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## Novel approach for synthesis of Magnesium Borohydride, $Mg(BH_4)_2$

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### Abstract

$Mg(BH_4)_2$  is a complex hydride with one of the highest hydrogen contents (~ 15%) known yet. Several synthesis routes have been reported for it, all based on the metathesis reaction of  $MgCl_2$  with  $NaBH_4$  performed in a ball-mill or in suitable solvents.

In the present study a new approach for synthesis of  $Mg(BH_4)_2$  will be presented in which the more reactive  $MgBr_2$  is used instead of  $MgCl_2$ . For this purpose a mixture of  $MgBr_2$  and  $NaBH_4$  (molar ratio: 1: 2 and 1:2.15) was ball-milled for 6, 12 and 18 h, respectively.  $Mg(BH_4)_2$  was extracted from the reaction product ( $Mg(BH_4)_2 + NaBr$ ) by Soxhlet with diethylether over a day. The remaining residue after solvent evaporation was dried in vacuum at 150 °C for 24 h and 5h at 190 °C. The intermediate and final products of the reactions were analyzed using XRD, DTA/TG, Mass and Vibrational Spectroscopy. The XRD diagrams of the mixture after ball milling showed only the characteristic reflections of NaBr and the patterns obtained after solvent extraction was in all cases consistent with  $\beta$ - $Mg(BH_4)_2$ . The additional weak  $MgBr_2$  reflections, decreased by increasing the ball milling time from 6 to 18 h. The DTA/TG coupled with MS revealed ~11% mass loss when the product was heated up to 600 °C. The result of MS detected that the exhaust gas is exclusively  $H_2$ .

Compared to  $MgCl_2$ , the use of  $MgBr_2$  has two advantages: the reaction time is considerably shorter and the excess of  $MgBr_2$  can act as additive lowering the onset temperature for hydrogen release from 290 °C - for pure  $Mg(BH_4)_2$  - to ~ 220 °C.

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## Introduction

Due to environmental pollution, diminishing and imbalance distribution of fossil fuels searching for alternative and sustainable energy sources always attracts too much of interests. Hydrogen, as the most abundant element in the universe, is one of the most promising clean energy sources. It is the lightest fuel, richest in energy per unit mass and can be easily stored unlike the electricity [1, 2].

There are some conventional methods for storing hydrogen which can be mainly categorized to physical storage ( $\text{LH}_2$ ,  $\text{CGH}_2$  and absorbents) and chemical storage (Complex Metal Hydrides Metal Hydrides) [3, 4]. The transport section requires cheap, safe and reliable way of storing hydrogen along with high storage capacity. Solid state hydrogen storage seems to be a prominent method for onboard applications [1, 3, 5, 6]. Among these, alkaline and alkaline-earth metal based borohydrides such as  $\text{LiBH}_4$ ,  $\text{Mg}(\text{BH}_4)_2$ , and  $\text{Ca}(\text{BH}_4)_2$  as being light weight compounds, have high gravimetric hydrogen energy density and potential to meet DOE requirements- in spite of some limitation in thermodynamics, kinetics and having several decomposition steps- become popular candidates among solid state hydrogen storage materials. [6-10].

Based on the hydrogen energy density values in Table 1,  $\text{Be}(\text{BH}_4)_2$  seems to be the first candidate among the metal borohydrides, as having low onset hydrogen release ( $123\text{ }^\circ\text{C}$ ) and low enthalpy of formation ( $27\text{ KJ/mole}$ ). However, all beryllium compounds are toxic and therefore not suitable for hydrogen storage [7, 11].  $\text{LiBH}_4$ , is the second candidate of choice with a theoretical hydrogen density of  $21.8\text{ wt}\%$  but practically it can release only  $13.8\text{ wt}\%$  hydrogen. The reason is that the thermal decomposition is not complete yielding  $\text{LiH}$  and  $\text{B}$  as final products. Moreover,  $\text{LiBH}_4$  has a moderate heat of formation of  $75\text{ KJ/mole}$  and extreme conditions in reversibility ( $873\text{K}$ ,  $35\text{Mpa}$  in 12 hours or  $1000\text{K}$ ,  $15\text{Mpa}$  in 10 Hours) [8]. With  $16.9\text{ wt}\%$  hydrogen content,  $\text{Al}(\text{BH}_4)_3$  is the third promising candidate. It has a very low enthalpy of formation ( $5.5\text{ KJ/mole}$ ) [29] and comparatively low hydrogen release temperature ( $150\text{ }^\circ\text{C}$ ). However, it is liquid at room temperature and pyrophoric [11]. Compared to aluminium borohydride, the title compound  $\text{Mg}(\text{BH}_4)_2$  has slightly lower hydrogen content ( $14.9\%$ ) but relatively low density ( $0.989\text{ g/cm}^3$ ), higher volumetric density ( $147\text{ kg/m}^3$ ) and a low enthalpy of formation ( $40\text{KJ/mole}$ ). With these properties, it has a high potential to become one of the most important hydrogen storage materials.  $\text{Mg}(\text{BH}_4)_2$  is tetramorph ( $\alpha$ ,  $\beta$ ,  $\gamma$  ( $2.5\%$  physically hydrogen storage) and  $\delta$  (porous)) with complex crystal structures. Each of the polymeric forms may reveal different decomposition pathways but the final product is in all cases the hydrogen free  $\text{MgB}_2$ . [7, 8, 12, 13].

