Synthesis and Properties of Magnesium Tetrahydroborate, $Mg(BH_4)_2$

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$Mg(BH_4)_2$ is one of the few complex hydrides which have the potential to meet the requirements for hydrogen storage materials, because it contains 14.9 mass% H and has suitable thermodynamic properties. It has not been investigated for hydrogen storage applications yet. In this study, several ways to synthesize solvated and desolvated magnesium tetrahydroborate by wet-chemical and
10 mechanochemical methods were tested and compared. A direct synthesis by a reaction of MgH_2 with aminoboranes yields magnesium tetrahydroborate quantitatively and in pure form. The method is also applicable to the synthesis of other tetrahydroborates. The products were characterised by elemental analysis, in-situ X-ray diffraction (XRD), infrared spectroscopy (FTIR), and thermal analysis methods, such as thermogravimetric analysis (TGA-DSC) and high-pressure
15 calorimetry under hydrogen atmosphere (HP-DSC).

1   Introduction

In search for new hydrogen storage materials with suitable properties for technical applications, a high hydrogen content
20 of the hydrogen carrier material is essential. Moreover, the thermodynamic properties are of significant importance, because they define the equilibrium conditions for hydrogen exchange, which may be considered to be the lower limits for the working temperature and loading pressure. High
25 gravimetric storage capacities for hydrogen make the use of light-weight materials indispensable. They consist of light elements, preferably from the first two or three rows of the periodic system. Hence, only a limited number of compounds have the potential of reaching these goals.

30 Hydrogen storage materials based on complex hydrides, such as tetrahydroaluminates, tetrahydroborates, and amides, have been considered promising for reversible hydrogen storage, [1-3] since it was demonstrated that transition metal dopants can considerably lower kinetic barriers for both hydrogen
35 absorption and desorption of $NaAlH_4$.[1] Thus, reversible amounts of more than 4.7 wt.% H have been reached under moderate operating conditions.[4] The system can reversibly desorb and absorb a maximum amount of 5.6 wt.% hydrogen (theoretical value) at temperatures below 120 °C. Other
40 compounds, such as $LiAlH_4$ containing 10.6 wt.% H [5] or $Mg(AlH_4)_2$ [6,7,8] with 9.3 wt.% H, cannot be used in practice due to their unfavorable thermodynamic properties that make them too unstable for reversible on-board storage.

Among other possible candidates, magnesium
45 tetrahydroborate seems to have the potential to meet these requirements. With a molecular weight of 53.99 g/mol, $Mg(BH_4)_2$ contains 14.9 mass% hydrogen, and even if only a part of it could be exchanged reversibly under moderate

pressure and temperature conditions, this would be a
50 considerable progress. Recently, the thermodynamic properties of $Mg(BH_4)_2$ and other boranates were estimated by Nakamori et al., [9] who reported about a correlation between the enthalpy of formation of the compounds and the Pauling electronegativity of the cation. According to their studies, the
55 enthalpy of formation of $Mg(BH_4)_2$ should amount to <208 kJ/mol, which would be <44 kJ/mol H_2, if the following decomposition reaction [10] and an enthalpy of formation of -76 kJ/mol for MgH_2 are assumed:

60 $$Mg(BH_4)_2 \; \rightarrow \; MgH_2 \; + 2\,B + 3\,H_2 \qquad (1)$$
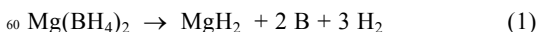
The estimated value would account for a low/medium-temperature hydride, which means that the compound would exhibit an equilibrium pressure of 1 bar below 100 °C. Up to
65 now, little has been known about the properties of pure magnesium tetrahydroborate and it has not yet been investigated as a material for hydrogen storage.

A synthesis route for magnesium tetrahydroborate was reported by Wiberg et al. in 1950. [12] However, the authors
70 were not aware of a stable solvent adduct forming under the experimental conditions described in the paper. The product cannot be desolvated completely without decomposing the compound, see below.

In the period following, Köster et al. [13] suggested a
75 synthesis of metal borohydrides based on the reaction of the respective metal hydride with *N*-alkylborazanes. However, properties of the products were not investigated.

A direct synthesis route from the elements was described by a German patent from 1957. [14] However, when reproducing
80 the procedure, we were not successful in obtaining sufficiently high yields and it was not possible to separate the product from the rest of the reaction mixture by solvent extraction and desolvation of the boranate. The authors reported that the process only works with a certain type of
85 amorphous boron which obviously differed from the type we

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used in our experiments. Nevertheless, the work of Görring may be of considerable importance, because it confirms the thermodynamic stability of the substance and the reversibility of the thermal decomposition by direct synthesis from the elements.

Konoplev et al. [10] reported about structural and thermal properties of $Mg(BH_4)_2$, but details of the synthesis and determination of purity were not given in the paper. The authors claimed to have prepared the pure compound. However, the X-ray diffraction patterns reported differ considerably from ours. In another paper by the same author [11] $Mg(BH_4)_2*2Et_2O$ was synthesized by a methatetical reaction and the compound was desolvated in vacuo at 210 °C. According to the elemental analysis, the material contained Mg and boron in the right ratio. However, the hydrogen was not determined directly in this work and the amount of residual carbon was also not analysed. Moreover, only the high temperature phase of the compound can be obtained by this method, due to the high desolvation temperature which is above the transition temperature, see below. The material was also not further characterized by other methods. Some of the thermal properties of $Mg(BH_4)_2$ were investigated in another paper by a Russian group, [15] but the synthesis was not described.

Recently, a synthesis by a mechanochemical method was reported. [9] However, there was no reprocessing of the product, the boranate was not separated from the by-product, and the XRD pattern of the product showed a largely amorphous material. The peaks identified belonged to the by-product LiCl.

