cell dimensions are calculated by linear extrapolation of the values for La, Ce and Pr. Fig. 7 thus predicts that the *a* and *c* axes of NdHO should be 7.79 and 5.49 Å, respectively. This is indeed close to the measured values. The question remains still open as to whether it is possible to make oxyhydrides of the heavier rare earths and whether they take the same crystal structure.

6. Conclusions

The present investigation has verified the formation of a new metal oxyhydride NdHO, obtainable from a reactant mixture of metal hydride (metal=Ca and Nd) and neodymium oxide under reducing atmosphere. The use of a small surplus of the metal hydride reactant gave the highest yield of NdHO in the resulting product. NdHO appears to be formed via a solid state reaction which involves interdiffusion of oxide and hydride ions. The oxide and hydride anions are fully ordered in the fluorite related structure. It can be speculated whether slight variations in the hydride to oxide ratio may be introduced by heterovalent doping, and whether the resulting material may provide a new material with mixed hydride ion and oxygen ion conducting properties.

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