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Synthesis of amorphous $Mg(BH_4)_2$ from MgB_2 and H_2 at room temperature

Claudio Pistidda[a], Sebastiano Garroni[b], Francesco Dolci[a], Elisa Gil Bardají[a], Ashish Khandelwal[c], Pau Nolis[d], Martin Dornheim[e], Rapee Gosalawit[e], Torben Jensen[f], Yngve Cerenius[g], Santiago Suriñach[b], Maria Dolors Baró[b], Wiebke Lohstroh[a], Maximilian Fichtner[a,*]

[a] Karlsruhe Institute of Technology, Institute of Nanotechnology, Postfach 3640, 76021 Karlsruhe, Germany
[b] Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
[c] Dipartimento di Ingegneria Meccanica, Settore Materiali and CNISM, Università di Padova, Via Marzolo 9, 35131 Padova, Italy
[d] Servei de Ressonància Magnètica Nuclear (SeRMN), Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain
[e] Institute of Materials Research, Materials Technology, GKSS Research Centre Geesthacht GmbH, Max-Planck-Straße 1, D-21502 Geesthacht, Germany
[f] Interdisciplinary Nanoscience Centre (iNANO) and Department of Chemistry, University of Aarhus, Langelandsgabe 140, DK-8000, Denmark
[g] MAX-lab, Lund University, S-22100 Lund, Sweden

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ABSTRACT

Due to its high hydrogen content and its favourable overall thermodynamics magnesium tetrahydroborate has been considered interesting for hydrogen storage applications. In this work we show that unsolvated amorphous magnesium tetrahydroborate can be obtained by reactive ball milling of commercial MgB_2 under 100 bar hydrogen atmosphere. The material was characterized by solid-state NMR which showed the characteristic features of $Mg(BH_4)_2$, together with those of higher borohydride species. High pressure DSC and TPD-MS showed thermal behaviour similar to that of $Mg(BH_4)_2$ but with broadened signals. *In situ* synchrotron X-ray powder diffraction confirmed the amorphous state of the material and showed the typical crystalline decomposition products of $Mg(BH_4)_2$ at elevated temperatures.

1. Introduction

Borohydrides have been considered interesting candidates for hydrogen storage applications due to their high gravimetric hydrogen content of up to 18.5 mass% in the case of $LiBH_4$. However, although $LiBH_4$, $NaBH_4$ and KBH_4 are readily available and store large amount of H_2, the reaction enthalpy for H_2 desorption is too high compared to a favoured value of $\sim 40\,kJ\,mol^{-1}$ H_2 required for having 1 bar H_2 equilibrium pressure at room temperature.

By means of empirical evaluations Kuznetsov and Dymova [1], Nakamori et al. [2], and Sarner [3], attributed to magnesium borohydride ($Mg(BH_4)_2$) an overall decomposition enthalpy value of about $40\,kJ\,mol^{-1}$ H_2 which was experimentally confirmed by Chlopek et al. [4] and Matsunaga et al. [5]. This feature, together with gravimetric hydrogen content of 14.9 mass%, made $Mg(BH_4)_2$ interesting for hydrogen storage applications and the reversible properties of the material gained centre stage. However, due to kinetic constraints the experimentally found desorption temperature for bulk $Mg(BH_4)_2$ is 300 °C and higher [4] and, under moderate conditions, only partial reversibility between Mg and MgH_2 has been found until now [6,7]. Recently, it was shown that almost full reversibility may be possible under high temperature and high pressure conditions. Severa et al. demonstrated that MgB_2 can be converted into $Mg(BH_4)_2$ with a yield of 75% when the boride is treated at 400 °C under 950 bar hydrogen atmosphere for 108 h [8]. The products were analyzed by TGA-DSC, XRD, IR, and solid-state NMR.

In another study, Barkhordarian et al. [9] reported the possibility to obtain borohydrides by solid–gas reaction at relatively moderate temperature and hydrogen pressure conditions using MgB_2 as source of boron instead of elemental boron. Although they synthesized $NaBH_4$, $LiBH_4$ and $Ca(BH_4)_2$ starting from NaH/MgB_2, LiH/MgB_2 and CaH_2/MgB_2, respectively, they could not obtain $Mg(BH_4)_2$ starting from a MgH_2/MgB_2 mixture.

In this work, we report another solvent-free route to synthesize $Mg(BH_4)_2$. Only magnesium diboride and high purity hydrogen gas are used as starting materials. The starting materials, as well as the reaction products were investigated by X-ray powder diffraction analysis (XRPD), high pressure differential scanning calorimetric techniques (HP-DSC), *in situ* X-ray diffraction at the synchrotron,

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* Corresponding author. Tel.: +49 0 724782 5340; fax: +49 0 724782 6368.
E-mail address: m.fichtner@kit.edu (M. Fichtner).