In this paper, several methods to synthesize pure magnesium tetrahydroborate by mechanochemical and wet chemical synthesis shall be described. One technique was successful in yielding a product free from solvent, in phase-pure form and with high purity. The method does not need separation from solid by-products and can also be applied to the synthesis of other boranates.

The materials were characterized by elemental analysis, in-situ powder X-ray diffraction, infrared spectroscopy, thermal desorption, and calorimetry. The thermal behavior (phase transformation and hydrogen release) of $Mg(BH_4)_2$ was analyzed.

2 Experimental

Synthesis operations were carried out on the bench using Schlenk tube techniques. The glassware was evacuated down to a pressure of 10^{-3} mbar and flushed with dry and oxygen-free nitrogen prior to use. Solids were handled in an argon-filled glove box equipped with a recirculation and regeneration system. Both the water and oxygen concentrations were kept below 1 ppm during operation.

2.1 Reagents

Tetrahydrofurane (THF) and diethyl ether (DEE) (both p.a., Merck) were distilled over sodium before use. Sodium tetrahydroborate (99%, Sigma Aldrich) and lithium tetrahydroborate (95%, Fluka), magnesium chloride (98%, Sigma Aldrich) and magnesium hydride (99%, Sigma Aldrich) were used as received. Borane triethylamine complex (97%, Sigma Aldrich) was degassed using the pump-thaw technique.

2.2 Instrumentation and analyses

High-energy ball milling was performed by a Fritsch P6 planetary mill at 600 rpm using an 80 ml vial and silicon nitride balls or an 80 ml stainless steel vial and balls. The vial was filled and sealed in the glove box; the ball-to-powder ratio always was 20:1.

Elemental analysis of carbon, nitrogen, and hydrogen was done with a CE Instruments Flash EA 1112 series analyzer using helium as purge gas. The powder samples were wrapped in tin capsules in the glove box and stored in gas-tight containers until weighing and measuring. The typical amount of a sample was 3-5 mg. For calibration, benzoic acid, nicotinamide, and $NaBH_4$ were used as standards. Control measurements were made before and after measuring the magnesium borohydride samples.

Solid-state infrared spectra of the boranates (as KBr pellets) were recorded in the range of 4000-370 cm^{-1} under nitrogen atmosphere and ambient conditions by using a Perkin-Elmer Spectrum GX FTIR spectrometer. The evaluation was done with the Perkin-Elmer Spectrum v. 2.00 Software.

Powder X-ray diffraction patterns were obtained with a Philips X´PERT diffractometer (Cu Kα radiation, 2 kW, with X´Celerator RTMS detector, automatic divergence slit). The powder was measured on an Si single crystal and sealed in the glove box by an air-tight hood made of Kapton foil, the foil being mounted out of the focus of the spectrometer. Temperature-dependent in-situ X-ray studies were performed with the same instrument *in vacuo* using a HTK 1200 sample holder made by Anton Paar GmbH. The material was measured on an Si single crystal, with a thermocouple mounted 2 mm underneath the sample. The data were taken in a stepwise manner, at nine different sample temperatures between room temperature and 480 °C. The measurement time at each temperature step was approximately 30 min. The heating ramp to the next temperature step was 2 K/min.The software for data acquisition and evaluation was PANalytical X´PERT Data Collector Ver. 2.1a and X´PERT HighScore Ver. 2.2.

Simultaneous thermogravimetric analysis and mass spectrometry (TGA-MS) were conducted under a vacuum between room temperature and 450 °C at a heating rate of 10 K/min using a NETZSCH STA 409C analyzer equipped with a BALZERS quadrupole mass spectrometer for the analysis of the evolved gas. Simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) were performed with the same instrument using the DSC setup. The TGA-DSC measurements were performed under a gas flow of 50 ml He/min.

Dynamic high-pressure differential scanning calorimetry (HP-DSC) was performed using a NETZSCH DSC 204 HP PHOENIX instrument at a pressure of 5 bar H_2, temperatures between room temperature and 450 °C, and a heating rate of 10 K/min. The calibration of the instrument was cross-validated by measuring hydrides with known decomposition enthalpy, MgH_2 for example. The deviation of the decomposition enthalpy compared to literature data was not more than 10 %.

3　　　Results and Discussion

3.1　　　Synthesis procedures

Various procedures based on mechanochemical and wet-chemical syntheses were used to prepare solvated and solvent-free magnesium tetrahydroborate. The direct synthesis routes for producing the compound will be described in the following sections.

3.1.1　　　Metathesis reactions

A common method to synthesize complex hydrides is the reaction of a halide with a tetrahydroaluminate or tetrahydroborate, whereby the anions are exchanged and the new compounds precipitate. [16,17] For the preparation of $Mg(BH_4)_2$, the following method is supposed to be feasible:

$$MgCl_2 + 2\ MBH_4 \rightarrow Mg(BH_4)_2 + 2\ MCl \qquad (2)$$
with M = Li, Na
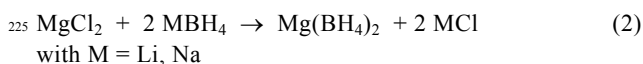
Several metathetical syntheses based on wet chemical and mechanochemical methods were tried, and the products were investigated. We found that high desolvation temperatures were needed for products synthesized from $NaBH_4$ and $LiBH_4$, in THF. This led to products which sometimes did not contain the full amount of hydrogen and/or still contained impurities of carbon from the solvent. Using diethylether as solvent gave a solvent adduct similar to the one described in [11] which could be desolvated so that product with a sufficient purity could be obtained.