Table 1: List of promising metal borohydrides

Metal Borohydride	Dehydrogenated form	H <sub>2</sub> Density (wt%)		H <sub>2</sub> Density (kg/m <sup>3</sup> )		Enthalpy of formation	Ref.
		Theo.	Exp.	Theo.	Exp.		
$\text{Be}(\text{BH}_4)_2$	$\text{Be}+2\text{B}$	20.8	20.8	146	146	27	8
$\text{LiBH}_4$	$\text{LiH}+\text{B}$	18.5	13.8	122	93	75	8,11
$\text{Al}(\text{BH}_4)_2$	$\text{Al}+3\text{B}$	16.9	16.9	133	133	6	11
$\text{Mg}(\text{BH}_4)_2$	$\text{Mg}+2\text{B}$	14.9	14.9	147	147	40	11
$\text{Ca}(\text{BH}_4)_2$	$2/3\text{CaH}_2+1/3\text{CaB}_6$	11.6	9.7	124	104	75.5	8,11

NaBH <sub>4</sub>	NaH+B	10.7	7.9	114.5	85	90	8,11
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The preparation of magnesium borohydride is quite challenging since the successful synthesis of it is critically depending on the experimental conditions. Mg(BH<sub>4</sub>)<sub>2</sub> undergoes a Lewis acid-base reaction with solvent molecules L yielding the stable adduct Mg(BH<sub>4</sub>)<sub>2</sub>.L (L=Solvent). Once the adduct is formed it is quite difficult to get the solvent free salt back again and needs extreme conditions for final heat treatments [14, 15]. Moreover, the mixture (Mg(BH<sub>4</sub>)<sub>2-n</sub>X<sub>n</sub>, n=0-2) is usually form in metathesis reaction from which Mg(BH<sub>4</sub>)<sub>2</sub> is difficult to separate or even to identify [15]. Several routes have been reported for the synthesis of magnesium borohydride, mostly based on the metathesis reaction of MgCl<sub>2</sub> with NaBH<sub>4</sub> or LiBH<sub>4</sub> performed in a planetary ball mills or in suitable solvents such as diethylether and THF [13, 16-18]. P.Zanella et.al. [15] proposed two alternative synthesis methods by using Al(BH<sub>4</sub>)<sub>3</sub> and BH<sub>3</sub>S(CH<sub>3</sub>)<sub>2</sub> which act as "BH<sub>4</sub>-donor" and Mg(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> as Mg source, respectively, in Toluene/Heptane with a relatively high yield. An overview of the reaction conditions for the some important synthesis methods of Mg(BH<sub>4</sub>)<sub>2</sub> are summarized in Table 2.

Table 2: overview of some known synthesis methods for Mg(BH<sub>4</sub>)<sub>2</sub> and their reaction conditions

