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## Towards room temperature, direct, solvent free synthesis of tetraborohydrides

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**Abstract.** Due to their high hydrogen content, tetraborohydrides are discussed as potential synthetic energy carriers. On the example of lithium borohydride LiBH<sub>4</sub>, we discuss current approaches of direct, solvent free synthesis based on gas solid reactions of the elements or binary hydrides and/or borides with gaseous H<sub>2</sub> or B<sub>2</sub>H<sub>6</sub>. The direct synthesis from the elements requires high temperature and high pressure (700°C, 150bar D<sub>2</sub>). Using LiB or AlB<sub>2</sub> as boron source reduces the required temperature by more than 300 K. Reactive milling of LiD with B<sub>2</sub>H<sub>6</sub> leads to the formation of LiBD<sub>4</sub> already at room temperature. The reactive milling technique can also be applied to synthesize other borohydrides from their respective metal hydrides.

### 1. Introduction

Tetraborohydrides M(BH<sub>4</sub>)<sub>n</sub> (n being the valence of the metal) are currently discussed as synthetic energy carriers [1]. Especially the lightweight alkali and alkaline earth metal borohydrides such as LiBH<sub>4</sub> which has a high gravimetric (18wt%) and volumetric hydrogen density (122kg/m<sup>3</sup>), are promising candidates for mobile applications. They form ionic crystals composed of positively charged metal ions [M]<sup>n+</sup>, and negatively charged borohydride [BH<sub>4</sub>]<sup>-</sup> ions. To exploit the high hydrogen content, the material ought to have convenient working conditions in terms of desorption temperature, equilibrium pressure and sorption kinetics. Furthermore, it should be easy to regenerate: technical application requires an efficient way to synthesize the borohydrides either on-board or off-board.

The first borohydrides were isolated by Stock et al. in 1935 [2-3] from the reaction of potassium amalgam and sodium amalgam with diborane. The reaction products were mistaken to be “disodium-diborane”  $\text{Na}_2\text{B}_2\text{H}_6$  and “dipotassium diborane”  $\text{K}_2\text{B}_2\text{H}_6$ . In 1949 Kasper et al. identified “disodium-diborane” to be sodium borohydride  $\text{NaBH}_4$  by its X-ray diffraction pattern [4]. The synthesis of  $\text{LiBH}_4$  from the reaction of gaseous diborane ( $\text{B}_2\text{H}_6$ ) with ethyllithium ( $\text{C}_2\text{H}_5\text{Li}$ ) was reported by Schlesinger and Brown in 1940 [5]. More conveniently,  $\text{LiBH}_4$  can be produced either by the reaction of  $\text{LiH}$  and  $\text{B}_2\text{H}_6$  (suspended in diethyl ether) or by the metathesis reaction of  $\text{NaBH}_4$  and  $\text{LiCl}$ , respectively [6]. To obtain the pure borohydride, by-products of the reaction and the solvent have to be removed. A comprehensive review of the currently applied methods is given by Hagemann and R Černý [7].

Within the last years several methods for the solvent-free synthesis were applied. These methods comprise (a) the high temperature / high pressure direct synthesis from the elements, (b) high temperature / high pressure reactions involving binary metal hydrides and binary metal borides and finally (c) the reaction of gaseous  $\text{B}_2\text{H}_6$  with the respective solid metal hydride. With the present paper we outline this development and give an overview over the current state of the art.

Diffraction techniques, especially neutron diffraction, are powerful tools to determine the crystalline structure of lightweight complex hydrides [8,9]. They are also used to recognize reaction pathways by the identification of intermediates and solid desorption products. The high penetration depth of neutrons allow to use massive sample environment, enabling in-situ experiments of high pressure – high temperature reactions in combination with volumetric measurements of the involved gases. The in-situ neutron diffraction experiments presented in this work were measured at the focusing diffractometer E6 at the 10 MW research reactor BERII of the Helmholtz Center for Materials and Energy in Berlin, Germany [10]. The neutron diffraction experiments were complimented by in-house X-ray diffraction and by imaging techniques.