Diethylether as solvent

A stoichiometric mixture of 1.904 g $MgCl_2$ (20 mmol) and 1.513 g $NaBH_4$ (40 mmol) were pre-milled in a Fritsch P6 planetary ball mill at 600 rpm for 2 hours (Si_3N_4 vial and balls, ball/powder ration 20:1). The fine white powder was transferred to a three-neck round bottom flask fitted with nitrogen inlet and attached to a condenser. After the addition of 200 ml diethylether, the suspension was vigorously stirred under reflux for 24 hours. The reaction mixture was filtered through a fine-grade glass frit and the solvent was removed under vacuum from the filtrate until the residue became viscous. The remaining liquid phase was then heated under vacuum at 190°C for 1 h, upon which it transformed into a white solid that was crushed, finely ground and dried at 180°C for 2 h in a rotating glass oven (Büchi B 585). The yield was 50% with respect to $Mg(BH_4)_2$. Elemental analysis showed that the product contained 0.4 mass% C, probably due to

residual solvent, and 13.6 mass% H (theor. 14.9 mass%). The purity related to the H content was 91 %, accordingly.

Other solvents with *N*-ligands instead of the stronger *O*-ligands were tested, such as trimethylamine (TMA), triethylamine (TEA), tetramethylethylenediamine (TMEDA), and pyridine. However, either the dissolving power of the solvent was too weak (TMA, TEA), such that the reactants were not dissolved and did not react, or the boiling point of the solvent was too high (TMEDA) and the coordination was so strong that the TMEDA could not be removed from the boranate without decomposing the substance.

Dry mechanochemical synthesis

2.5 g $MgCl_2$ (0.026 mol) and 1.142 g $LiBH_4$ (0.052 mol) were milled under an argon atmosphere in a planetary ball mill at 600 rpm in a 80 ml stainless steel vial and balls. Samples were taken during the procedure and analyzed by XRD. Milling was performed for 80 h until the reflections of $LiBH_4$ (educt) or Li_2MgCl_4 (intermediate) had disappeared and signals from LiCl and a second phase only were present.

3.1.2　　　Direct synthesis

A direct synthesis of $Mg(BH_4)_2$ was developed based on a proposition made by Köster. [13] 34.9 mmol (0.918 g) of pre-milled magnesium hydride were added to 76.8 mmol (8.83 g) of the triethylamine borane complex under argon atmosphere. The mixture was heated under reflux at 100 °C for one hour with vigorous stirring and afterwards at 145 °C for another six hours. After this time, the mixture was cooled down to room temperature, followed by the addition of 30 ml of n-hexane. The suspension was then stirred for eight hours at RT and subsequently filtered, washed with n-hexane (3 x 30 ml), and dried under vacuum. The solid obtained in this way is a triethylamine adduct of magnesium borohydride. The pure, solvent-free magnesium borohydride was obtained after drying the complex mentioned for a total of 15 hours at various stages (100 °C/1h; 130 °C/1h; 170 °C/3h; and 160 °C/12h under a vacuum (p ~ 1 x 10-3 mbar). The yield was 1.79 g (95%) with respect to MgH_2.

The Mg content was determined by ICP-OES and reached the theoretical value (99 ± 1 %, calculation based on $Mg(BH_4)_2$). Boron could not be determined quantitatively by the method, which was probably due to the unpredictable loss of volatile borohydride species during preparation and/or measurement. This was also found when analyzing other tetrahydroborates of known composition by the method. The carbon and nitrogen content determined by elemental analysis was zero, the hydrogen content was 14.6 ± 0.1 wt.% H (theoretical value 14.9 wt% H). Based on the hydrogen content, the purity of $Mg(BH_4)_2$ was approx. 98%. Pure $Ca(BH_4)_2$ and transition metal boranates were prepared in pure form by the same procedure. The results will be published in a forthcoming paper.

3.2　　　Characterization

3.2.1　　　Infrared spectroscopy

FTIR spectra were taken from the products produced by wet chemical and mechanochemical synthesis. Figure 1 shows the FTIR spectra of $Mg(BH_4)_2$ prepared by ball milling (in a mixture with the by-product LiCl) and by direct wet chemical synthesis as low-temperature (α) phase and high-temperature (β) phase annealed at 240°C. Typical features of the $[BH_4]$ group can be observed in the spectra, i.e. the stretching and deformation of B-H bonds in the regions between 2150-2400 cm^{-1} and 1100-1300 cm^{-1}, respectively. The B-H1 absorption band is split into three contributions at 2387 cm^{-1}, 2296 cm^{-1}, and 2230 cm^{-1}. The B-H2 bending vibration is split into two contributions at 1126 cm^{-1} and 1261 cm^{-1}. The presence of an absorption band around 2390 cm^{-1} is an indication of an H bridge or H interaction between the complex anion and the metal, similar to a monodentate hydroborate complex. [18] The only difference between the spectra of the low- and the high-temperature phases is the occurrence of a small peak at 1020 cm^{-1} in the former phase. The other signals are exactly at the same position. A small signal is present at 1370 cm^{-1} in the data of the ball-milled product, but is missing in the products of direct wet chemical synthesis. Only a weak bump at around 1400 cm^{-1} can be observed in these samples. Table 1 summarizes the absorption data of the dried samples from wet chemical metathesis and the samples from the direct synthesis methods.

3.2.2 Thermal analysis

Thermal analysis was performed with α-$Mg(BH_4)_2$ from direct wet chemical synthesis in order to study the decomposition behavior of the material. TGA-MS, TGA-DSC, and high-pressure DSC experiments were performed to examine the temperatures of the various transformation steps, the decomposition products, and the transformation enthalpies.