Synthesis method	Precursor 1	Precursor 2	Ratio (1/2)	Synthesis		Solvent	Heat treatment		Product(s)	Yield %	Ref
				Temp. (C)	Time (h)		Temp. (C)	Time (h)			
Planetary ball mill-Stirring	MgCl <sub>2</sub>	MBH <sub>4</sub> (M=Li,Na)	1:2	R.T.	2+24	Diethylether	190 180	1 2	α and β Mg(BH <sub>4</sub> ) <sub>2</sub>	50	13
Planetary ball mill Stirring	MgCl <sub>2</sub>	LiBH <sub>4</sub>	1:2	R.T.	80	–	–	–	LiCl- Mg(BH <sub>4</sub> ) <sub>2</sub>	–	
	MgH <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N-BH <sub>3</sub>	1:2.2	100 145 R.T. (*)	1 6 8	–	100 130 170 160	1 1 3 12	α and β Mg(BH <sub>4</sub> ) <sub>2</sub>	95	
Direct	MgCl <sub>2</sub>	LiBH <sub>4</sub>	1:2	320 (**)	3	–	–	–	LiCl	–	16
Stirring	Mg(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	Al(BH <sub>4</sub> ) <sub>3</sub>	1.35:1	-78 to 25	15	Toluene/Heptane	R.T. 60	– –	α- Mg(BH <sub>4</sub> ) <sub>2</sub>	85	15
Stirring	Mg(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	BH <sub>3</sub> S(CH <sub>3</sub> ) <sub>2</sub>	1:3.6	25	2	Toluene/Heptane	R.T. 75	6 13	α- Mg(BH <sub>4</sub> ) <sub>2</sub>	93	15
Stirring	MgCl <sub>2</sub>	LiBH <sub>4</sub>	1:2.51	R.T.	Over-night	Diethylether	180	1	α- Mg(BH <sub>4</sub> ) <sub>2</sub>		18
	MgCl <sub>2</sub>	LiBH <sub>4</sub>	1:3	R.T.	Over-night	Diethylether	200	1	α- Mg(BH <sub>4</sub> ) <sub>2</sub>		
Stirring	MgCl <sub>2</sub>	NaBH <sub>4</sub>	1:2	R.T.	15	Amine solution	R.T. 155 200	1 2 2	α and β Mg(BH <sub>4</sub> ) <sub>2</sub>	41	
Stirring	MgCl <sub>2</sub>	NaBH <sub>4</sub>	1:3	R.T.	6	Diethylether	155 200	2 2	β- Mg(BH <sub>4</sub> ) <sub>2</sub>	15	
Pipe ball mill	MgCl <sub>2</sub>	NaBH <sub>4</sub>	1:3	R.T. (*)	24	Diethylether	R.T. 80 235	– – 5	β- Mg(BH <sub>4</sub> ) <sub>2</sub>	77.5	

\* with addition of 30 ml n-hexane

\*\* under 10 Mpa H<sub>2</sub> atmosphere

## Experimental Procedure

The convenient synthesis of Mg(BH<sub>4</sub>)<sub>2</sub> is based on metathesis reaction of anhydrous MgCl<sub>2</sub> with LiBH<sub>4</sub> or NaBH<sub>4</sub> followed by solvent extraction with diethylether or THF. In the present study an alternative preparation is followed in which the more reactive MgBr<sub>2</sub> is used instead of MgCl<sub>2</sub>. The equation for the metathesis reaction is given below:



The reactants, magnesium bromide (MgBr<sub>2</sub>, 98% anhydrous) and sodium borohydride (NaBH<sub>4</sub>, granular 98%) were purchased from Aldrich as analytical reagent grade. Diethylether (Merck) was used as solvent for extraction and purification of the target compound, Mg(BH<sub>4</sub>)<sub>2</sub>. An excess of NaBH<sub>4</sub> with respect to the stoichiometric ratio was employed to investigate its effect on the formation of Mg(BH<sub>4</sub>)<sub>2</sub>. The ratio of reactants and the reaction times of ball milling are summarized in Table 3.

Table 3: synthesis conditions for reaction in reaction 1

Series	MgBr <sub>2</sub> (mole)	NaBH <sub>4</sub> (mole)	Time (h)
1	1	2	6
	1	2	12
	1	2	18
2	1	2.15	6
	1	2.15	12
	1	2.15	18

The mechanochemical synthesis was performed in Fritsch P7 planetary ball mill at 600 rpm with a 20 ml zirconia vials using 3 mm zirconium oxide balls. The ball to powder mass ratio was 20:1. All sample manipulations and powder loading were performed under inert conditions (glove-box, N<sub>2</sub>, O<sub>2</sub> ≤ 1ppm, H<sub>2</sub>O ≤ 1ppm). The very hygroscopic white crude product obtained after ball milling was then transferred into the glove box and placed into the thimble of the Soxhlet extraction vessel. In this work diethylether was chosen as a solvent for extraction/purification because THF needs high desolvation temperature which leads to the loss of hydrogen and can result in carbon impurity in the final product [13]. The extraction takes approximately 24 h, after which all Mg(BH<sub>4</sub>)<sub>2</sub> was dissolved while NaBr remained as residue in the thimble. The solvent removal occurred under vacuum (10<sup>-3</sup> mbar) at room temperature yielding a colorless viscous residue which then turned into white waxy mass after heating in silicon oil bath to 150 °C for 24 h in vacuum and was annealed for 5 h at 190 °C to remove the residual solvent.

