



Preparation of a series of lanthanide borohydrides and their thermal decomposition to refractory lanthanide borides

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This work is dedicated to prof. Z. R. Grabowski in memoriam.

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ABSTRACT

Several solvent-free borohydrides of trivalent lanthanides (Nd–Lu) and their composites with LiBH₄ have been targeted utilizing mechanochemical synthesis, and physicochemically characterized. Overall, the eight new borohydride phases are reported, which include the two polymorphs of the previously elusive Eu(BH₄)₃, completing the series of the known inorganic borohydrides of trivalent lanthanides. Thermolysis of borohydrides yielded refractory lanthanide borides; the attempts of purification of the post-thermolysis composites were unsuccessful.

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1. Introduction

Metal borohydrides are among the most hydrogen-rich chemical compounds, hence they attract attention as potential on-board chemical hydrogen storage materials [1,2]. This stimulated investigation of numerous new borohydride systems. Among them, the solvent-free lanthanide borohydrides gained recent interest due to release of pure hydrogen, revealed ionic conductivity and interesting magnetic and luminescent properties [3–13].

As the borohydrides of La, Ce and Pr have been rather extensively characterized [3,14,15] we focus our present study on borohydrides of the heavier lanthanides: Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. We characterize their polymorphic forms structurally and investigate their thermal decomposition process, including their composites with the high LiBH₄ content. The case of Eu is special here, since despite the experimental effort made to date, no quasi-binary borohydride of the trivalent Eu has been

unambiguously reported [5,7,8]. The reason for that is that Eu(III) is easily reduced in borohydride environment, and the resulting Eu(II) is the most stable divalent lanthanide cation, which resembles strontium in many aspects.

Borohydrides have usually been studied as sources of hydrogen; however, the solid residue of their decomposition is also of interest. As the evolution of hydrogen from most of RE(BH₄)₃ results in remaining of metal and boron in the sample, it can lead to formation of metal borides. Therefore, we also tested a few selected metal borohydrides as precursors towards the refractory metal borides [16]. The said borides are usually synthesized from the elements or their binary compounds under extremely harsh temperature conditions (ca. 2000 °C) [17,18], while thermal decomposition of borohydrides occurs at a few hundred centigrade, thus bypassing the extreme thermal regime needed for their synthesis.

2. Experimental

All reactions were performed and samples were stored in argon atmosphere of the MBRAUN glovebox (O₂ < 1 ppm, H₂O < 1 ppm). All reagents were fine quality anhydrous chemicals purchased from Sigma Aldrich (LiBH₄ > 95%, RECl₃ > 99.9%).

Mechanochemical reactions were carried out in stainless steel

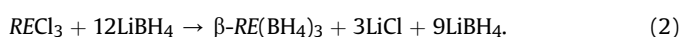
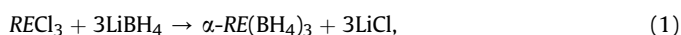
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bowl with a disc-shaped milling element, using LMW–S vibrational mill from Testchem (1400 rpm, ca. 23.3 Hz). Milling was performed in 5 min periods. Between the periods the milling bowl was slightly cooled using liquid nitrogen to avoid overheating and thermal decomposition of the products.

In case of mechanochemical reaction (Eq. (1)) for $RE = \text{Eu}$ three different synthetic protocols were applied: $T = -200^\circ\text{C}$ (LN2), $T = 0^\circ\text{C}$, and room temperature (RT) conditions ($T = 25^\circ\text{C}$). PXRD measurements for all products were performed at 230 or 240 K, followed by the measurements at RT. All other samples were routinely synthesized at RT, when a typical milling time for reaction (Eq. (1)) and (Eq. (2)) being 20 min and 60 min, respectively (more technical data is contained in Table 1 and Table 2). It is worth mentioning that larger RE^{3+} require longer time of milling to complete both reactions.



Powder X-Ray diffraction (PXRD) measurements were performed using Bruker D8 Discover diffractometer with parallel beam and the $\text{CuK}_{\alpha 1}$ and $\text{CuK}_{\alpha 2}$ radiation with intensity ratio of ca. 2:1. Samples were sealed under the argon atmosphere inside of 0.3 or 0.5 mm quartz capillaries.

Rietveld refinements were performed using Jana2006 [19]. These results for most of the new compounds are placed in ESI. The preliminary structural models used for refinement were $\alpha\text{-}Y(\text{BH}_4)_3$ and $\beta\text{-}Y(\text{BH}_4)_3$ [6,20], for all $\alpha\text{-}RE(\text{BH}_4)_3$ and $\beta\text{-}RE(\text{BH}_4)_3$ respectively, $\text{LiY}(\text{BH}_4)_4$ [28] for $\text{LiRE}(\text{BH}_4)_{4-x}\text{Cl}_x$ and $[\text{ErCl}_2(\text{H}_2\text{O})_6]\text{Cl}$ [38] for $[\text{TmCl}_2(\text{H}_2\text{O})_6]\text{Cl}$. Peak shapes were described using pseudo-Voigt functions. If needed, peak asymmetry has been accounted for using Berar–Baldinazzi function. The background was described by 30 Legendre polynomials. During the Rietveld refinement application of a set of restraints was necessary: H–B–H angles and B–H distances in BH_4 groups have been fixed at 109.47° and 1.15 \AA with a standard uncertainty s.u. = 0.01° and 0.001 \AA , respectively. The ADP (Atomic Displacement Parameters) of hydrogen atoms were fixed as 1.2 ADP of boron atoms. Additionally, in case of $\text{LiYb}(\text{BH}_4)_4$ the ADP of lithium atoms were fixed to be the same as those of boron atoms. The RE–H distances for coordinating hydrogens from borohydrides groups were fixed to be equal (with s.u. = 0.001 \AA). Vesta software has been used for visualization of the structures [21].