TGA-DSC measurements were performed under a He flow at ambient pressure. In order to obtain quantitative information about the transitions, the experiments were repeated in an HP-DSC instrument under a 5 bar hydrogen atmosphere, with the same heating rate. Figure 2 shows the results of a TGA-DSC, and a HP-DSC experiment.

The major events of the transformation are all endothermic. The first event with a peak temperature 193 °C (He flow) and 195 °C (5 bar H_2) was identified to be a polymorphic transition from the alpha to the beta phase. It is not associated with a mass loss of the sample, as can be seen from the TGA curve in the upper part of the diagram. Moreover, the polymorphic transition is not reversible, as was shown by a HP-DSC experiment, where the sample was heated up to 240 °C and then cooled down to 100 °C at different heating rates. This indicates that the alpha phase is metastable and irreversibly transforms into the beta phase when heated.

A considerable mass loss was detected together with the following endothermic events. A mass spectrometric analysis of the gas phase above the sample showed that the desorbed gas consisted almost exclusively of hydrogen, with a trace of B_2H_6. The weight loss detected between 290 °C and 500 °C was 13 wt.%, which is close to the total hydrogen content of

the material. Most of the weight is lost between 300 °C and 400 °C.

The HP-DSC data provide a picture which differs slightly from the one obtained in the experiments under He flow. The first decomposition peak is located at 320 °C (5 bar H_2) compared to around 310 °C under He atmosphere. It should be noted that there is a shoulder at around 310 °C which appears in the HP-DSC trace. Moreover, there is a minor contribution at 320 °C in the DSC data under He flow also. The second major event was found in both experiments at the same temperature (367 °C). The third event is located at 383 °C (He flow) or 403 °C (5 bar H_2). It is likely that the peak shifts to higher temperature are due to the background pressure of hydrogen in the HP-DSC experiments. Such an effect points at decomposition reactions which occur in equilibrium with hydrogen. Hence, it is assumed that the events at 320 °C and at 403 °C are such processes, most likely the first decomposition step of the $Mg(BH_4)_2$ into MgH_2, and the decomposition of the MgH_2 in the second step. The DSC data exhibits that the transformation of the $Mg(BH_4)_2$ is a rather complex process where the decomposition occurs in at least 4-5 subsequent transformation steps.

Evaluation of the area under the desorption event between 280 °C and 450 °C yields an overall desorption enthalpy of 67 +- 7 kJ/mol $Mg(BH_4)_2$. It should be noted that this value includes the whole event of the decomposition of the compound and is considerably smaller than the values which are expected from enthalpy of formation data in the literature which were, e.g., predicted by theoreticians. The low decomposition enthalpy together with the comparably high decomposition temperature points toward a transformation process which is kinetically hindered.

3.2.3 Powder X-ray Diffraction

Samples from mechanochemical synthesis

Batches prepared by mechanochemical synthesis were investigated as a product mixture of boranate and the inert by-product and an evolution was observed of the product composition with time. During the first hours of ball milling, a mixture was obtained, which consisted of $LiBH_4$, Li_2MgCl_4, traces of $LiBH_4$, and a fourth phase, the reflections of which were assigned to the low-temperature phase of $Mg(BH_4)_2$ according to the reaction

$$2\ MgCl_2 + 4\ LiBH_4 \rightarrow Li_2MgCl_4 + 2\ LiBH_4 + Mg(BH_4)_2\ (\alpha)$$

$$(4)$$
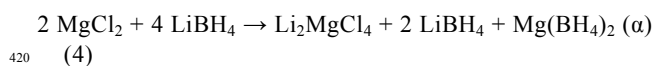
After approx. 36 h, the ternary chloride started to decompose and LiCl was detected additionally in the sample due to the following reaction:

$$Li_2MgCl_4 + 2\ LiBH_4 \rightarrow 4\ LiCl\ + Mg(BH_4)_2 \qquad (5)$$

The ternary chloride could not be detected after 80 h of ball milling and the sample mixture had converted into LiCl and at least one additional phase, see Figure 3. Most of the reflections of this phase could be assigned to the low-

temperature modification of $Mg(BH_4)_2$. However, there is also one signal at 19.3°, the position and intensity of which does not fit to the nearest reflections of the alpha phase at 18.7° or 19.9°. Moreover, the position is not close to the highest signal of the beta phase at 18.75°.

Samples from wet chemical reactions

The wet chemical metathesis reaction with THF produced a compound which was identified as $Mg(BH_4)_2 \cdot 3$ THF. The structure of this compound was determined earlier [19] and its structural data were used to calculate a powder XRD pattern which fits to the experimental data. Distinct patterns were obtained when drying the material at different stages, probably showing the partly desolvated intermediates to the end product $Mg(BH_4)_2$. However, it was not possible to obtain the fully desolvated material without decomposing the substance, as was mentioned above.

In the following, the properties of the products obtained from direct wet chemical synthesis are described. The data of the product obtained by metathesis reaction in diethylether is similar. However, due to the desolvation temperature of 180 °C which is necessary to remove the ether, a small amount of the low temperature phase had already converted into the beta phase so that it was not possible to obtain the material phase-pure.

Low-temperature modification

The product showed good crystallinity, see Figure 4. The position of the reflections, the d-spacing, and the relative intensities are listed in Table 2.

High-temperature modification

The material was annealed under argon atmosphere at 210 °C for 2 h to convert the low-temperature into the high-temperature modification which is more stable. The diffraction pattern of the product, measured at room temperature, is shown in Figure 5. The position of the reflections, the d-spacing, and the relative intensities are summarized in Table 2.