## 2. Direct synthesis from the elements

Even though  $\text{LiBH}_4$  possesses a high negative heat of formation ( $\Delta H_f = -185\text{kJ/mol}$ ) [11], the direct synthesis from the elements requires elevated temperature and high pressure. Goerrig observed the direct synthesis from lithium, boron and hydrogen at  $650^\circ\text{C}$  and 150 bar  $\text{H}_2$  and claimed general applicability to group IA and IIA metals [12]. A significant activation energy barrier prevents the formation of  $\text{LiBH}_4$  at lower temperatures. The activation barrier is attributed to the general chemical inertness of boron [13-15], which may be due to the strongly bound boron atoms ( $\Delta H_{\text{B(s)} \rightarrow \text{B(g)}} = 560\text{ kJ/mol}$ ), compared to Li ( $\Delta H_{\text{Li(s)} \rightarrow \text{Li(g)}} = 159.3\text{ kJ/mol}$ ) and H ( $\Delta H_{\text{H}_2\text{(g)} \rightarrow 2\text{H(g)}} = 218\text{ kJ/mol}$ ) [16] and/or a natural passivating oxide layer [17–19]. However, The results by Goerrig could not be reproduced so far [20,21].

We achieved the direct synthesis of  $\text{LiBH}_4$  and  $\text{LiBD}_4$  from the elements by exposing pre-milled boron powder and lithium to a hydrogen (deuterium) atmosphere of 150 bar at a temperature of  $700^\circ\text{C}$  [22], which is slightly higher than the temperature observed by Goerrig and above the melting point of  $\text{LiH}$  ( $688^\circ\text{C}$ ). Above this temperature no passivating hydride layer is formed and all Li completely converts to  $\text{LiH}$  and liquid  $\text{LiH}$  intercalates the boron leading to an intermixing of Li, H and B on the atomic scale, facilitating the formation of  $\text{LiBH}_4$ .

The formation of  $\text{LiBH}_4$  and  $\text{LiBD}_4$  can be improved by Li intercalation into B [22-24] prior to a subsequent hydrogenation. At low Li-concentrations Li is dissolved into the interstitial sites of the boron lattice, leading to a stressed and expanded boron structure and causing the decrepitation of boron particles. At higher concentrations, stoichiometric  $\text{LiB}$  forms. The reaction of  $\text{LiB}$  with  $\text{D}_2$  to  $\text{LiBD}_4$  involves  $\text{LiD}$  as an intermediate product. The diffraction data in figure 1 show that the nucleation of  $\text{LiD}$  is accompanied by the decomposition of the  $\text{LiB}$  compound. The absence of the boron diffraction peaks indicates that the boron resulting from the D-induced decomposition of  $\text{LiB}$

has no crystalline long-range order that is observed in the as-purchased boron. The crystalline order that is still observed in ball-milled boron is obviously destroyed after the formation of B from the decomposition of the binary LiB compound.

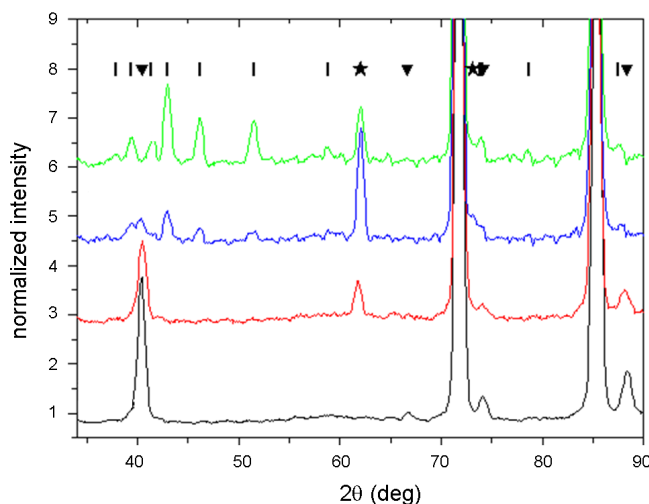


Figure 1: Neutron diffraction pattern recorded during the reaction of LiB with D<sub>2</sub> (180bar). From bottom to top: as prepared sample, after heating to 200°C, 350°C and 500°C. Ticks (|) mark the position of LiBD<sub>4</sub> reflections, down triangles (▼) mark the positions of the LiB reflections and the star (\*) marks the reflection of LiD. The strong reflections at 72° and at 85° originate from the sample container. The curves are offset for clarity [24].