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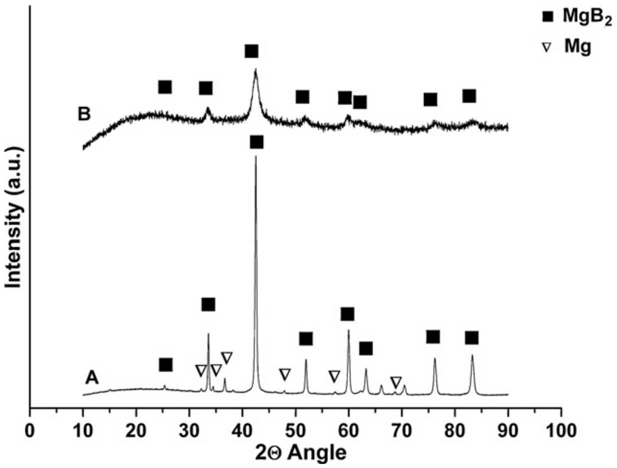

Fig. 1. XRD patterns of the MgB_2 as purchased (pattern A) and the same after 100 h of ball milling under 100 bar and of hydrogen pressure (pattern B). Symbols: ▽ Mg, ■ MgB_2.

and solid-state nuclear magnetic resonance (ssNMR). The gas evolution of the reaction product during thermal programmed desorption (TPD) were examined by means of mass spectrometry technique (MS).

2. Experimental details

The starting materials, MgB_2 (purity >96%) and H_2 (purity 99.999%) were purchased from Sigma–Aldrich and Air Liquide, respectively and used as received. The MgB_2 was charged into a hardened steel high pressure vial, with a ball to powder ratio of 30:1. The handling of the material and the sealing of the high pressure vessel were performed in a glove box under a purified argon atmosphere (O_2 < 1 ppm and H_2O < 1 ppm). The vial was then evacuated ($\sim 10^{-2}$ mbar) and subsequently a hydrogen pressure of 100 bar was applied. The material was milled in a FRITSCH planetary mill (P6) at a rotation speed of 600 rpm for up to 100 h. For comparison, $Mg(BH_4)_2$ (LT-phase) was synthesized by wet chemistry in our laboratory, and used as reference material [4].

X-ray diffraction analysis was carried out using a Philips XPERT diffractometer (Bragg-Brentano configuration) with XCelerator RTMS detector, using Cu Kα radiation (λ = 0.15406 nm). The powder was spread onto a silicon single crystal and sealed in the glove box with an airtight hood of Kapton foil.

In situ XRD measurement was performed at the MAX II Synchrotron, at beamline I711 (Lund, Sweden). The selected wavelength was 0.979 Å. A special sample holder designed for *in situ* monitoring of solid/gas reactions was used [10–12]. All the raw SR diffraction data were elaborated and converted to powder patterns by the use of the FIT2D program [13].

Thermal analysis was performed in a high pressure DSC 204 HP Phoenix from Netzsch. The measurements were carried out at the constant pressure of 3 and 5 bar helium, with a heating rate of 5 °C/min. The HP-DSC apparatus was located in a dedicated glove box under a continuously purified argon atmosphere. Furthermore, temperature programmed desorption was carried out by a homemade TPD-MS apparatus operating at high vacuum ($\sim 10^{-8}$ mbar). The evolved gas was examined by a mass spectrometer from Hiden Analytical.

Solid-state Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker Advance 400 MHz spectrometer with a wide bore 9.4 T magnet employing a boron-free Bruker 4 mm CPMAS probe. The spectral frequency was 128.33 MHz for the ^{11}B nucleus and the NMR shifts are reported in parts per million (ppm) externally referenced to BF_3Et_2O. The powder materials were packed into 4 mm ZrO_2 rotors in an argon-filled glove box and were sealed with tight fitting Kel-F caps. Sample spinning was performed using dry nitrogen gas. The one-dimensional (1D) ^{11}B MAS-NMR spectra were acquired after a 2.7 μs single $\pi/2$ pulse (corresponding to a radiofield strength of 92.6 kHz) and with application of a strong ^1H signal decoupling by using the two-pulse phase modulation (TPPM) scheme [14]. The recovery delay was set to 10 s. Spectra were acquired at 20 °C controlled by a BRUKER BCU unit.

