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# Polymorphism and hydrogen discharge from holmium borohydride, $\text{Ho}(\text{BH}_4)_3$ , and $\text{KHo}(\text{BH}_4)_4$ \*

Wojciech Wegner<sup>a</sup>, Tomasz Jaron<sup>b,\*</sup>, Wojciech Grochala<sup>b</sup>

<sup>a</sup> Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

<sup>b</sup> Centre of New Technologies, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw, Poland

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## ABSTRACT

Holmium borohydride,  $\text{Ho}(\text{BH}_4)_3$ , its composites with  $\text{LiBH}_4$ , and a mixed-cation derivative,  $\text{K}[\text{Ho}(\text{BH}_4)_4]$ , have been prepared via mechanochemical reaction between  $\text{HoCl}_3$ ,  $\text{LiBH}_4$  (and also  $\text{KBH}_4$  in case of  $\text{K}[\text{Ho}(\text{BH}_4)_4]$ ). These compounds are isostructural to the related rare earth borohydrides, adopting  $\alpha\text{-Y}(\text{BH}_4)_3$ ,  $\beta\text{-Y}(\text{BH}_4)_3$ , and  $\text{Na}[\text{Sc}(\text{BH}_4)_4]$ -type structures, respectively. The relative amount of  $\alpha\text{-Ho}(\text{BH}_4)_3$  and  $\beta\text{-Ho}(\text{BH}_4)_3$  can be controlled by the composition of reagents. While  $\beta\text{-Ho}(\text{BH}_4)_3$  has not been obtained from stoichiometric mixtures of  $\text{HoCl}_3$  and  $\text{LiBH}_4$ , the excess of  $\text{LiBH}_4$  favours it as the main product. Thermal decomposition of  $\alpha\text{-Ho}(\text{BH}_4)_3$ , as well as  $\text{K}[\text{Ho}(\text{BH}_4)_4]$  commences above 170 °C, with the fastest rate within 250–260 °C, which is slightly lower than for the corresponding borohydrides of yttrium.  $\text{LiBH}_4$  is destabilised thermally in the composites with  $\beta\text{-Ho}(\text{BH}_4)_3$ , which leads to desorption of >40% total amount of  $\text{H}_2$  below 450 °C, while in case of pure  $\text{LiBH}_4$  only <20% total amount of  $\text{H}_2$  is released in these conditions. The catalytic mechanism is as yet unknown.

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## Introduction

Storage of hydrogen fuel is a crucial unresolved problem hampering application of hydrogen as an energy carrier [1,2]. Utilisation of hydrogen-rich chemical compounds for on-board hydrogen storage appears one of the most promising solutions. Metal borohydrides rank among the most hydrogen-rich groups of compounds and attract attention as potential chemical hydrogen stores [3,4]. However, the borohydrides explored so far reveal serious drawbacks, e.g. either too high or too low temperature of hydrogen release, difficult reversibility and contamination of evolved hydrogen with

$\text{B}_2\text{H}_6$ , which obstruct their application but also triggers the search towards new systems. Consequently, various novel borohydride-based materials have been prepared and investigated lately, including simple or mixed-cation borohydrides (e.g.  $\text{Cd}(\text{BH}_4)_2$  [5],  $\text{Li}_3\text{MZn}_5(\text{BH}_4)_{15}$ ,  $\text{M} = \text{Mg}, \text{Mn}$  [6]), anion-substituted borohydrides (e.g.  $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$  [7]), borohydride ammoniates and related compounds (e.g.  $\text{Mg}(\text{BH}_4)_2 \cdot \text{NH}_3$ ,  $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ ,  $\text{Li}_2(\text{NH}_2\text{BH}_3)(\text{BH}_4)$  [8–10]), as well as composite materials (e.g.  $\text{LiBH}_4/\text{MgH}_2$  [11]).

While the transition metal borohydrides have drawn significant attention in the mid XX century [12–14], the upsurge of interest in solvent-free homoleptic borohydrides of rare-earth (RE) metals has been seen only recently, particularly

\* This work is dedicated to Prof. Grzegorz Chalasinski at his 65th birthday.

\* Corresponding author.

E-mail address: [tjaron@uw.edu.pl](mailto:tjaron@uw.edu.pl) (T. Jaron).