The structures of both modifications are still unknown. Although several suggestions were made by theoreticians, [9,20] none of the structures suggested fit to the experimental powder diffraction pattern. Hence, further work is under way in order to synthesize a deuterated version of the material, which shall be studied by neutron diffraction. It may be worth noting that none of the powder diffraction patterns in the ICDD data bank (PDF #261212 and PDF #261213) published by Konoplev [10] fit to our experimental patterns obtained for the products of direct wet chemical and mechanochemical synthesis.

In-situ XRD

Temperature-resolved in-situ XRD studies were performed under a vacuum ($< 1 \times 10^{-3}$ mbar) at temperatures up to 480 °C, see Figure 6. The alpha phase of the $Mg(BH_4)_2$ was detected at room temperature and up to 170 °C. The measurement at 170 °C already exhibited a mixture of the

low-temperature and the high-temperature phase. The pattern at 240 °C shows the pure high-temperature phase of the $Mg(BH_4)_2$ only. No traces of the low-temperature phase, MgH_2, or Mg are detected. When the decomposition has started at 290 °C, MgH_2, MgB_2, and Mg are predominant in the pattern. This mixture is also present at 355 and 390 °C, with an increasing amount of Mg and decreasing concentration of MgH_2. At 450 °C and above, the MgH_2 has vanished and Mg, MgB_2, and another unknown phase are present. The reflections of this phase do not fit to the ICDD-PDF data bank patterns of B, MgB_4, MgB_6, and MgB_{12}. MgB_2 was assigned based on its second and third largest peak at 33.5° and 59.9° (2Θ), respectively. The most intense reflection is obscured by a broad signal at around 42° (2Θ), however. This signal and a second one at around 62° can be assigned to MgO. The oxide was detected in the sample at temperature levels above 290 °C, probably due to the reaction between the decomposing material and a background level of oxygen in the analysis chamber. The broad signal at 14° was due to the sample holder. The observations suggest a decomposition scheme according to:

$$Mg(BH_4)_2 \rightarrow MgH_2 + 2\ B + 3\ H_2 \rightarrow Mg + 2\ B + 4\ H_2 \rightarrow MgB_2 + 4\ H_2 \qquad (6)$$
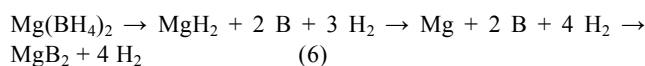
It was found in ex-situ experiments that the product spectrum during the composition may vary depending on the conditions under which the temperature treatment was performed. Heating rapidly up to 390 °C under a vacuum, keeping the temperature for 30 min, and then quenching to room temperature gave a product mixture which consisted of MgH_2, Mg, and MgB_4, the formation of which may be described by the following reaction:

$$3\ Mg(BH_4)_2 \rightarrow Mg + MgB_4 + MgH_2 + 11\ H_2 \qquad (7)$$
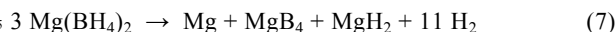
Conclusions

A direct wet chemical synthesis, where Mg hydride reacts with an aminoborane as BH_3 donor was found to be the only method capable of yielding the alpha phase of $Mg(BH_4)_2$ and other tetrahydroborates in high purity, and in quantitative yields. The resulting material is free of any solvents and contains an almost theoretical amount of hydrogen. A particular advantage of this method is that there is no solid by-product which has to be separated from the borohydride, as in case of the other methods investigated in this paper.

When heated under inert or hydrogen atmosphere or under a vacuum, the material first undergoes a polymorphic phase transition to the beta phase at around 190 °C. The transition is not reversible, which indicates a low-temperature phase that is metastable. The thermal decomposition under inert gas or a vacuum proceeds under the formation of hydrogen with traces of diborane and in four or more endothermic steps, as is indicated by simultaneously taken TGA, MS, and DSC data. MgH_2 is detected in the early phase of the decomposition, which might fit to the decomposition reaction (1). However, the diffraction data do not fully prove this assumption,

because elemental boron could not be detected. Moreover, elemental Mg, MgB$_2$, and, depending on the ambient conditions, MgB$_4$ were found in the decomposition product at temperatures around 290 °C already, where the decomposition starts.

The thermal data indicate that the experimental value for the overall decomposition reaction is about 67 kJ/mol Mg(BH$_4$)$_2$, which is considerably lower than the estimate value of less than 132 kJ/mol Mg(BH$_4$)$_2$ predicted earlier by theoretical calculations. The results show that further work is necessary in order to elaborate the reaction schemes and determine the factors which have an influence on the product spectrum and, hence, on the transition enthalpies. In first cycling experiments, it was possible to partly rehydrogenate the material, but only up to an amount which can be explained by the re-formation of MgH$_2$. Therefore, a detailed investigation of the early decomposition steps is necessary, in order to understand, and to be able to lower the obvious kinetic barriers which interfere with the transformation of the material.

