Hydrogen storage properties of rare earth (RE) borohydrides
(RE = La, Er) in composite mixtures with LiBH₄ and LiH.

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Abstract

Mixtures of 6LiBH₄-RECl₃-3LiH (RE=La, Er) have been produced by mechanochemical milling and their structure, thermal decomposition and reversibility have been studied. Hydrogen desorption starts around 300 °C in both composites. Heating to 400 °C yields LaB₆, ErB₄ and REH₂+δ as major decomposition products. LiBH₄ is destabilized by REH₂+δ formed through decomposition of the parent borohydrides LiLa(BH₄)₃Cl and Er(BH₄)₃, respectively, and its hydrogen release temperature is reduced by 100 °C as compared to pure ball-milled LiBH₄. The lanthanum-containing composite releases 4.2wt% H between 300 and 350 °C and shows a limited reversibility of ~20% (340 °C, 10 MPa) probably due to hydrogen uptake by some amorphous boron-containing phases. For 6LiBH₄-ErCl₃-3LiH about 3wt% H is evolved up to 400 °C. Desorption against 0.5 MPa backpressure results in an increased reversibility (~80

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% as compared to vacuum (~66 %). Rehydrogenation (340 °C, 10 MPa) shows the formation of ErH₃ and LiBH₄ at drastically reduced conditions compared to pure LiBH₄ (>400 °C, >10 MPa).

**Introduction**

Rare earth (RE) borohydrides have received considerable attention during the past 5 years due to their rich crystal chemistry [1-7] and potential as both solid state hydrogen storage materials [8-15] and solid state electrolytes [16-18]. Special interest has been directed lately towards the development of easy and facile synthesis routes for solvent-free borohydrides [19-21]. Mechanochemical synthesis that utilizes a metathesis reaction between a RE-chloride and an alkali metal borohydride (mostly LiBH₄) is now the standard technique for the synthesis of RE-borohydrides. We have recently reviewed the crystal chemistry and thermal properties of ball-milled mixtures between RECl₃ and LiBH₄ [2]. We observe the formation of a series of RE-borohydrides with four distinct structure types which are determined by the ionic radius of the RE and its electronic configuration. The early lanthanides La, Ce, Pr, and Nd form LiRE(BH₄)₃Cl compounds (cubic; I-43m), Sm, Gd, Tb, Er and Yb form α-RE(BH₄)₃ (cubic; Pa-3) with a possible polymorphic transition to β-RE(BH₄)₃ for Y, Yb (cubic; Pm-3m or Fm-3m) [1-3, 5-7, 11, 16, 17]. The smallest lanthanides Yb and Lu form tetrahedral [RE(BH₄)₄]⁻ anionic complexes that are stabilized by Li⁺ cations (tetragonal; P-42c) in analogy to LiSc(BH₄)₄ [22]. Furthermore, Sm and Gd show transitions to the LiRE(BH₄)₃Cl structure type that is observed for the largest lanthanide ions [17].

The RE-borohydrides obtained by mechanochemical synthesis decompose between 200 and 300 °C [5, 6, 11, 12, 16, 17], which is considerably lower than pure LiBH₄ [23]. With the exception of Yb-based compounds [3], they release primarily hydrogen and form RE-hydrides and borides as the major decomposition products. Gennari et al. have recently reported the destabilization of LiBH₄ via the formation of RE-hydrides in 6LiBH₄-RECl₃ composites (RE= Ce, Gd) [13]. We have extended this study to a
wide range of novel RE borohydrides [2]. Here, we present new experimental results based on ex-situ powder X-ray diffraction (PXD), thermogravimetric and caloric measurements (TG/DSC), and cycling experiments for La- and Er-based borohydrides in composite mixtures with LiBH₄ and LiH. We elucidate the nature of products formed during different experimental conditions, e.g. decomposition under back pressure and vacuum. Finally, we compare the hydrogen storage properties and benchmark the reversibility of the La- and Er-based composites against previously investigated 6LiBH₄-RECl₃-3LiH systems (RE=Ce, Gd).