Fourier Transform Infrared (FTIR) spectra in the $4000\text{--}400 \text{ cm}^{-1}$ range were measured using Vertex 80v FTIR spectrometer from Bruker. Anhydrous KBr (Sigma Aldrich) was

used as a pellet material (200 mg per pellet of 12 mm diameter).

Thermal decomposition of the samples placed inside Al_2O_3 crucibles has been investigated with combined thermogravimetry (TGA) and differential scanning calorimetry (DSC) measurements, using Netzsch STA 409 PG. Measurement was performed at a constant flow (80 mL/min) of argon (purity: 5–6 N) and at $5^\circ\text{C}/\text{min}$ heating rate. The evolved gas was analyzed using a quadrupole mass spectrometer (MS) from Pfeiffer Vacuum (QMS 403C), connected to the Netzsch device by quartz capillary preheated to 200°C to avoid condensation of low-boiling volatiles. After the measurement, samples were slowly cooled down to room temperature, and the solid products of thermal decomposition were analyzed using PXRD and FTIR. In order to obtain larger batch of solid residue, a tubular furnace from Carbolite (model GHA 12/300) was used with constant flow of argon. Samples were loaded into a Pt boat placed inside a quartz sample tube.

SEM images have been obtained using a Merlin electron microscope from Zeiss. The selected products of thermal decomposition after TGA/DSC measurements were examined.

3. Results and discussion

3.1. Synthesis of lanthanide borohydrides and analysis of the products

Although the homoleptic monometallic borohydrides of most lanthanides and of related yttrium have been prepared, yet not in the pure form; most often the composite samples with the large excess of the LiBH_4 precursor were studied (e.g. a mechanochemical reaction of RECl_3 with six equivalents of LiBH_4 was carried out [5]). In such composites the remaining LiBH_4 is destabilized by the presence of borohydride, and effectively, more hydrogen is released from the system as compared to the hypothetical $RE(\text{BH}_4)_3$ system alone [12]. The reported composites, however, often contained significant amount of different impurities, which can alter the thermal decomposition pathways, rendering their analysis problematic.

Recently, two new methods of borohydride synthesis have been introduced to overcome these problems – the first one is based on a metathesis mediated by dimethyl sulfide (DMS), and the second employs the weakly coordinating anion (WCA) salts [22,23]. While the latter method is predominantly used to prepare mixed-cation borohydrides, the first approach delivers quasi-binary borohydride salts, such as those targeted in this work. Regretfully, synthetic protocol results in a DMS-containing intermediate which needs to be later desolvated at elevated temperature while yielding the homoleptic metal borohydride. The applicability of the method

Table 1
Crystalline products of the type (1) reaction for $RE = \text{Nd-Lu}$ and the products of their thermal decomposition to 650°C . nd – not determined, [] – signals fade in time at RT in the X-ray beam.

RE	Reaction conditions	Crystalline products (synthesis)	Crystalline products (heating to 650°C)
Nd	20 min	NdCl_3 , LiCl	nd
Sm	20 min	$\alpha\text{-Sm}(\text{BH}_4)_3$, LiCl, $[\text{SmCl}_3]$	nd
	60 min	$\alpha\text{-Sm}(\text{BH}_4)_3$, LiCl	Sm_2O_3^a , LiCl
Eu	30 min (LN2, 0°C)	EuCl_3	nd
	30 min (RT)	EuCl_3 , LiCl, $[\alpha\text{-Eu}(\text{BH}_4)_3]$	nd
Gd	20 min	GdCl_3 , $\alpha\text{-Gd}(\text{BH}_4)_3$, LiCl	Gd_2O_3^a , LiCl
Tb	20 min	$\alpha\text{-Tb}(\text{BH}_4)_3$, LiCl, TbCl_3	Tb_2O_3^a , LiCl
Dy	20 min	$\alpha\text{-Dy}(\text{BH}_4)_3$, LiCl	DyB_4 , Dy_2O_3^a , LiCl
Ho	60 min	$\alpha\text{-Ho}(\text{BH}_4)_3$, LiCl	HoB_4 , Ho_2O_3^a , LiCl
Er	20 min	$\alpha\text{-Er}(\text{BH}_4)_3$, LiCl	ErB_4 , Er_2O_3^a , LiCl
Tm	60 min	$\alpha\text{-Tm}(\text{BH}_4)_3$, LiCl	TmB_4 , Tm_2O_3^a , LiCl
Yb	20 min	$\text{LiYb}(\text{BH}_4)_3\text{Cl}$	nd
Lu	20 min	$\text{LiLu}(\text{BH}_4)_3\text{Cl}$	LuB_2 , Lu_2O_3^a , LiCl

^a - RE_2O_3 formed after exposure unknown phase in sample to air.

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