Similar temperatures can be achieved by exposing ball milled mixtures of LiH and B to H<sub>2</sub> [25, 26]. Chen et al. directly prepared LiBH<sub>4</sub> at 300 °C – 500 °C at 350 bar H<sub>2</sub> starting from high energy ball milled LiH/B mixtures under 100 bar H<sub>2</sub> atmosphere [26]. The milling reduces the particle size and induces mechanical alloying of LiH and B, reducing the solid diffusion pathway. The pre-treatment also deoxidizes the surface oxides. Chen et al., discuss several possible rate limiting steps that control the reaction kinetics, such as diffusion, nucleation and growth, or movement of phase boundaries. In a careful kinetic investigation, solid state diffusion was concluded to be the rate limiting step of the formation of LiBH<sub>4</sub> from LiH, B and H<sub>2</sub>.

### 3. Synthesis paths involving metals, metal hydrides and metal borides

Binary compounds such as MgB<sub>2</sub> or AlB<sub>2</sub> can play an important role as destabilizing agents during hydrogen desorption. Vajo et al. [27] studied the hydrogen sorption behaviour of LiBH<sub>4</sub> using MgH<sub>2</sub> as additive. Including 2–3 mol% TiCl<sub>3</sub> as a catalyst, the reaction follows the equation:



The formation of MgB<sub>2</sub> upon dehydrogenation stabilizes the dehydrogenated state and, thereby, destabilizes the MgH<sub>2</sub> and the LiBH<sub>4</sub>. The reduced decomposition temperature of the combined system as compared to the individual hydrides makes this system attractive for hydrogen storage. LiBH<sub>4</sub> + MgH<sub>2</sub> is thereby a prototype system for a whole class of pseudo-binary hydrides containing a complex hydride (as LiBH<sub>4</sub>) and a binary metal hydride (as MgH<sub>2</sub>) called *reactive hydride composites* (RHC).

Synthesis reactions according to



have been realized at  $p_{\text{H}_2}=350\text{bar}$  and at  $T=400^\circ\text{C}$  and by Barkhordarian et al. [28]. Closer investigations showed that the  $\text{Ca}(\text{BH}_4)_2$  synthesis already takes place at  $p_{\text{H}_2}=150\text{ bar}$  and at  $T=350^\circ\text{C}$  [29]. Due to their reduced working temperature, enhanced kinetics and reversibility, RHC are currently in the focus of many research activities. Choosing the hydride and the boride from the same metal, pure borohydrides may be synthesized.  $\text{Ca}(\text{BH}_4)_2$  prepared from  $\text{CaB}_6$  and  $\text{CaH}_2$  under 700 bar  $\text{H}_2$  at about  $400^\circ\text{C}$  is an example for such a reaction [30].

The hydrogenation of metal hydride / metal boride mixtures may also result in the concurrent formation of the borohydride (from the respective metal hydride) and the elemental metal (from the metal boride). The most studied system in this respect is  $\text{AlB}_2 + 2\text{LiH} + 3\text{H}_2 \rightarrow 2\text{LiBH}_4 + \text{Al}$ . The reaction was observed to take place between  $350^\circ\text{C}$  and  $400^\circ\text{C}$  in applied hydrogen pressures between 70 bar and 150 bar [31–34]. Compared to the re-hydrogenation temperature of pure  $\text{LiBH}_4$  these temperatures and pressures are more moderate and therefore a step towards technical application. Unfortunately, the system suffers from a severe capacity loss during cycling. A phase separation of Al and B during the decomposition of  $\text{LiBD}_4$  was identified as the main reason for the hydrogen capacity loss and the decreasing kinetics upon subsequent cycling [35].