Experimental

Sample Preparation: LiBH₄ (Sigma-Aldrich, >95%), LaCl₃ and ErCl₃ (both Sigma-Aldrich, > 99.99%) in a 6:1 ratio were first milled in a Fritsch Pulverisette 6 at 400 rpm with a milling time of 5 hours. In the second step, LiH (Sigma-Aldrich >95%) was added (molar ratio LiH:RE = 3) and milled for an additional hour. Stainless steel vial and balls were used and a ball-to-powder ratio of 40:1 was applied. All sample handling was performed under strictly inert conditions and samples were stored in an MBraun glove box fitted with recirculation system and oxygen/humidity sensors. Oxygen and water levels were kept below 1 ppm during all operations.

PXD: Patterns were collected in transmission mode using Cu-Kα radiation (1.5418 Å) in a Bruker AXS D8 Advance diffractometer equipped with a Göbel mirror and LynxEye™ 1D strip detector. In addition, Synchrotron Radiation (SR) PXD patterns with a wavelength of 0.50513 Å were recorded at the Swiss-Norwegian Beam Line (SNBL, BM01B) at ESRF, Grenoble, in France. Data were collected with a Dexela-Perkin Elmer 2923 CMOS pixel detector. All samples were contained in rotating boron glass capillaries (0.5 mm diameter) filled and sealed under Ar atmosphere.
Simultaneous TG/DSC experiments were conducted under flowing Argon gas (flow: 50 ml/min) in a Netzsch STA 449 F3 Jupiter instrument between room temperature (RT) and 400 °C with a heating rate of 2 °C/min. Samples were contained in Al crucibles fitted with pierced lids. The data were baseline corrected using two empty Al pans in the reference and sample position which were heated under identical conditions. The desorbed gases were analyzed with a MKS Microvision-IP residual gas analyzer (RGA) by mass spectroscopy (MS).

Dehydrogenation and rehydrogenation: The 6LiBH₄·RECl₃ and 6LiBH₄·RECl₃·3LiH (RE=La, Er) composite mixtures were cycled in a Sieverts apparatus that was built in-house. Decomposition was either performed under vacuum or against 0.5 MPa backpressure at 400 °C for 12 hours. Rehydrogenation was performed at 340 °C under 10 MPa hydrogen pressure for 12 hours.

Results

6LiBH₄·LaCl₃·3LiH: The PXD pattern of as-milled 6LiBH₄·LaCl₃·3LiH in Fig. 1 shows the presence of three major crystalline phases: LiCl, LiBH₄, and LiH, and their peak positions have been indicated by tick marks. Crystalline LiLa(BH₄)₃Cl which is the major constituent phase after the initial milling of 6LiBH₄·LaCl₃ [2] (see Fig. 1 Top) is no longer detected after ball-milling with LiH. Instead a broad and featureless bump is visible between 5 and 10° in 2θ and a modulation of the background at higher scattering angles. This indicates additional amorphous and/or nanocrystalline phases, possibly LaH₂⁺δ. A similar nanostructured CeH₂⁺δ phase has been observed during thermal decomposition of Ce(BH₄)₃ [24]. The PXD pattern after desorption (400°C, 0.5 MPa) shows four major crystalline phases: LaB₆, LiCl, LaH₂⁺δ and LiH, which are also present in the rehydrogenated sample. The two strongest peaks for the LaH₂⁺δ phase
are now clearly visible in the PXD pattern. The peak positions (lattice parameter) related to LaH$_{2+\delta}$ remain unchanged after rehydrogenation.