The crude (after ball mill) and purified reaction products were analyzed using powder X-ray diffraction method. PXRDs were done with BRUKER D2 Phaser diffractometer (Cu radiation with LYNXEYETM detector). The samples were prepared in the glove box and Kapton foil was used to keep the holder air tight during the measurement. The thermal behavior of the specimen was determined by Differential Thermal Analysis – Thermogravimetry (DTA/TG). The evolved gases were analyzed by Mass Spectrometry. DTA/TG ( SII EXSTAR 6300) – MS (PFEIFFER Vacuum GDS 301 T3) measurements were conducted under argon gas flow from room temperature to 600 °C with the heating rate of 10 K/min using platinum sample holders. In each test nearly 10 mg sample was loaded in to Pt sample holders and transferred using an air tight container. The samples were further characterized by Raman Spectroscopy. The measurements were done using nearly 5 mg of sample in sealed pyrex tube (Ø

= 4 mm) in the range of 2500-1000  $\text{cm}^{-1}$  with a BURKER RFS 100/S spectrometer (Nd: YAG-Laser, 1064 nm, 200 mW).

## Results and Discussion

In the first reaction series the stoichiometric mixture of  $\text{MgBr}_2/\text{NaBH}_4$  (1:2) were ball milled for 6h to 18h. PXRD analyses in both cases confirmed an incomplete reaction. After 6 hours of ball mill only precursors can be detected, while, after 18 hours PXRD pattern shows NaBr with some amount of unreacted  $\text{MgBr}_2$ .

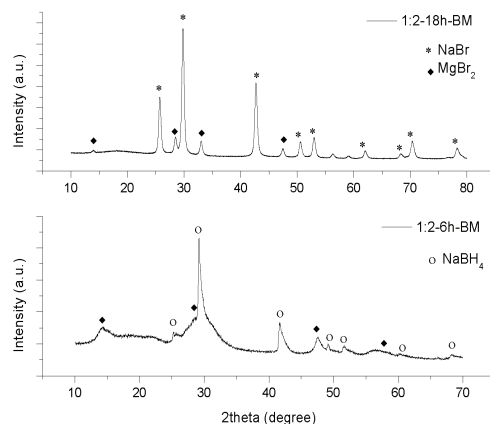


Figure 1: PXRD patterns of ball milled samples with stoichiometric ratio of 1:2 at 6h (bottom) and 18h (top)

For the second reaction series ( $\text{MgBr}_2/\text{NaBH}_4$  1:2.15, and 6h to 18h ball milled) the PXRD patterns revealed in all conditions solely NaBr indicating a complete reaction (Fig. 2a). After purification,  $\text{MgBr}_2$  peaks emerged in all powder diagrams whose intensity decreased significantly by increasing ball mill time from 6 hours to 18 hours. After the final heat treatment at 190 °C,  $\beta\text{-Mg}(\text{BH}_4)_2$  became the only detectable phase (Fig. 2b) in the patterns. As was reported by several authors [21, 22], the absence of  $\text{Mg}(\text{BH}_4)_2$  reflections in all reaction products indicates that the compound formed under this conditions is an amorphous type.

As can be seen in figure 3a, MS spectra revealed in all cases nearly 11% mass loss on the heating to 600 °C. The result shows that the exhaust gas is exclusively  $\text{H}_2$ . According to figure 3b even small amounts of  $\text{MgBr}_2$  effect on both onset temperature of  $\text{H}_2$  release and maximum of  $\text{H}_2$  release. The presence of  $\text{MgBr}_2$  shifts  $\text{H}_2$  release temperature from 290 °C [13] or 250 °C [19, 20] for pure  $\text{Mg}(\text{BH}_4)_2$  to near to 220 °C. Another effect of  $\text{MgBr}_2$  addition is the change of the temperature of maximum hydrogen release for  $\text{Mg}(\text{BH}_4)_2$ . The relationship is demonstrated in Fig.4b in which the maxima of hydrogen release peaks in the Mass spectra undergo a shift of almost 10 °C towards lower temperatures with increasing amount of  $\text{MgBr}_2$ ; i.e. from sample with 18 h to 6 h ball milling time. The TG curves of the two samples (Fig. 4a) show beside the above mentioned effects also a slight difference of in the total mass loss (~ 2% ) which can be referred to partial hydrolyses of the specimen during the transfer into the measuring cell of the DTA device.