A common feature of the RCH is the prevention elemental boron as reactant, circumventing the breaking of B-B bonds during the synthesis. The boride serves as a source of boron during the hydrogen adsorption while the formation of the boride during hydrogen desorption binds the boron and avoids the formation of B-B bonds.

#### 4. Synthesis paths involving diborane

The previous experiments suggest that the boron supply is crucial for the synthesis of  $\text{LiBD}_4$ . Breaking of the B-B or the B-metal bonds and the formation of B-H seem to be the limiting steps. Consequently, reaction paths involving diborane ( $\text{B}_2\text{H}_6$ ), in which the B-H bonds are already established, should further facilitate the formation of  $\text{LiBD}_4$  at lower temperatures and pressures.

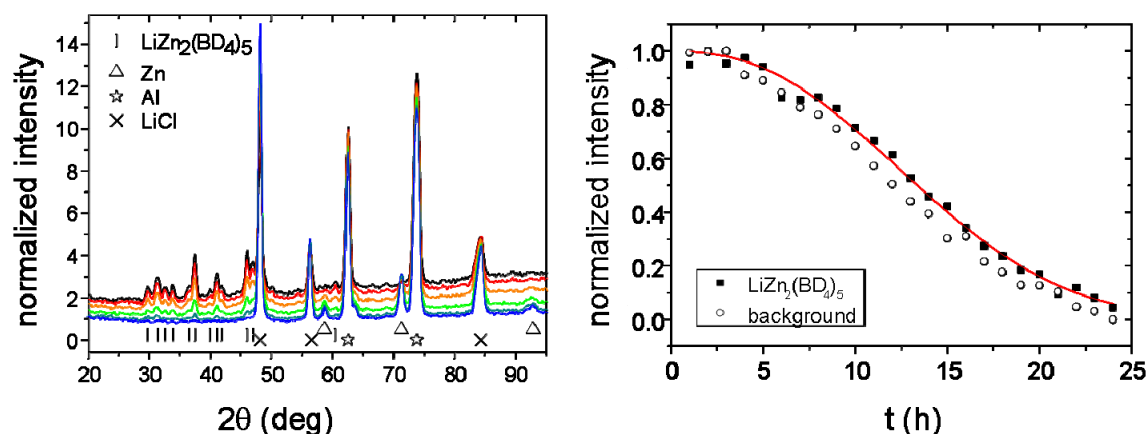
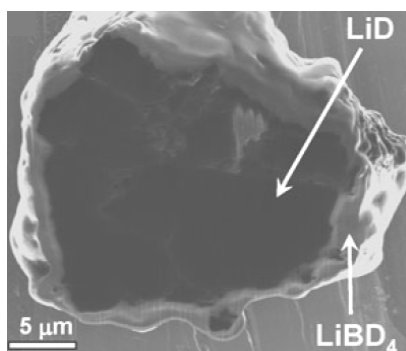


Figure 2a (left): Top to bottom: Temporal evolution of the neutron powder diffraction pattern of a ball milled mixture of  $\text{LiBD}_4$  and  $\text{ZnCl}_2$ , recorded in a sealed container at  $T=85^\circ$ . Figure 2b (right): Temporal evolution of the integrated intensity of the  $\text{LiZn}_2(\text{BD}_4)_5$  reflection (filled symbols) and of the integrated background intensity (open symbols).

Diborane is a toxic, thermodynamically unstable gas. On the lab-scale small amounts of  $B_2H_6$  are released, together with  $H_2$ , in a 1:1 ratio, from a ball milled mixture of  $LiBH_4$  and  $ZnCl_2$  [36]. Ravensbæk et al. identified the resulting compound to be the double cation lithium zincborohydride, formed according to  $5LiBH_4 + 2ZnCl_2 \rightarrow LiZn_2(BH_4)_5 + 4LiCl$  [37].