Figure 1

Fig. 2 shows the TG/DSC measurements of the 6LiBH$_4$-LaCl$_3$-3LiH composite at different stages, i.e. after ball-milling, desorption and rehydrogenation. The result for 6LiBH$_4$-LaCl$_3$ after ball-milling is shown for comparison and has been discussed in [2]. The DSC curves have been divided into three major regions as indicated by vertical dashed lines in Fig. 2b and labelled (1) to (3). Below 300$^\circ$C, the DSC trace of the as-milled 6LiBH$_4$-LaCl$_3$-3LiH composite shows endothermic signals at 105 and 285 $^\circ$C, caused by the orthorhombic to hexagonal structure transformation and melting of LiBH$_4$, respectively. After milling with LiH, the endothermic events in region (2) have disappeared. They are caused by the partial decomposition of LiLa(BH$_4$)$_3$Cl and the presence of a LiLa(BH$_4$)$_3$Cl-LiBH$_4$ composite [2]. Indeed, LiLa(BH$_4$)$_3$Cl was found to be absent in the PXD pattern for 6LiBH$_4$-LaCl$_3$-3LiH after ball-milling (see Fig. 1). Finally, between 300 and 350 $^\circ$C a broad and intensive endothermic signal with a peak maximum at 320 $^\circ$C is visible that is accompanied by a loss of about 4.2 wt% H. The DSC curves after desorption against 0.5 MPa backpressure and rehydrogenation (10 MPa) show no presence of LiBH$_4$. The TG-trace after rehydrogenation details a continuous small weight loss of about 0.8 wt% H between 150 and 330 $^\circ$C which indicates a very limited reversibility (< 20%) under the present experimental condition. Since the lattice parameter of the LaH$_{2+\delta}$ phase in the PXD does not change after rehydrogenation, and no LiBH$_4$ is detected from the DSC curves after rehydrogenation, it follows that the small uptake of hydrogen for the 6LiBH$_4$-LaCl$_3$-3LiH composite must stem from some amorphous boron-containing phases.
6LiBH₄-ErCl₃-3LiH: The PXD pattern of as-milled 6LiBH₄-ErCl₃-3LiH in Fig. 3 shows the presence of three major crystalline phases: LiCl, LiBH₄ and LiH. Crystalline Er(BH₄)₃ which is the major constituent phase after the initial milling of 6LiBH₄-ErCl₃ (see Fig. 3 Top) is no longer detected after ball-milling with LiH. Instead the pattern exhibits a modulated background due to some amorphous and/or nanocrystalline components and broad shoulders on either side of the LiCl peaks, which could be attributed to the presence of ErH₃ and possibly ErH₂. However, ErH₂ is difficult to verify since it has almost identical lattice constant as LiCl, and/or could be hidden under the broad and modulated background. The sample desorbed against 0.5 MPa H₂ shows LiCl, ErB₄ and LiH as the major crystalline phases. The rehydrogenated sample also exhibits peaks corresponding to LiCl, ErB₄ and LiH, and in addition weak reflections caused by LiBH₄. The most intense peaks after rehydrogenation stem from ErH₃, which was not present in the desorbed sample.

Fig. 4 shows the TG/DSC measurements of the 6LiBH₄-ErCl₃-3LiH composite at different stages, i.e. after ball-milling, desorption and rehydrogenation. The result for 6LiBH₄-ErCl₃ after ball-milling is shown for comparison and has been discussed in [2]. The 6LiBH₄-ErCl₃ mixture shows the orthorhombic to hexagonal phase transition for LiBH₄ at 100 °C, and multiple endothermic events in the range 150 -200 °C, associated with the amorphization and partial decomposition of the parent borohydride phase, α-
Er(BH$_4$)$_3$, as previously reported [2, 11]. Finally, between 220 and 350 °C, a series of endothermic events is visible, with two relatively sharp ones around 240 and 290 °C, corresponding to the major decomposition of the parent borohydride phase and melting of LiBH$_4$, respectively. Superimposed is a broad and featureless endothermic peak that stretches from 220 to 330 °C. For the 6LiBH$_4$-ErCl$_3$ composite after ball-milling a total mass loss of about 5.2 wt% H is detected between RT and 400 °C. After the addition of LiH and a second milling procedure, the 6LiBH$_4$-ErCl$_3$-3LiH composite shows two major endothermic events (Fig. 4b) at about 105 and 285 °C, which are attributed to the presence of LiBH$_4$. The thermal decomposition of 6LiBH$_4$-ErCl$_3$-3LiH starts at about 300 °C, and is accompanied by a mass loss of about 3 wt% H. The TG/DSC trace of the dehydrogenated sample against 0.5 MPa backpressure is flat and exhibits no signals from LiBH$_4$.

