

**Synthesis and Investigation of Hydrogen Storage Properties of $\text{Mg}(\text{BH}_4)_2$
and Investigation on Structural Modification in MgB_2**

by

Ali Bateni

**A Thesis Submitted to the
Graduate School of Engineering
in Partial Fulfillment of the Requirements for
the Degree of**

Doctor of Philosophy

in

Material Science and Engineering

Koç University

September 2015

Koç University
Graduate School of Sciences and Engineering

This is to certify that I have examined this copy of a Ph.D. 's thesis by

Ali Bateni

and have found that it is complete and satisfactory in all respects,

and that any and all revisions required by the final

examining committee have been made.

Committee Members:

Prof. Dr. Mehmet Somer (Advisor)

Prof. Dr. Sema Z. Baykara

Assoc. Prof. Dr. Emre Erdem

Assoc. Prof. Dr. Özgür Birer

Assist. Prof. Dr. Melis Şerefoğlu Kaya

Date:

Abstract

Complex metal borohydrides, such as MBH_4 ($\text{M}^+ = \text{Li}, \text{Na}, \text{K}$), $\text{M}(\text{BH}_4)_2$ ($\text{M}^{2+} = \text{Mg}, \text{Ca}, \text{Zn}, \text{Sn}, \text{Cu}$) and $\text{M}(\text{BH}_4)_3$ ($\text{M}^{3+} = \text{Al}$) have attracted a great deal of interest for their potential use as solid-state hydrogen storage materials due their high gravimetric and volumetric storage capacities. One of the most promising and extensively investigated candidate in this series is $\text{Mg}(\text{BH}_4)_2$ which is available only in small quantities on preparative scale. The complex synthesis procedure and the comparatively high price of the material has been one of the main drawbacks in its more widely use, both in research and for technical applications. In the present study, five different multi steps mechanochemical and wet mixing synthesis – all based on the metathesis reaction of MgX_2 ($\text{X} = \text{Cl}, \text{Br}$) with NaBH_4 – were performed in a planetary ball-mill or in diethyl ether to develop an easy and convenient preparation route for $\text{Mg}(\text{BH}_4)_2$. In addition, a novel and expedient approach was tested at relatively high pressure and high temperature in an autoclave using diethyl ether as solvent. $\text{Mg}(\text{BH}_4)_2$ was extracted from the reaction product by Soxhlet method overnight. 97% pure $\text{Mg}(\text{BH}_4)_2$ with 63% yield in only 6 h mixing time was obtained after solvent removal.

In contrast to MgCl_2 , MgBr_2 is at least partially soluble in diethyl ether. Thus, using bromide should enhance the reaction rate and the yield of $\text{Mg}(\text{BH}_4)_2$. The synthesis results surprisingly not only in formation of pure magnesium borohydride and NaBr but yielding also the mixed phases $\text{NaBr}_{1-x}(\text{BH}_4)_x$ and/or $\text{Na}(\text{BH}_4)_{1-y}\text{Br}_y$, as consequence of solid solution formation. The effect of milling speeds, time and reactant ratios for sample prepared by ball milling and various temperatures, time and reactant ratios for mixtures prepared in autoclave are investigated in detail with respect to solid solution formation by XRPD and ATR-FTIR. Finally, dehydrogenation behavior of $\text{Mg}(\text{BH}_4)_2$ has been investigated in combination with metal amides and MgBr_2 . For the systems of $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$, the decomposition pathways were predicated using XRPD, DTA-TG-MS, DSC and ATR-FTIR spectroscopy. The mentioned systems show an improvement in H_2 onset temperature release while NH_3 and B_2H_6 liberation is decreased in a great extend or suppressed. Interestingly, hydrogen desorption in

Mg(BH₄)₂-Mg(NH₂)₂ mixtures occurs in two steps, unlike the other blends and pure Mg(BH₄)₂ which release their hydrogen in three and four steps, respectively.

MgB₂ is the ultimate product of thermal decomposition of Mg(BH₄)₂ at 600 °C. This simple compound is a binary superconductor with a great potential for several engineering applications. In the second part of this thesis, investigation of the synthesis of nano structured MgB₂, as well as its structural modification will be coming to the fore. Micron sized MgB₂ is obtained from the boron and magnesium powders by solid-state reaction route under Ar. However, the synthesis of nano-sized material succeeds only when nano sized boron powder was used as precursor, as proved by SEM and TEM images. Rietveld analysis revealed also a reduction in MgO content when nano boron was employed. The defect structures of MgB₂ bulk and nano particles, have been investigated mainly by the aid of X-band electron paramagnetic resonance (EPR) spectrometer which proved the presence of Mg vacancies in nanoscale MgB₂. In addition, the microscopic defect structures of carbon-doped MgB₂ were systematically investigated by means of XRPD, Raman spectroscopy and EPR. Mg vacancies and C-related dangling-bond active centers were distinguished. By the help of EPR in the temperature range of 40 to 10 K, the reduction in the critical temperature T_c was observed due to C doping.