3. Results and discussion

The X-ray diffraction patterns of the as received MgB_2 before and after 100 h of ball milling under 100 bar of hydrogen pressure are shown in Fig. 1. Due to purity between 96% and 100% for the starting material (pattern A), a little amount of free Mg is visible together with MgB_2. The material obtained after reactive ball milling (pattern B) is characterized by the presence of residual MgB_2 plus an amorphous signal with a maximum at approximately 23°. Despite Mg presence in the starting material, peaks related to free Mg, MgH_2 or $Mg(BH_4)_2$ cannot be detected among the final products which indicates that these compounds were either not present or in the amorphous state.

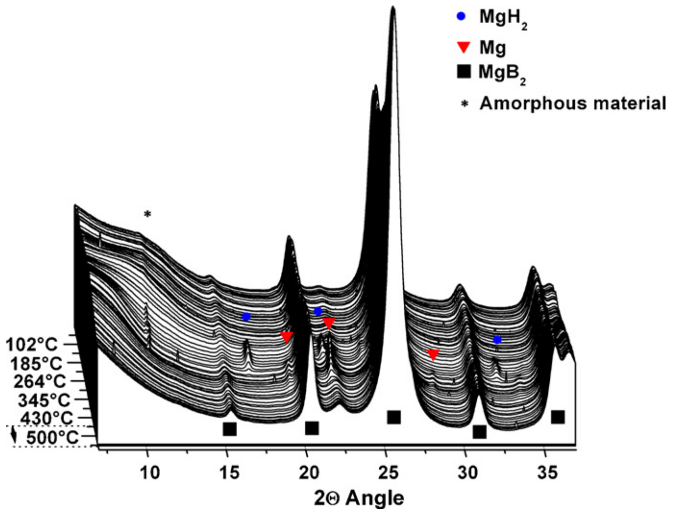

Fig. 2. Series of SR-PXD patterns (wavelength = 0.979 Å) of MgB_2 milled for 100 h under 100 bar of H_2. The sample was heated (5 °C/min) under dynamic vacuum ($\sim 10^{-2}$ bar) from room temperature to 500 °C.

In order to investigate more in detail the synthesized material the desorption process was studied by SR-PXD technique (Fig. 2). The measurement was performed under dynamic vacuum ($\sim 10^{-2}$ bar), heating up the material from room temperature up to 500 °C with a constant heating rate of 5 °C/min. As mentioned above the starting material contains un-reacted MgB_2 and amorphous reaction products (amorphous background at 11.5 2θ angles), among which $Mg(BH_4)_2$ is the predominant phase, see below. Upon heating, due to the thermal cell expansion the MgB_2 peaks shift toward lower 2θ angles. At around 200 °C and above, the intensity of the amorphous background at 11.5 2θ angles starts to decrease. This phenomena is most likely due to a partial decomposition of the amorphous $Mg(BH_4)_2$. At 280 °C MgH_2 appears. Along with the MgH_2 formation the complete disappearance of the amorphous background and a slight increment of the MgB_2 diffracted intensity are observed. The MgH_2 is stable until a temperature of 340 °C is reached, and it rapidly decomposes into free Mg at higher temperatures. In the range between 440 and 480 °C the Mg reflections are markedly attenuated. Simultaneously the MgB_2 intensities increase, indicating an ongoing reaction between Mg and a boron containing species (possibly $Mg(B_nH_m)_y$) to form MgB_2.

For the characterization of the amorphous content of the sample, $^{11}B\{^1H\}$ ssNMR was chosen which is a sensitive and distinct method for the characterization of solid tetrahydroborates and related species, also in amorphous samples [15]. Hence, single pulse $^{11}B\{^1H\}$ ssNMR analysis was performed under MAS conditions of boron chemical environment for the mechanically/hydrogen treated MgB_2. Four main peaks can be distinguished, see Fig. 3. The broad peak at 94.97 ppm can be assigned to MgB_2 by direct comparison with the starting material. The integration of the peak indicates that approximately 18% of the boron atoms are still present as MgB_2. However, as determined by the characteristic $[BH_4]^-$ anion chemical shift position around −40 ppm (side band at ∼53 ppm, 12 kHz sample spinning) and by direct spectral comparison with the LT-$Mg(BH_4)_2$ used as standard (Fig. 3C) it is apparent that a tetra-