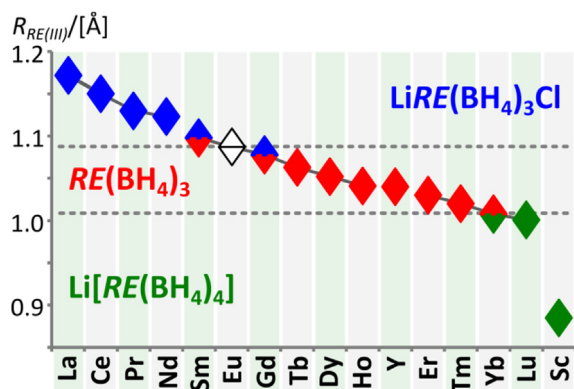
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for lanthanide borohydrides [15–20]. Miscellaneous borohydride materials containing rare-earth metals have been synthesised mechanochemically in reaction of  $\text{RECl}_3$  with  $\text{LiBH}_4$  in various stoichiometric ratios (1:3–1:6), Fig. 1. The actual products of such synthesis depend on the ionic radius of  $\text{RE}^{3+}$  ion: for the biggest cations ( $\text{La}^{3+}$ – $\text{Nd}^{3+}$ ) only the cubic borohydride chloride,  $\text{LiRE}(\text{BH}_4)_3\text{Cl}$ , have been detected, while for slightly smaller  $\text{Sm}^{3+}$  and  $\text{Gd}^{3+}$   $\text{LiRE}(\text{BH}_4)_3\text{Cl}$  compounds coexist with cubic simple borohydride,  $\text{RE}(\text{BH}_4)_3$ , which is the only product for  $\text{Tb}^{3+}$ – $\text{Tm}^{3+}$  as well as for  $\text{Y}^{3+}$ . The smallest  $\text{RE}^{3+}$  cations,  $\text{RE} = \text{Yb}, \text{Lu}, \text{Sc}$ , act here as the strongest Lewis acids and show tendency to form complex  $[\text{RE}(\text{BH}_4)_4]^-$  anions. In consequence, the simple  $\text{RE}(\text{BH}_4)_3$ , for  $\text{RE} = \text{Lu}$  and  $\text{Sc}$ , have not been reported, and a mechanochemical reaction between  $\text{RECl}_3$  and  $\text{LiBH}_4$  leads in these cases to tetragonal mixed-cation borohydrides,  $\text{Li}[\text{RE}(\text{BH}_4)_4]$ , as the only borohydride-containing products [20,21]. This simple picture of RE borohydride materials prepared in mechanochemical reactions is complicated by the polymorphism of  $\text{RE}(\text{BH}_4)_3$  [22,23,30], and also by the redox properties of Sm, Eu and Yb (i.e. their stable + II oxidation state). In fact, despite the attempts of synthesis of  $\text{Eu}(\text{BH}_4)_3$ , no europium(III)-containing borohydride has been identified yet [20].

$\text{RE}-\text{BH}_4$  systems release most of hydrogen between 200 and 300 °C, which is considerably lower than in case of the alkaline metal borohydrides (e.g.  $\text{LiBH}_4 > 380$  °C,  $\text{NaBH}_4 > 400$  °C [24]). Beyond hydrogen storage, such systems are also interesting as potential ionic conductors – high lithium ion conductivity has been reported for lanthanide borohydride chlorides,  $\text{LiRE}(\text{BH}_4)_3\text{Cl}$ ,  $\text{RE} = \text{La}, \text{Ce}, \text{Gd}$  [25,26], as well as the polymerisation catalysts (various RE complexes containing borohydride anion) [27,28]. Moreover, as metal borides,  $\text{REB}_x$ ,  $x = 4, 6$ , are often the final thermal decomposition products of RE borohydrides [29,30], the latter could serve as the precursors towards those refractory metal borides, which are usually synthesised from the elements under harsh temperature conditions [31,32].

Herein we expand the chemistry of RE borohydrides reporting on the synthesis and polymorphism of novel



**Fig. 1** – Borohydride phases prepared in mechanochemical reactions of  $\text{RECl}_3$  and  $\text{LiBH}_4$  compared to the  $\text{RE}^{3+}$  crystal ionic radii in octahedral environment [50]. Note that no borohydride of europium has yet been identified. Data from the refs [15,20,21], Ho – this work.

holmium compounds:  $\text{Ho}(\text{BH}_4)_3$ , and its derivative,  $\text{K}[\text{Ho}(\text{BH}_4)_4]$ . We put an emphasis on their structural and thermal characterisation, as well as discuss the control of relative amount of  $\alpha$ - $\text{Ho}(\text{BH}_4)_3$  and  $\beta$ - $\text{Ho}(\text{BH}_4)_3$  polymorphs by varying composition of the disc-milled reagent mixture.