Figure 4

However, the DSC curve of the rehydrogenated 6LiBH$_4$-ErCl$_3$-3LiH sample contains two endothermic signals clearly caused by the presence of LiBH$_4$, and a broad endothermic signal similar to the one observed for the as-milled composite. The rehydrogenated sample exhibits an accumulated mass loss of about 2.4 wt% H up to 400 °C, and thus shows an excellent reversibility (~80%) after desorption against 0.5 MPa backpressure. With desorption against vacuum the mass loss for the rehydrogenated sample is ~2.0 wt% H up to 400 °C (not shown) and thus reaches ~66% reversibility.

These findings are in contrast to the composite containing lanthanum (see above) where only very limited reversibility of ~19% was found. In light of the PXD and TG/DSC results it can be concluded that the improved capacity on rehydrogenation compared to the lanthanum containing composite is caused
by the formation of ErH3 and the rehydrogenation of LiBH4. This is a remarkable result since the rehydrogenation of pure LiBH4 requires usually much harsher conditions, >400 °C and >10 MPa H2 [25, 26].

**Discussion**

The as-milled 6LiBH4-RECl3 samples (RE= La, Er) contain LiLa(BH4)3Cl and Er(BH4)3 in product mixtures with excess LiBH4 and LiCl according to previous publication [2]. These composites release hydrogen at around 210 °C (La) and 180 °C (Er), respectively, and yield about 5.5 wt% H (La) and 5.2 wt% H (Er) in total up to 400 °C. The thermal decomposition of both 6LiBH4-RECl3 composites follows a complicated multistep process that involves several intermediate phases until the final products, mainly LaB6, ErB4 and traces of REH2+δ are formed [2]. The formation of REH2+δ species through decomposition of the parent borohydride phase destabilizes the excess LiBH4 and leads to a gas release at significantly lower temperatures (~200 °C) compared to pure ball-milled LiBH4 (~400 °C) [13]. A similar destabilization effect has also been observed in other composites containing LiBH4 and metal hydrides, e.g. 6LiBH4-CaH2 [27, 28], 6LiBH4-CeH2 [24, 27, 28] and 4LiBH4-YH3 [27].

6LiBH4-RECl3-3LiH (RE = La,Er) that are formed after the additional milling procedure with LiH show a simplified thermal decomposition as compared to composites without LiH (see Figs. 2 and 4). Although desorption starts at higher temperatures (~300 °C), both systems still liberate 4 wt% H (La) and 3 wt% H (Er) respectively, in a narrow temperature interval between 300 and 350 °C. The kinetics of hydrogen desorption appear to be enhanced as compared to 6LiBH4-RECl3. For 6LiBH4-LaCl3-3LiH, 4 wt% H are desorbed within a temperature range of 50 °C, whereas the same amount of gas is released within 100 °C in the 6LiBH4-LaCl3 composite. Since all TG/DSC experiments were carried out with the same heating rate, it follows that gas desorption is almost twice as fast for 6LiBH4-LaCl3-3LiH. The effect is less
pronounced for 6LiBH₄-ErCl₃-3LiH, yet 3 wt% H are released within an interval of 75 °C, whereas the same amount of gas is desorbed within 100 °C from the 6LiBH₄-ErCl₃ composite.