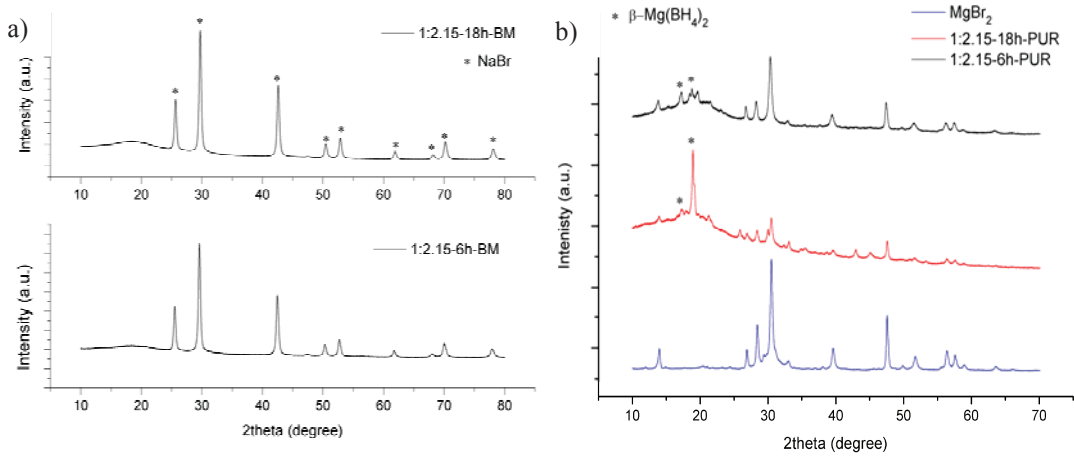


Figure 2: a) XRD patterns of ball milled samples with 1:2.15 ratio at 6h (bottom) and 18h (top), b) XRD patterns of purified samples in which  $\text{MgBr}_2$  pattern is given as a reference.

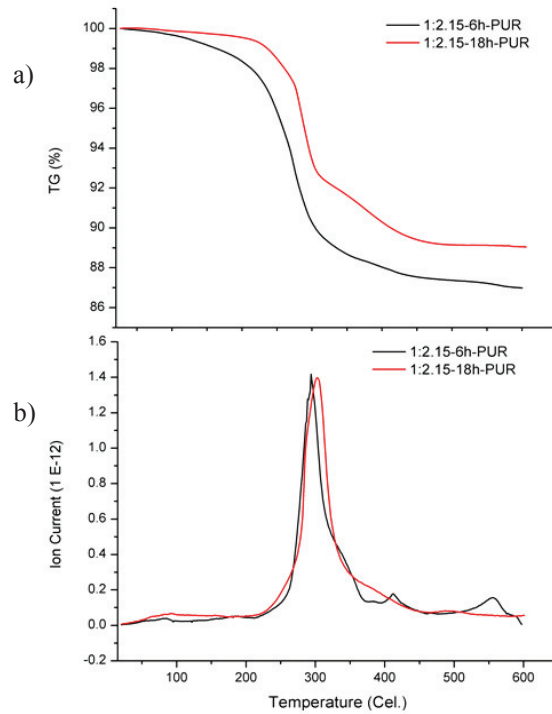


Figure 3: TG spectra of synthesized  $\beta\text{-Mg}(\text{BH}_4)_2$  with 6h(red) and 18h(black) (a) and MS spectra of it with 6h(red) and 18h(black) (b) heating rate 10 K/min under Ar flow

Raman spectrum of purified  $\beta\text{-Mg}(\text{BH}_4)_2$  is shown in Figure 4 in comparison with that of  $\text{NaBH}_4$  which is used as a reference. Both the frequencies as well as the distribution of the band intensities are in good agreement with those previously reported for  $\beta\text{-Mg}(\text{BH}_4)_2$  [12, 21, 22]. The (B–H) bending modes

are observed at 1202 and 1391  $\text{cm}^{-1}$ , respectively. Due to the different structural environment of the  $[\text{BH}_4]^-$  units in the crystal, the symmetric (B-H) stretch splits up and is observed as two bands at 2195 and 2305  $\text{cm}^{-1}$ . The antisymmetric stretch is localized at 2510  $\text{cm}^{-1}$ .