Özet

Mg(BH₄)₂ Sentezi ve Hidrojen Depolama Özelliklerinin İncelenmesi ve MgB₂ Yapısal Modifikasyonunun İncelenmesi

Kompleks metal bor hidrürlerin, MBH₄ (M⁺ = Li, Na, K), M(BH₄)₂ (M²⁺ = Mg, Ca, Zn, Sn, Cu) ve M(BH₄)₃ (M³⁺ = Al), yüksek gravimetrik ve volumetrik depolama kapasiteleri nedeniyle katı-hal hidrojen depolama malzemesi olarak kullanımları oldukça ilgi çekmektedir. Mg(BH₄)₂ ise bu serinin en yüksek potansiyele sahip olan ve üzerinde yoğun bir şekilde araştırmalar yapılmasına rağmen ancak küçük ölçekte üretimi gerçekleştirilebilen bir malzemedir. Oldukça kompleks sentez işlemi ve nispeten yüksek maliyetli bir malzeme olması birçok alanda kullanımını engellemiş ve teknik ve bilimsel uygulamalar için dezavantaj oluşturmuştur. Bu çalışmada, çok adımlı beş farklı mekanokimyasal ve ıslak karıştırma senteziyle -tümü MgX₂ (X = Cl, Br) ve NaBH₄ metatez reaksiyonuna dayandırılan- değirmende ya da dieterler içinde yapılan ve kolay ve uygun bir şekilde Mg(BH₄)₂ sentezi çalışılmıştır. Buna ek olarak, yeni ve uygun bir yöntem olarak olarak, dieter etilin, bir otoklav içinde nispeten yüksek bir basınç ve yüksek sıcaklıkta çözünürlüğü test edilmiştir. Mg(BH₄)₂, gece boyunca Soxhlet yöntemle reaksiyon ürünü olarak elde edilmiştir. Çözücü buharlaştırıldıktan sonra %63 verim ile yüksek derecede saflıkta (%97) Mg(BH₄) sadece 6 saat içinde elde edilmiştir.

MgBr₂, MgCl₂ nin aksine, dieterler içinde çok az ve kısmen çözünmektedir. Bu sebepten dolayı, bromit kullanımı reaksiyon hızını ve Mg(BH₄)₂ verimini artırmaktadır. Şaşırtıcı bir şekilde, sentez sonucunda sadece saf magnezyum borohidrid ve NaBr değil ve aynı zamanda karışık fazlarda NaBr_{1-x}(BH₄)_x ve/veya Na(BH₄)_{1-y}Br_y, da katıhal oluşumunda görülmüştür. Otoklavda farklı sıcaklıklarda hazırlanan numuneler, değirmen hızının, karıştırma zamanının ve tepkimeye giren malzeme oranının etkilerinin incelenmesi amacıyla, XRPD ve ATR-FTIR ile katı çözelti oluşumu ile ilgili olarak ayrıntılı bir şekilde incelenmiştir. Son olarak, Mg(BH₄)₂ nin hidrojen giderme davranışı, metal amidler ve MgBr₂ ile kombinasyonlar halinde incelenmiştir. Mg(BH₄)₂-NaNH₂, Mg(BH₄)₂-LiNH₂, Mg(BH₄)₂-Mg(NH₂)₂ sistemleri için, ayrışma yolu XRPD, DTA-TG-MS, DSC ve ATR-FTIR spektroskopisi analiz sonuçları esas alınmıştır. Söz konusu sistemlerde,

H₂ başlangıç sıcaklığı salınımında bir iyileşme sağlanırken, NH₃ ve B₂H₆ salınımı büyük oranda azaltılmış ya da bastırılmıştır. Saf Mg(BH₄) ve karışımlarda hidrojen salınımı sırasıyla üç yada dört adımda gerçekleşirken, farklı olarak, Mg(BH₄)₂-Mg(NH₂)₂ karışımlarında hidrojen salınımı iki aşamada gerçekleşir.