Acknowledgements

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Figure Captions

Double column figure/scheme (below)

Single column image (no caption) (below)
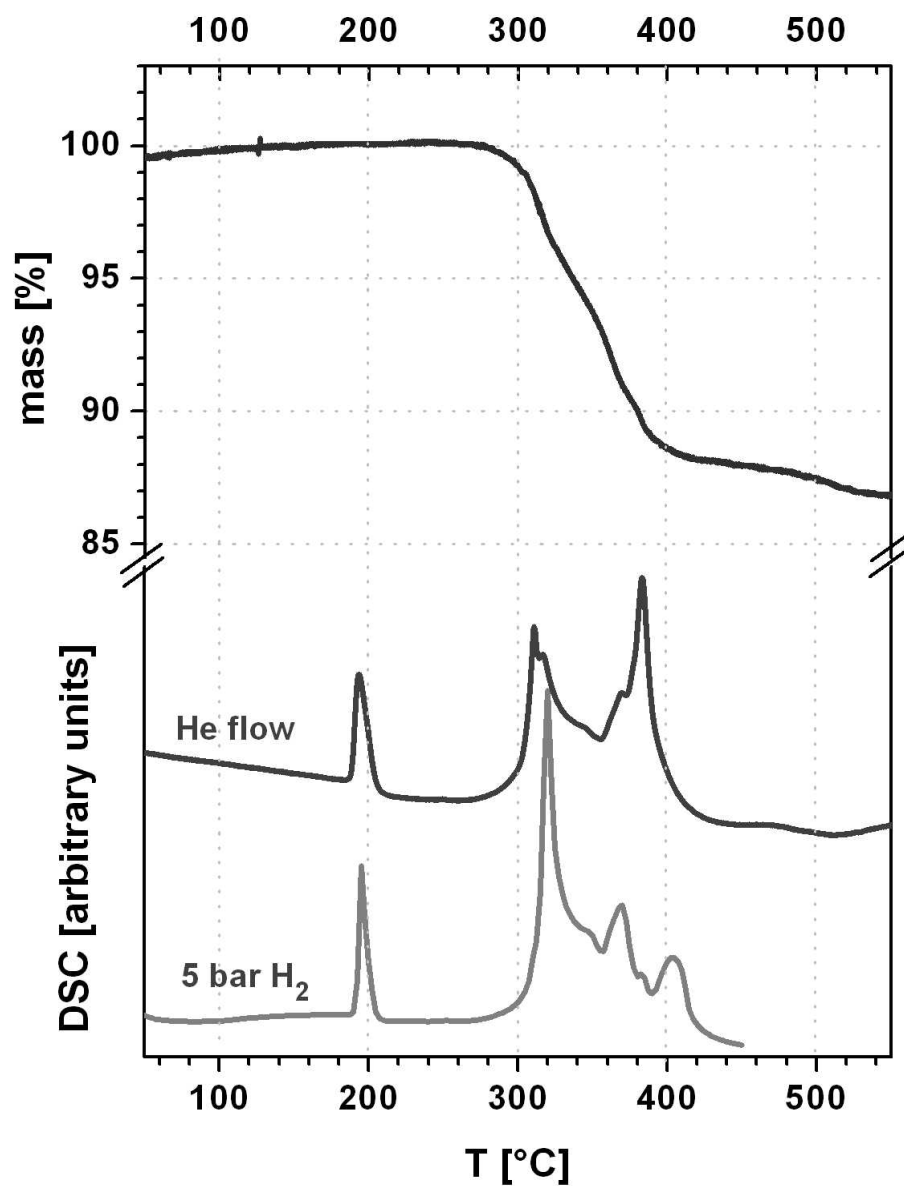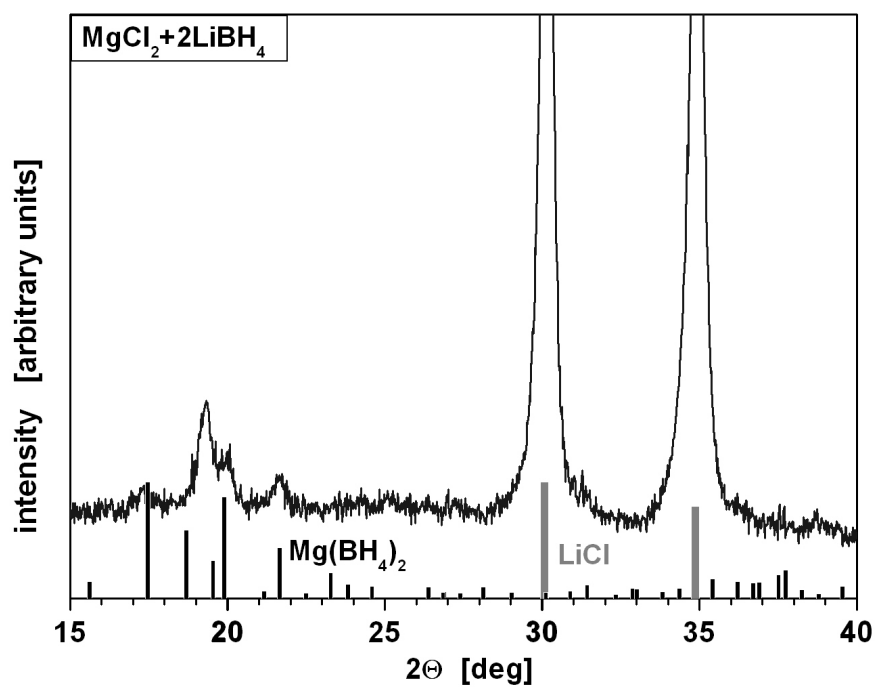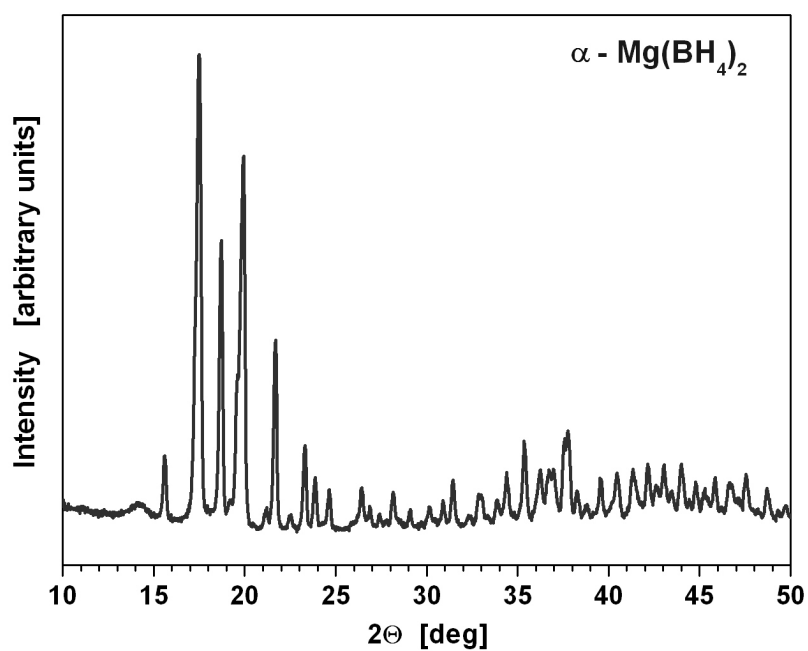
Fig. 1:

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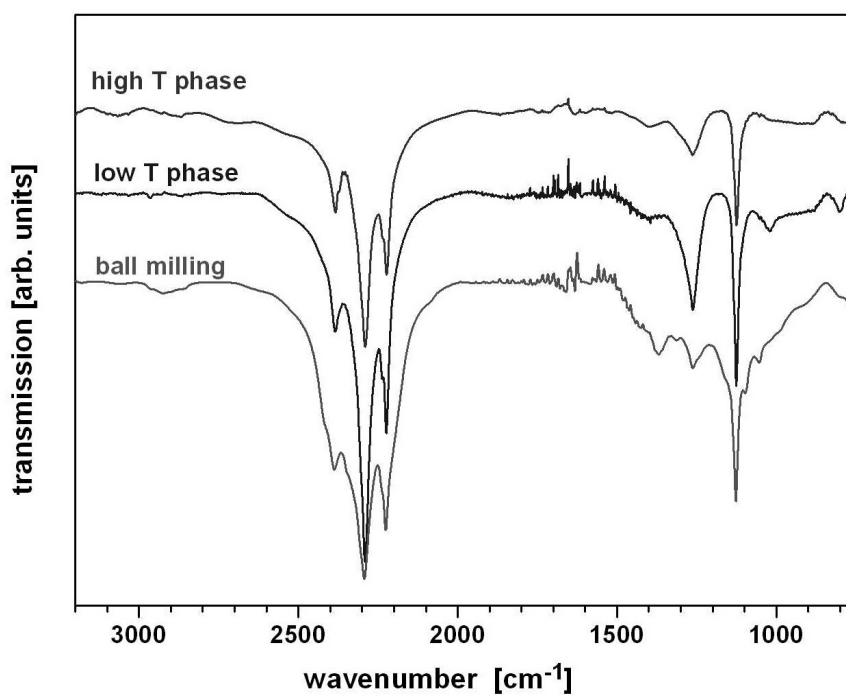
Fig. 2:
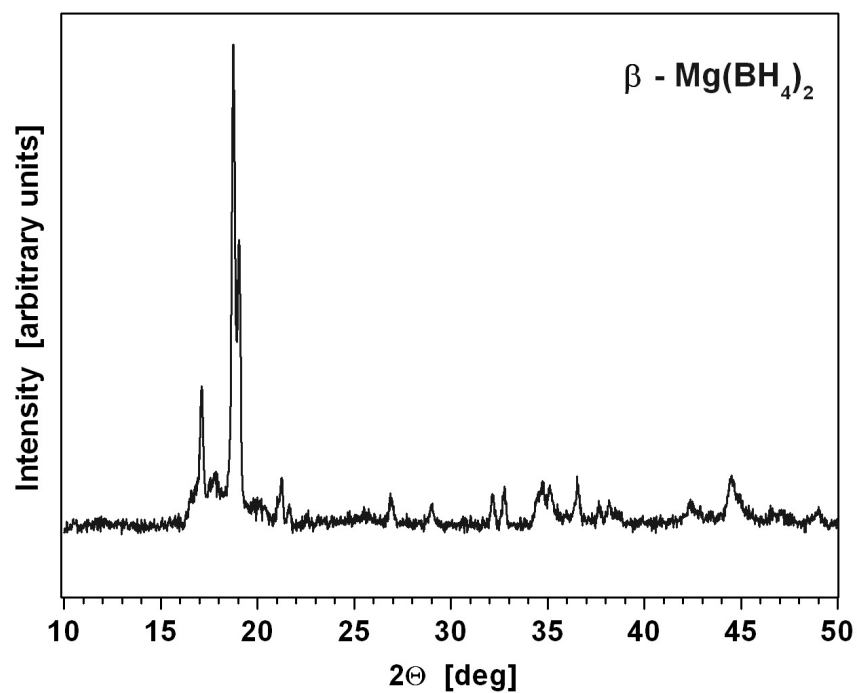
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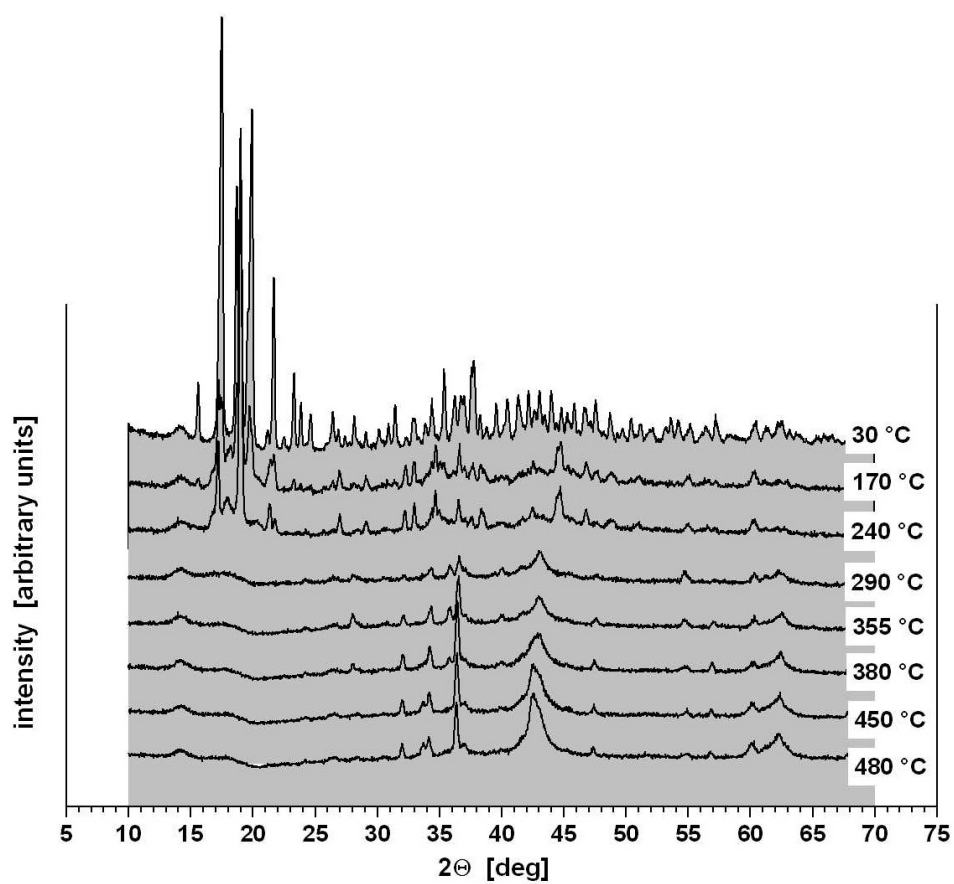