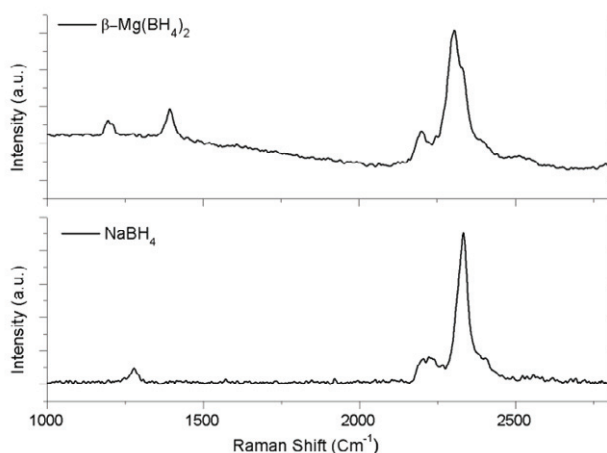


Figure 4: Raman spectra of synthesized  $\beta\text{-Mg}(\text{BH}_4)_2$  (top) and purchased  $\text{NaBH}_4$  (bottom).

## Conclusion

Magnesium borohydride was successfully synthesized by metathesis reaction of  $\text{MgBr}_2$  and  $\text{NaBH}_4$ . For the stoichiometric ratio (1:2) the reaction was incomplete even after 18h ball milling. For mixtures with the molar ratio 1:2.15  $\text{NaBr}$  was the only crystalline product that could be observed in the X-ray powder diagram. In accordance with other reports  $\text{Mg}(\text{BH}_4)_2$  which forms as second phase under this reaction conditions is amorphous so that no powder patterns were available. TG analysis of the purified magnesium borohydride has shown nearly 11% mass loss stemming solely from  $\text{H}_2$  release. In some cases the extracted magnesium borohydride was slightly contaminated by  $\text{MgBr}_2$ . This has two consequences on the thermal behaviour of  $\text{Mg}(\text{BH}_4)_2$ . The  $\text{MgBr}_2$  impurity reduces the onset temperature of hydrogen release from 250  $^\circ\text{C}$  to 220  $^\circ\text{C}$ . On further increasing of the magnesium bromide content in the samples, the peak maximum of hydrogen release shifts towards lower temperatures.

## References

- [1] I.P.Jain, Pragma Jain, Ankur Jain, Novel hydrogen storage materials: A review of lightweight complex hydrides, *J alloy Comp*, 2010, 503, 303-339.
- [2] Gustavo Adolfo Lozano Martinez, *Development of Hydrogen Storage Systems using Sodium Alanate*, PhD thesis Technischen Universität Hamburg, 2010.
- [3] Ulrich Eberle, Michael Felderhoff, and Ferdi Schth, Chemical and Physical Solutions for Hydrogen Storage, *Angew Chem Int*, 2009, 48, 6608 – 6630.
- [4] Trygve Riis, Gary Sandrock, Øystein Ulleberg, Preben J.S. Vie, Hydrogen Storage – Gaps and Priorities, *IEA HIA*, 2005.
- [5] Lyci George, Surendra K. Saxena, Structural stability of metal hydrides, alanates and borohydrides of alkali and alkali- earth elements: A review, *Int J hydro Energy*, 2010, 35, 5454-5470.
- [6] Rebecca J. Newhouse, Vitalie Stavila, Son-Jong Hwang, Leonard E. Klebanoff, and Jin Z. Zhang, Reversibility and Improved Hydrogen Release of Magnesium Borohydride, *J Phys Chem C* 2010, 114, 5224–5232.
- [7] Ewa Ronnebro, Development of group II borohydrides as hydrogen storage materials, *Cur Op Solid State Mat Sci*, 2011, 15, 44-51.
- [8] Hai-Wen Li, Yigang Yan, Shin-ichi Orimo, Andreas Züttel and Craig M. Jensen, Review: Recent Progress in Metal Borohydrides for Hydrogen Storage, *Energies*, 2011, 4, 185-214.