Gennari et al. [13] recently investigated the thermal behavior and reversibility of 6LiBH₄-RECl₃ composites (RE=Ce, Gd) with and without addition of LiH. The authors state that the presence of LiH in the second milling step leads to the formation of CeH₂⁺. In the current study for 6LiBH₄-LaCl₃-3LiH, peaks for nanoscale LaH₂⁺ are visible after ball-milling from the PXD pattern in Fig 1. This finding combined with the TG/DSC result in Fig. 2 indicates the disappearance of LiLa(BH₄)₃Cl after ball-milling with LiH, and strongly suggests that LaH₂⁺ is formed via the interaction of LiH with the parent borohydride phase LiLa(BH₄)₃Cl:

\[
\text{LiLa(BH₄)₃Cl} + 3\text{LiH} \rightarrow \text{LaH₂⁺} + 3\text{LiBH₄} + \text{LiCl} + (1-\delta)/2\text{H₂} \quad (1)
\]

The thermal decomposition of 6LiBH₄-LaCl₃-3LiH yields 4.2 wt% H during the first cycle and 0.8 wt% H during the second cycle after rehydrogenation. The system shows only a very limited capacity for rehydrogenation (~19%) under these experimental conditions. In a previous report on 6LiBH₄-LaCl₃ mixtures desorbed against vacuum we also observed only 18% recovery at 300 °C and 36% at 415 °C [2]. Neither the addition of LiH nor the application of backpressure in the present study seems to have a beneficial effect on the reversibility in the lanthanum containing composites. This is a surprising result since backpressure is expected to promote the formation of LaB₆ over amorphous boron and the addition of LiH should enhance the reversibility of LaB₆. It is at present not clear why the lanthanum containing composite shows such a poor reversibility whereas the 6LiBH₄-CeCl₃-3LiH system investigated
by Gennari et al. (note both parent RE-borohydrides are isostructural) is able to recover between 45 and 80% of its initial hydrogen capacity [13].

In this paper we have compared for the first time the thermal properties of erbium-based 6LiBH4-RECl3 composites with and without addition of LiH. For 6LiBH4-ErCl3, we observe a mass loss of about 5.2 wt% H in the temperature region between RT and 400 °C. The mixture releases 1.4 wt% H after rehydrogenation (415 °C, 10 MPa) during the second dehydrogentation cycle, which corresponds to ~25% reversibility [2]. In comparison, Gennari et al. have reported a gas release of about 5 wt% H from a gadolinium-based 6LiBH4-GdCl3 composite during the first dehydrogenation cycle and 2.0 and 1.7 wt% H gas evolution during the second dehydrogenation cycle under vacuum and against 0.5 MPa backpressure, respectively [13]. Since the parent borohydrides Er(BH4)3 and Gd(BH4)3 in both mixtures are isostructural [1, 2], and similar decomposition products (ErB4 vs. GdB4) are formed, we can expect similar behavior during decomposition.

In contrast, as-milled 6LiBH4-ErCl3-3LiH desorbs only about 3.0 wt% H up to 350 °C. Samples decomposed against vacuum and backpressure release 2.0 wt% H and 2.4 wt% H after rehydrogenation, respectively. The 6LiBH4-ErCl3-3LiH composite shows therefore a reversibility of 66% under vacuum and 80% against 0.5 MPa backpressure. The decomposition of the parent Er(BH4)3 phase in 6LiBH4-ErCl3-3LiH is proposed to follow two pathways according to (2) and (3):

\[
\text{Er(BH}_4\text{)}_3 \rightarrow 0.25\text{ErH}_2 + 0.75\text{ErB}_4 + 5.75\text{H}_2 \quad (2)
\]