Fig. 4:

645 Fig. 5:

Fig. 6

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Double column image (no caption) (below)

Single column numbered equation/reaction (below)

Single column table (below)

Table 1: Absorption bands (in $[cm^{-1}]$) obtained for samples from different synthesis methods. The data for the low-temperature and high-temperature phases were obtained using the direct wet chemical synthesis product. IR data of $LiBH_4$ are added for comparison.

Ball-milling	α-phase	β-phase	
2386	2384	2384	
2293	2292	2292	
2224	2223	2224	
1371	(1400)	(1400)	
1262	1262	1262	
1127	1126	1125	

Double column table (below)

655

Table 2: Experimental powder diffraction patterns for the low- and the high-temperature modification of $Mg(BH_4)_2$, including the d-spacing, the 2Θ values (for Cu Kα radiation), and the relative signal intensities. Signals weaker than 1% of the maximum intensity were omitted.

Low temperature phase (α)			High temperature phase (β)		
2Θ [°]	d [Å]	I(rel.) [%]	2Θ [°]	d [Å]	I(rel.) [%]
15.62	5.675	15	16.90	5.242	5
17.47	5.076	100	17.10	5.181	21
18.69	4.749	59	17.66	5.018	6
19.54	4.542	32	17.99	4.927	5
19.90	4.461	87	18.74	4.731	100
21.17	4.197	6	19.02	4.663	53
21.66	4.103	43	20.00	4.437	5
22.49	3.953	4	21.21	4.186	8
23.28	3.821	22	21.61	4.108	2
23.83	3.733	12	23.66	3.758	3
24.59	3.620	10	26.86	3.317	7
26.39	3.378	10	28.98	3.079	4
26.85	3.320	5	32.12	2.784	7
27.41	3.255	4	32.74	2.733	9

28.13	3.172	10	34.67	2.585	12
29.04	3.075	5	35.12	2.553	11
30.12	2.967	5	36.51	2.459	10
30.89	2.895	7	37.61	2.390	2
31.43	2.846	12	38.38	2.344	8
32.33	2.769	3	42.45	2.128	11
32.87	2.722	9	44.45	2.037	17
33.01	2.718	8	44.86	2.019	13
33.83	2.648	6	47.02	1.931	5
34.37	2.607	9	48.85	1.863	3
35.42	2.532	17	51.11	1.786	4
36.21	2.479	14	55.27	1.661	2
36.71	2.446	13			
36.90	2.434	14			
37.51	2.396	20			
37.74	2.382	24			
38.24	2.351	8			
38.79	2.320	4			
39.54	2.277	10			
40.43	2.229	12			
41.30	2.184	13			
42.14	2.143	14			
42.57	2.122	9			
43.02	2.101	14			
43.41	2.083	7			
43.98	2.057	14			
44.76	2.023	10			
45.22	2.004	7			
45.82	1.979	11			
46.65	1.945	12			
47.53	1.911	13			
48.72	1.867	9			
49.68	1.834	4			
50.39	1.810	7			
51.11	1.786	6			
52.05	1.755	4			
53.12	1.723	5			
53.57	1.709	7			
54.16	1.692	6			
55.15	1.664	4			
56.43	1.629	4			
57.19	1.610	7			
58.25	1.583	3			
60.22	1.536	3			
61.30	1.511	4			
62.49	1.485	7			
63.15	1.471	4			
63.85	1.457	3			
65.92	1.416	3			

66.52	1.405	3
68.74	1.365	2
70.12	1.341	3
72.18	1.308	3
76.75	1.241	3
78.24	1.221	3
81.04	1.186	1
83.83	1.153	1