Figure 2a (top curve) shows a series of neutron powder pattern during the decomposition of a deuterated  $LiBD_4/ZnCl_2$  sample. Each individual diffractogram was recorded within one hour; the time lag between two depicted measurements equals five hours. Figure 1b shows the normalized temporal evolution of the integrated intensity of the strongest  $LiZn_2(BD_4)_5$  reflection at  $2\theta=37.47^\circ$ , together with the integrated background intensity. The strong initial background is obviously related to the presence of  $LiZn_2(BD_4)_5$ , most probably due to the presence of amorphous  $LiZn_2(BD_4)_5$ . In agreement with earlier studies, elemental zinc is observed within the solid residue [38].

Exposing  $LiH$  to a diborane/deuterium atmosphere of 10 bar at  $100^\circ C$  leads to the formation of  $LiBD_4$ . The reaction stops after about 50% of  $LiH$  is consumed for the formation of  $LiBD_4$ . The reaction proceeds in one step, no intermediate products are visible [36]. A core-shell structure of lithium hydride surrounded by lithium borohydride is observed, as shown in figure 3 [39].



*Figure 3: Secondary electron image (induced by 30 keV ion beam) of  $LiH$  after reaction with  $B_2H_6$  showing a cross sectional view of a grain. The core shell structure is clearly visible. The chemical composition of the inner part of the grain and the outer layer were determined by electron loss spectroscopy [36].*

The reaction stops due to kinetic constraints originating from the increased diffusion path of either B–H species into the grain or Li towards the exterior. The results are in agreement with the passivation layer proposed by Schlesinger et al., who synthesized different borohydrides in solvents in order to prevent the formation of the passivation layer [6]. Upon reactive ball milling the passivation layer is constantly broken and  $LiBH_4$  forms already even at room temperature [39]. As long as sufficient gas is supplied, no influence on the pressure was detected. As long as fresh surface is provided, the reaction proceeds. Details of the reaction mechanism were studied by Gremaud et al. [40]. They found evidence for the heterolytic splitting of diborane on the alkali hydrides. The resulting  $[BH_4]^-$  anion is subsequently exchanged with a  $[H]^-$  ion of the underlying hydride. The alkali hydride surface is ionic and polarizes the  $B_2D_6$  prior splitting, assisting the necessary charge transfer for binding of the negatively charged  $[BD_4]^-$ .

The synthesis of a borohydride by reactive ball milling is not limited to  $\text{LiBH}_4$ . The direct, solvent free method of synthesizing borohydrides from the respective binary hydride has been successfully applied to  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$  [39] and  $\text{Y}(\text{BH}_4)_3$ . Figure 4 shows the resulting XRD pattern of  $\text{LiBH}_4$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Y}(\text{BH}_4)_3$  (from top to bottom).