MgB₂, Mg(BH₄)₂ nin 600°C 'de termal bozunması sonucunda elde edilen nihai üründür. Bu basit bileşik, iki bileşenli süperiletken malzeme olarak çeşitli mühendislik uygulamalarında kullanımı için büyük potansiyele sahiptir. Bu tezin ikinci bölümünde, nano yapılı MgB₂ sentezinin yanısıra, yapısal modifikasyonu da ön planda tutularak incelenmiştir. Mikron büyüklüğündeki MgB₂ parçacıkları Ar gazı ortamında bor ve magnezyum tozlarının katıhal reaksiyonu sonucunda elde edilir. Ancak, nanoboyuttaki malzeme sentezi, SEM ve TEM görüntüleri ile ispatlandığı üzere ancak nanoboyutlu bor tozu, öncü olarak kullanıldığında başarılı olur. Nanoboyutta boron kullanıldığı zaman MgO içeriğinde bir azalma görüldüğü Rietveld analizi ile doğrulanmıştır. Hacimsel ve nanoparçacık MgB₂ nin kusur yapıları temel olarak, MgB₂ içindeki Mg boşluk kusurlarının nano ölçekte varlığının kanıtlandığı X-bant elektron paramanyetik rezonans (EPR) spektrometresi yardımıyla incelenmiştir. Buna ek olarak, karbon katkılanırılmış MgB₂ nin mikroskopik yapı kusurları XRPD, Raman spektroskopisi ve EPR ile sistematik olarak incelenmiştir. Mg boşluk kusurları ve C-ilişkili sarkık bağ aktif merkezleri ayırt edilmiş ve karbon radikalleri tespit edilmiştir. EPR analizi yardımıyla 10-40 K arasında bir sıcaklık aralığında, C katkılanmasından kaynaklanan kritik sıcaklık, T_c, değerinde düşüş tespit edilmiştir.

ACKNOWLEDGEMENTS

There are a number of people I would like to thank for helping and supporting me during my research. Without their supports in various ways, this thesis would not have been possible.

First and foremost, I would like to express my thanks to my supervisor Professor Dr. Mehmet Somer for all his invaluable supports and guidance during my PhD. He was like a father mentoring me in my life as well as advising me as a supervisor for my research.

I would also like to thanks Assoc. Prof. Dr. Emre Erdem, master of EPR, for his friendly help in the second part of my thesis. Without his guidance writing these sections would be almost impossible.

I want to thank to all my professors and instructors at Koç University, particularly Dr. Annamaria Miko who keeps her door open for me for any kinds of discussion. I am also thankful of Assist. Prof. Dr. Melis Şerefoğlu Kaya and Dr. Durata Hacıu and Assoc. Prof. Dr. Özgür Birer for their support during my PhD. Thanks much to Cansu Yildirim and Dr. Barış Yağci at KUYTAM for their help in measurments and insightful comments.

I was lucky to work with Dr. Selcuk Acar at beginning of my PhD. He instructed me in using many devices and supported me in dealing with problems. Many thanks to current and graduated Inorganic Chemistry Laboratory research group, Ali Baş, Ahmet Topcu, Burcu Uslu, Mujde Yahyaoğlu, and Kamil Kiraz for motivation and discussion during my thesis. I would like to express my gratitude to many summer and undergraduate students, Irem Magazci, Tuğçe Üstün, Fatih Karabulut, Emir Pilten, Antonion Medina, Stephan Scherpe, BegümErkin, who handed me in part of experiments. Thanks to Muherrem Güler, master of glass, for all glass works.

Thanks to my friends who I met all at Koç University, Alireza Aleali, Iman Zafarparandeh, Ahad Khaleghi, Farhad Ghorbani, Mohammadreza Khodabakhsh for their moral support and their friendships and specially thanks to Şebnem Yazici who has given me some technical supports and stress relief times over the years.

Finally, I would like to thanks my lovely parents, Mehri and Iraj, and my beautiful sister, Maryam for their love and unlimited support and patience during my whole education.