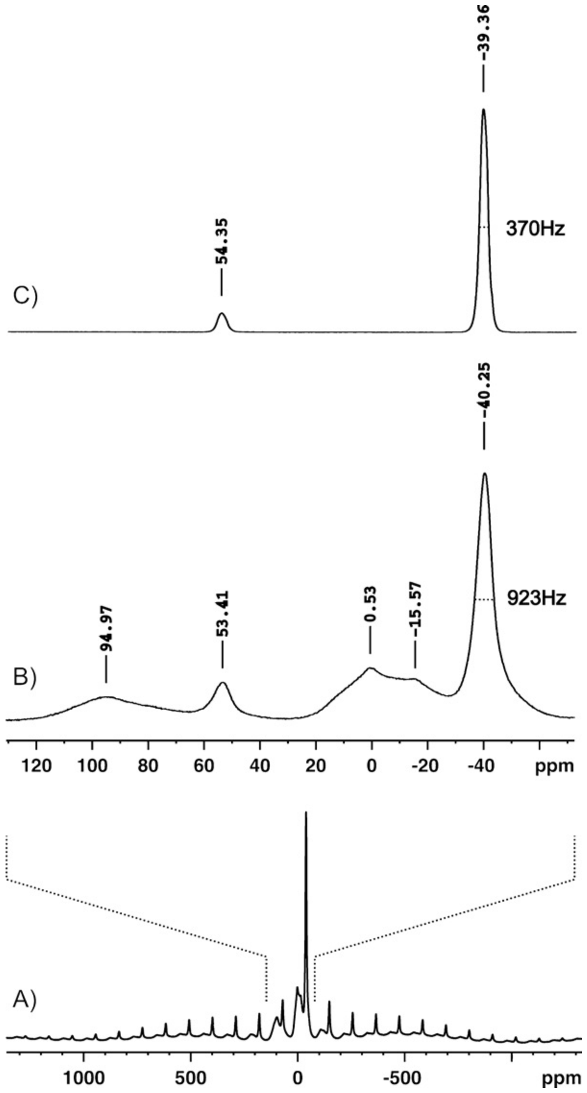

Fig. 3. (A) $^{11}B\{^1H\}$ MAS (12 kHz) single pulse NMR spectrum of MgB_2 milled for 100 h under 120 bar of H_2. (B) Expanded plot of spectrum (A). (C) Bulk $Mg(BH_4)_2$ as reference.

borohydride species has been synthesized which yields the same chemical shift as $Mg(BH_4)_2$. According to the integration of the ssNMR signals the yield of a reaction to $Mg(BH_4)_2$ can be estimated to 50%. The peak of the obtained product is broadened compared to the crystalline reference material, which confirms the amorphous structure of the product obtained by reactive milling. In the range from 20 to −30 ppm a very broad signal is observed, with two shoulders at 0.53 ppm and −15.57 ppm (∼32% signal). In earlier work, this signal has been attributed to a mixture of several $Mg(B_nH_m)_y$ species which were observed during the decomposition process of $Mg(BH_4)_2$ or similar $M(BH_4)_n$ materials [15–17].

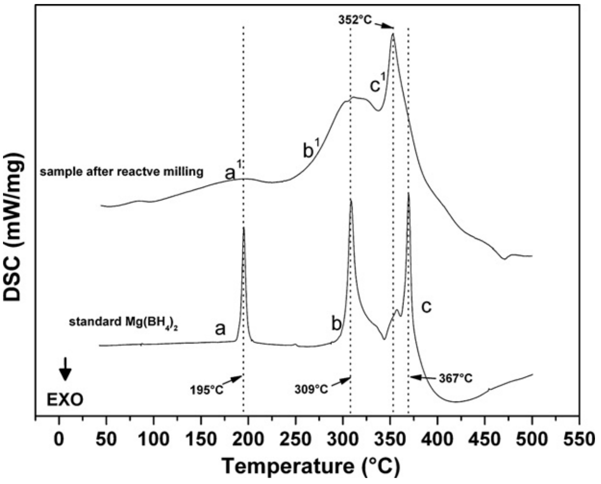

Fig. 4. HP-DSC traces recorded under 3 bar of He pressure for the $Mg(BH_4)_2$ synthesized by reactive milling and under 5 bar of He pressure for the standard $Mg(BH_4)_2$ from RT to 500 °C (5 °C/min heating rate).