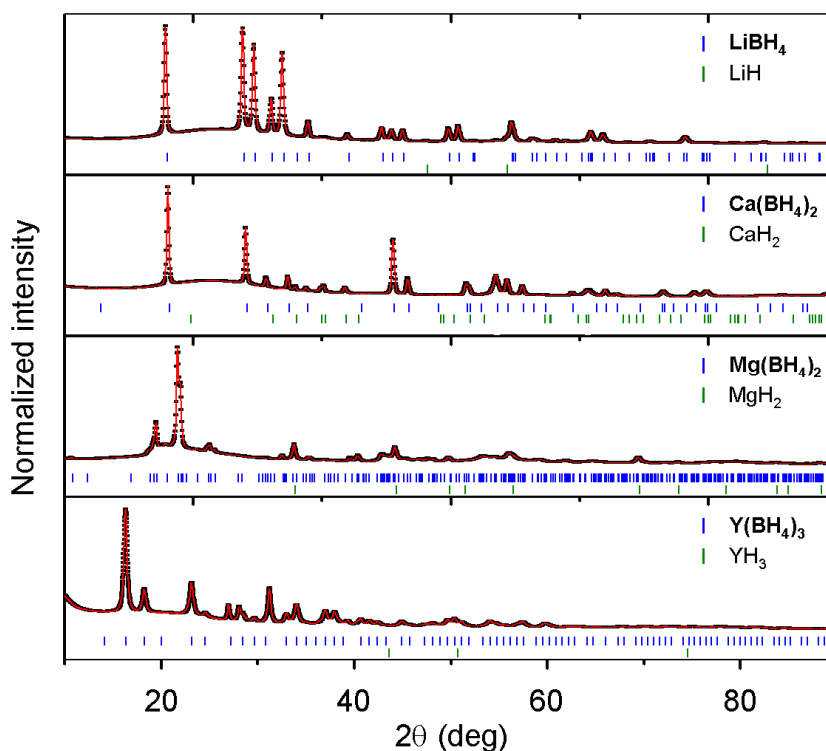


Figure 4: X-ray diffraction pattern of the products achieved by reactive ball milling of  $\text{LiH}$ ,  $\text{CaH}_2$ ,  $\text{MgH}_2$  and  $\text{YH}_3$  (from top to bottom) in a mixed  $\text{B}_2\text{H}_6/\text{H}_2$  atmosphere. The main product is the respective borohydride, the educt is the only detectable solid contaminant.

The reactive ball milling is not generally applicable. The formation of the borohydride competes with the formation of the respective boride analogous to the reaction of  $\text{TiH}_2$  and  $\text{B}_2\text{H}_6$ . The formation of a borohydride is generally accompanied by a reduction of the overall pressure in the milling vial due to the absorption of diborane. In the case of  $\text{TiH}_2$  and  $\text{B}_2\text{H}_6$  a pressure increase is observed, indicating the release of a gas. Figure 5 displays the pressure within the vial during the milling. Until saturation, the pressure increases from an initial value of 10.1 bar by 3.6 bar. The solid product has been identified as  $\text{TiB}_2$ , as shown in the inset to fig.5.

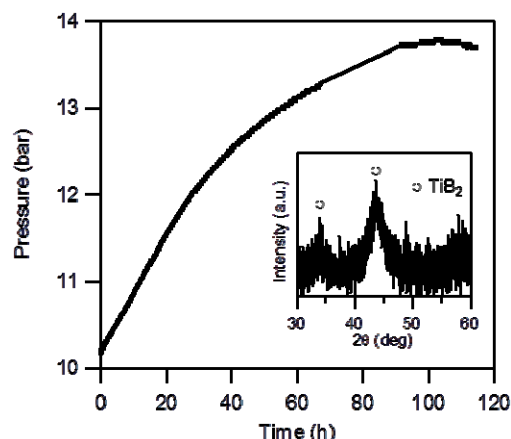


Figure 5: Pressure increase during the ball milling of  $TiH_2$  in  $B_2H_6$  atmosphere. The inset shows the XRD pattern of the reaction product, identified as  $TiB_2$ .

The applicability of the gas solid diborane synthesis is obviously limited by thermodynamics. The borohydride is only formed when it is more stable than the corresponding boride. Moreover, the increase of entropy originating from the net release of 3 formula units of gaseous products favours the formation of the boride instead of the borohydride.

## 5. Conclusion

Among the various methods to prepare borohydrides, the direct, mechanically assisted gas-solid reactions offer solvent free routes, circumventing the necessity to remove solvents or unwanted by-products that are unavoidable in metathesis reactions. Combining NPD, XRD, Raman spectroscopy and imaging techniques, the fundamental reaction mechanisms could be unveiled. The formation of the B-H bonds is the crucial step, mainly responsible for the activation energy needed for the direct synthesis from the elements. Lower barriers can be achieved by using additives that destabilize the stable borohydrides and that prevent the formation of B-B bonds during hydrogen desorption. Room temperature synthesis can be achieved starting from diborane, where the B-H bonds are already established.

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