## Experimental details

All reactions were performed and samples were stored in argon atmosphere of the MBRAUN Labmaster DP glovebox ( $\text{O}_2$  &  $\text{H}_2\text{O} < 1$  ppm). All reagents were fine quality anhydrous chemicals bought from Sigma Aldrich ( $\text{LiBH}_4 > 95\%$ ,  $\text{KBH}_4 > 99.9\%$ ,  $\text{HoCl}_3 > 99.99\%$ ).

Mechanochemical reactions were carried out in stainless steel and silicon carbide (SiC) bowls using LMW–S vibrational mill from Testchem (1400 rpm, ca. 23.3 Hz). Reactants were weighted, introduced to the bowl and milled for 1 h at room temperature. The milling was performed in 5 min periods, while the bowl was slightly cooled with liquid nitrogen to avoid overheating and thermal decomposition of the products. Milling was done for the mixtures of  $\text{HoCl}_3$  and  $\text{LiBH}_4$  in molar ratios of 1:3.15 (5% excess of  $\text{LiBH}_4$ ), 1:4, 1:9 and 1:12. Also milling of the mixture of  $\text{HoCl}_3$ ,  $\text{LiBH}_4$  and  $\text{KBH}_4$  in molar ratios of 1:3:1 was performed for preparation of  $\text{K}[\text{Ho}(\text{BH}_4)_4]$ .

Fourier Transform Infrared spectra (FTIR) in the 4000–400  $\text{cm}^{-1}$  range were measured using Vertex 80v FTIR spectrometer (Bruker). Anhydrous KBr was used as a pellet material (200 mg per pellet).

Powder X-ray diffraction (PXRD) measurements were performed using Panalytical X'Pert Pro diffractometer (parallel beam; the  $\text{CoK}\alpha_1$  and  $\text{CoK}\alpha_2$  radiation intensity ratio of ca. 2:1); a fine PXD measurement of  $\text{K}[\text{Ho}(\text{BH}_4)_4]$  has been performed using Bruker D8 Discover diffractometer (parallel beam; the  $\text{CuK}\alpha_1$  and  $\text{CuK}\alpha_2$  radiation intensity ratio of ca. 2:1). Samples were sealed under argon inside 0.3 mm quartz capillaries to avoid exposition to the atmospheric moisture. Rietveld refinement has been performed in Jana2006 [33]. The pseudo-Voigt peak shape function and Berar–Baldinazzi asymmetry correction were used; the background was described with 25–30 Legendre polynomials. The structures of  $\alpha$ - $\text{Ho}(\text{BH}_4)_3$ ,  $\beta$ - $\text{Ho}(\text{BH}_4)_3$  and  $\text{K}[\text{Ho}(\text{BH}_4)_4]$  were refined in the previously reported structures of  $\alpha$ - $\text{Y}(\text{BH}_4)_3$ ,  $\beta$ - $\text{Y}(\text{BH}_4)_3$  and  $\text{Na}[\text{Sc}(\text{BH}_4)_4]$ , respectively [15,23,36]. During the Rietveld refinement of all structures described here the restraints have been applied to the H–B–H angles and B–H distances in  $\text{BH}_4$  groups: 109.47° (with a standard uncertainty, s.u. = 0.01°) and 1.15 Å (s.u. = 0.001 Å), respectively. In case of  $\text{K}[\text{Ho}(\text{BH}_4)_4]$  and both polymorphs of  $\text{Ho}(\text{BH}_4)_3$ , Ho–H distances concerning bridge hydrogen atoms of tridentate  $\text{BH}_4^-$  anions were set equal with s.u. = 0.05 Å and s.u. = 0.001 Å, respectively. Moreover, the atomic displacement parameters (ADP) of hydrogen atoms were fixed as 1.2 ADP of boron atoms.

The details of the crystal structures of the new compounds may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: [crysdata@fizkarlsruhe.de](mailto:crysdata@fizkarlsruhe.de)) on quoting their CSD numbers: 427981 –  $\alpha$ - $\text{Ho}(\text{BH}_4)_3$ , 427982 –  $\beta$ - $\text{Ho}(\text{BH}_4)_3$ , 427983 –  $\text{K}[\text{Ho}(\text{BH}_4)_4]$ .

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