- [9] Elisa Gil Bardaji, Zhirong Zhao-Karger, Nancy Boucharat, Angeloclaudio Nale, Michiel J. van Setten, Wiebke Lohstroh, et al.,  $\text{LiBH}_4\text{-Mg}(\text{BH}_4)_2$ : A Physical Mixture of Metal Borohydrides as Hydrogen Storage Material, *J Phys Chem C*, 2011, 115, 6095–6101.
- [10] Junzhi Yang, Dichen Li, He Fu, Gongbiao Xin, Jie Zhenga and Xingguo Li, In situ hybridization of  $\text{LiNH}_2\text{-LiH-Mg}(\text{BH}_4)_2$  nano-composites: intermediate and optimized hydrogenation properties, *Phys. Chem. Chem. Phys.*, 2012, 14, 2857–2863.
- [11] Grigorii L. Soloveichik, Metal Borohydrides as Hydrogen Storage Materials, *Mat Matter*, 2007, 2.2, 11.
- [12] Yaroslav Filinchuk, Bo Richter, Torben R. Jensen, Vladimir Dmitriev, Dmitry Chernyshov, and Hans Hagemann, Porous and Dense Magnesium Borohydride Frameworks: Synthesis, Stability, and Reversible Absorption of Guest Species, *Angew. Chem Int Ed*, 2011, 50, 11162–11166.
- [13] Chłopek, K.; Frommen, C.; Léon, A.; Zabara, O.; Fichtner, M. Synthesis and Properties of Magnesium Tetrahydroborate,  $\text{Mg}(\text{BH}_4)_2$ , *J Mater Chem*, 2007, 17, 3496–3503.
- [14] Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Grigorii L. Soloveichik, Job Rijssenbeek, Matthew Andrus, et al., Structure of unsolvated magnesium borohydride  $\text{Mg}(\text{BH}_4)_2$ , *Acta Cryst*, 2007, B63, 561–568.
- [15] Pierino Zanella, Laura Crociani, Norberto Masciocchi, and Giovanni Giunchi, Facile High-Yield Synthesis of Pure, Crystalline  $\text{Mg}(\text{BH}_4)_2$ , *Inorg Chem*, Vol. 46, No. 22, 2007, 9039–9041.
- [16] Matsunaga, T.; Buchter, F.; Miwa, K.; Towata, S.; Orimo, S.; Züttel, A., Magnesium borohydride: A New Hydrogen Storage Material. *Renew. Energy*, 2008, 33, 193–196.
- [17] Soloveichika, G.L.; Gao, Y.; Rijssenbeek, J.; Andrus, M.; Kniajanski, S.; Bowman, R.C., et al., Magnesium Borohydride as a Hydrogen Storage Material: Properties and Dehydrogenation Pathway of Unsolvated  $\text{Mg}(\text{BH}_4)_2$ , *Int J Hydro Energy*, 2009, 34, 916–928.
- [18] Grigorii L. Soloveichik, Matthew Andrus, Yan Gao, J.-C. Zhao, Sergei Kniajanski, Magnesium borohydride as a hydrogen storage material: Synthesis of unsolvated  $\text{Mg}(\text{BH}_4)_2$ , *Int J Hydro Energy*, 34, 2009, 2144-2152.
- [19] Hanada, N.; Chłopek, K.; Frommen, C.; Lohstroh, W.; Fichtner, M., Thermal Decomposition of  $\text{Mg}(\text{BH}_4)_2$  Under He flow and  $\text{H}_2$  Pressure. *J Mater Chem*, 2008, 18, 2611–2614.
- [20] Junzhi Yang, Xuanzhou Zhang, Jie Zheng, Ping Songa and Xingguo Lia, Decomposition pathway of  $\text{Mg}(\text{BH}_4)_2$  under pressure: Metastable phase and thermodynamic parameters, *Scr Mater*, 2011, 64, 225-228.
- [21] H.-W. Li, K. Kikuchi, Y. Nakamori, K. Miwa, S. Towata and S. Orimo, Effect of ball milling and additive on dehydrating behaviors of well-crystallized  $\text{Mg}(\text{BH}_4)_2$ , *Scr Mater*, 2007, 57, 679–682
- [22] Yuko Nakamori, Kazutoshi Miwa, Akihito Ninomiya, Haiwen Li, Nobuko Ohba, Shin-ichi Towata, et al., Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiments, *Phys Rev B*, 2006, 74, 045126.