The thermodynamic properties of the products were investigated by HP-DSC technique. Fig. 4 shows the HP-DSC traces recorded under 3 bar of He pressure for the $Mg(BH_4)_2$ synthesized by reactive milling and under 5 bar of He pressure for the standard $Mg(BH_4)_2$, both in a ramp from room temperature up to 500 °C, with a heating rate of 5 °C/min. The DSC trace of $Mg(BH_4)_2$ obtained by reactive milling resembles that of standard $Mg(BH_4)_2$, confirming that a large fraction of the MgB_2 has been reacted to form $Mg(BH_4)_2$. Hence peaks a^1 and b^1 belong to the decomposition of $Mg(BH_4)_2$ to MgH_2 (and a not defined B–H species) and peak c^1 belongs to the subsequent decomposition of MgH_2 which occurs between 350 and 400 °C. It is not clear at the moment whether peak c^1 is due to a shift of c in the bulk phase to lower temperature or whether c^1 is the enhanced little peak at 355 °C which is visible prior to the large event at 367 °C in the bulk. The nature of the peak at 355 °C is presumably due to residual MgH_2 [18]. We assume that the change in the pattern is due to the particular microstructure of the sample which still contains MgB_2 in an intimate mixture with $Mg(BH_4)_2$. It is also apparent that there is no exothermic signal which could be related to a possible crystallization of $Mg(BH_4)_2$ upon heating which is in accordance to the results of the *in situ* XRD measurements shown in Fig. 2.

The decomposition was further analyzed by a coupled TPD-MS analysis. The measurement was carried out at a pressure of $\sim 10^{-8}$ bar. The range of temperature investigated and the heating rate used were the same chosen for HP-DSC analysis. For the mass spectroscopic analysis of the evolving gases we focused our attention on the intensities of $m/z = 2$ amu for hydrogen, and 24, 25, 26, and 27 amu as a fingerprint for diborane. The results of the TPD-MS measurement are shown in Fig. 5. Considering the

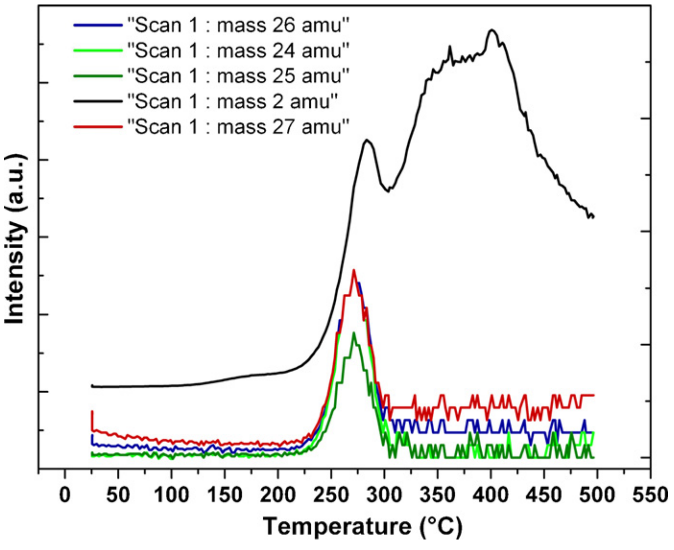

Fig. 5. TPD-MS analysis of the MgB_2 after 100 h of ball milling under 100 bar of hydrogen, measured against 10^{-8} bar of pressure from room temperature to 500 °C (5 °C/min heating rate). Monitored m/z intensities: 2, 24, 25, 26, and 27.

fact that the TPD-MS measurements were carried out at pressures much lower than the one used for HP-DSC analysis a shift towards lower temperatures is expected for the events that are observed by TPD-MS analysis. The gas evolution profiles recorded by means of TPD-MS technique show a first hydrogen release at 110 °C, then a second stronger desorption with a maximum at 290 °C followed by a third peak with onset at 310 °C. The respective intensity ratios for the masses 24, 25, 26, and 27 amu, are in accordance with the fingerprint intensities of diborane [19]. They indicate a diborane release starting at 200 °C, with a maximum at 270 °C, and ending at 305 °C.

In spite of several attempts, the characterization of the produced material by infrared (IR) and Raman spectroscopy was not possible. Obviously, due to the dark color of the material the high radiation absorption led to a decomposition of the sample and a very high background.

4. Conclusions

In summary, amorphous $Mg(BH_4)_2$ can be synthesized by solid–gas reaction with a yield of approximately 50% from MgB_2 and hydrogen by high pressure ball milling. This work is a route for synthesizing unsolvated $Mg(BH_4)_2$ by direct solid-state reaction at more moderate conditions which has not been reported yet for this material. Similarly to earlier reports $Mg(B_nH_m)_y$ species was formed in parallel to the desired $Mg(BH_4)_2$. The particular microstructure of the sample prevents crystallization, as indicated by *in situ* XRD and HP-DSC measurements. The material was characterized by solid-state NMR showing the characteristic features of $Mg(BH_4)_2$ and other $Mg(B_nH_m)_y$ species which were also found in other work where direct synthesis was performed under high temperature and pressure conditions. *In situ* synchrotron X-ray powder diffraction confirmed the amorphous state of the material and showed the typical crystalline decomposition products of $Mg(BH_4)_2$.

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