\[
\text{Er(BH}_4\text{)}_3 \rightarrow \text{ErH}_2 + 3\text{B} + 5\text{H}_2 \quad (3)
\]
The experimental conditions will have a strong influence on the relative ratio between these two alternative pathways, and desorption under backpressure is expected to favor the formation of ErB$_4$ over elemental boron. A similar effect has been observed for the combination of LiBH$_4$ with reactive additives such as MgH$_2$ [29-31], CaH$_2$ [28] and Al [32, 33]. Indeed analysis of the relative intensities for ErB$_4$ and LiCl in the PXD patterns show a slight intensity increase for ErB$_4$ after desorption against 0.5 MPa hydrogen as compared to vacuum. 6LiBH$_4$-ErCl$_3$-3LiH shows good reversibility (~66%) for samples desorbed under vacuum and even higher reversibility (~80%) after dehydrogenation under hydrogen backpressure. Hydrogen uptake of the mixture could be realized through the interaction between the decomposition product ErB$_4$, LiH and hydrogen. This will result in the formation of ErH$_2$ and LiBH$_4$. This assumption seems plausible and is furthermore supported by experimental observations, in particular the reappearance of LiBH$_4$ in the DSC-curve (Fig. 4b) and peaks belonging to ErH$_3$ (cubic, a=5.27 Å) in the PXD pattern (Fig. 3) for the rehydrogenated samples.

For 6LiBH$_4$-GdCl$_3$-3LiH composites, Gennari et al.[13] have reported a slightly higher gas release under vacuum than against backpressure (5.0 % vs. 4.9 %) during the first dehydrogenation cycle and a slightly larger difference during the second dehydrogenation cycle (2.0 % vs 1.7 %). This is in contrast to what we observe for 6LiBH$_4$-ErCl$_3$-3LiH, where the sample desorbed against backpressure shows a larger gas release (2.4% vs. 2.0%) after rehydrogenation. These findings could be caused by differences in experimental conditions such as temperature, pressure and time during the cycling experiments, sample morphology and/or final composition in the 6LiBH$_4$-RECl$_3$-3LiH composites after ball-milling.

**Conclusion**
The mechnochemical reaction between LiBH₄, LaCl3 / ErCl₃ and LiH in a molar ratio of 6:1:3 has led to the formation of composite mixtures that release between 3 wt% H (Er) and 4.2 wt% H (La) above 300 °C. In both composites RE-hydride species, REH₂₊δ, are formed during heating which destabilize excess LiBH₄ and lower its desorption temperature by about 100 °C. The kinetics of hydrogen release is significantly increased compared to 6LiBH₄-RECl₃ composites without LiH. The lanthanum-containing mixture shows only a limited rehydrogenation capacity of <20% (340 °C, 10 MPa). The erbium-containing samples regain 66% of their original hydrogen storage capacity after rehydrogenation when desorbed against vacuum. This value increases up to 80% when desorbed against 0.5 MPa backpressure.

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Figure Captions

**Figure 1**: SR-PXD pattern (\( \lambda = 0.50513 \) Å) of 6LiBH₄-LaCl₃ mixture obtained after ball-milling (Top) and 6LiBH₄-LaCl₃-3LiH after ball-milling, desorption against 0.5 MPa backpressure and rehydrogenation (340 °C, 10 MPa).

**Figure 2**: (A) TG-trace of 6LiBH₄-LaCl₃ composite obtained after ball-milling and 6LiBH₄-LaCl₃-3LiH after ball-milling, desorption against 0.5 MPa backpressure and rehydrogenation (340 °C, 10 MPa). (B) DSC trace of the composite mixtures described under (A) in the temperature region between RT and 400 °C.

**Figure 3**: SR-PXD pattern (\( \lambda = 0.50513 \) Å) of 6LiBH₄-ErCl₃ mixture obtained after ball-milling (Top) and 6LiBH₄-ErCl₃-3LiH after ball-milling, desorption against 0.5 MPa backpressure and rehydrogenation (340 °C, 10 MPa).

**Figure 4**: (A) TG-trace of 6LiBH₄-ErCl₃ composite obtained after ball-milling and 6LiBH₄-ErCl₃-3LiH composite mixtures after ball-milling, desorption against 0.5 MPa backpressure and rehydrogenation (340 °C, 10 MPa). (B) DSC trace of the composite mixtures described under (A) in the temperature region between RT and 400 °C.
Figure 1:
Figure 2:
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References