Table of content

Table of Figures.....	XIII
Table of Tables.....	XVIII
Aims and scope of this thesis.....	XIX
Chapter 1	1
Introduction	
1.1 Non-renewable vs. renewable energy	1
1.2 Hydrogen.....	2
1.3 Hydrogen storage methods.....	3
1.4 Chemical storage of hydrogen.....	6
1.4.1 Metal Hydrides.....	6
1.4.2 Complex Hydrides	7
1.4.2.1 Alanate	7
1.4.2.2 Amides/imides.....	8
1.4.2.3 Borohydrides	9
1.5 References	10
Chapter 2	14
Synthesis of Magnesium Borohydride, $\text{Mg}(\text{BH}_4)_2$	
2.1 Introduction.....	14
2.2 Experimental Procedure.....	20
2.2.1 Metathesis reaction of MgCl_2 and NaBH_4 using furnace or using ball mill followed by furnace heat treatment.....	21
2.2.2 Solid-state metathesis reaction of MgBr_2 and NaBH_4 using ball mill.....	21
2.2.3 Metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether in round bottom flask in ambient condition.....	22

2.2.4	High pressure-high temperature metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether using Autoclave	23
2.2.5	High pressure-high temperature metathesis reaction of MgCl_2 and NaBH_4 in diethyl ether using Autoclave	24
2.3	Results and discussion.....	28
2.3.1	Metathesis reaction of MgCl_2 and NaBH_4 using furnace or using ball mill followed by furnace heat treatment.....	28
2.3.2	Solid-state metathesis reaction of MgBr_2 and NaBH_4 using ball mill.....	29
2.3.3	Metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether in round bottom flask in an ambient conditions	35
2.3.4	High pressure-high temperature metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether using Autoclave	37
2.3.5	High pressure-high temperature metathesis reaction of MgCl_2 and NaBH_4 in diethyl ether using Autoclave	38
2.4	Conclusion.....	42
2.5	References.....	42
Chapter 3		45
Solid solution formation		
3.1	Introduction	45
3.2	Experimental Procedure	48
3.3	Result and Discussion	50
3.3.1	Effect of milling time on solid solution	50
3.3.2	Effect of ball mill speed on substitution	52
3.3.3	Effect of reactant ratio on substitution using ball milling.....	55
3.3.4	Effect of time, temperature and reactant ratio on anion substitution using autoclave	63
3.4	Conclusion.....	67

3.5	References	68
Chapter 4		71
Hydrogen desorption modification of $\text{Mg}(\text{BH}_4)_2$		
4.1	Introduction.....	71
4.2	Experimental Procedure.....	75
4.2.1	$\text{Mg}(\text{NH}_2)_2$ synthesis.....	75
4.2.2	Mixtures preparation for $\text{Mg}(\text{BH}_4)_2\text{-M}(\text{NH}_2)_2$ (M=Li, Na, Mg) system.....	77
4.2.3	Mixture preparation in $\text{Mg}(\text{BH}_4)_2\text{-MgBr}_2$ system.....	77
4.3	Results and Discussion.....	78
4.3.1	$\text{Mg}(\text{BH}_4)_2\text{-M}(\text{NH}_2)_2$ (M=Li, Na, Mg) system.....	78
4.3.2	$\text{Mg}(\text{BH}_4)_2\text{-MgBr}_2$ system.....	93
4.4	Conclusion.....	95
4.5	References.....	96
Chapter 5		99
Superconductivity and MgB_2		
5.1	Superconductivity.....	99
5.1.1	Critical Temperature (T_c).....	100
5.1.2	Meissner Effect	100
5.1.3	Vortex states and flux pinning:	102
5.1.4	BSC Theory	103
5.1.5	High- T_c superconductors.....	104
5.2	Magnesium diboride (MgB_2)	104
5.2.1	MgO role in MgB_2	106
5.2.2	Doping effect in MgB_2	107
5.2.3	Effect of strain and defect in MgB_2	108

5.3	References	108
Chapter 6		112
Defect structure of ultrafine MgB₂ Nanoparticles		
6.1	Introduction	112
6.2	Experimental procedure	114
6.3	Results and Discussion.....	115
6.4	Conclusion.....	121
6.5	References	122
Chapter 7		125
PXRD, Raman and EPR spectroscopy studies on C-doped MgB₂		
7.1	Introduction	125
7.2	Experimental Procedure	127
7.2.1	Synthesis of carbon-doped MgB ₂ powders.....	127
7.2.2	Methods of sample characterization	128
7.3	Result and Discussion	129
7.3.1	Structural analysis.....	129
7.3.2	Raman spectroscopy	131
7.3.3	EPR spectroscopy	133
7.4	Conclusion.....	136
7.5	References	137
Chapter I.....		140
Appendix: Characterization methods and analysis theory		
ii.	Powder X-ray Diffraction	140
iii.	X-ray Fluorescence Spectroscopy (XRF)	141

iv. Thermal analysis (Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric (TG)	144
v. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR)...	146
vi. Raman spectroscopy	148
vii. Scanning Electron Microscope (SEM).....	150
viii. CNHS/O Analyzer.....	153
ix. Electron Paramagnetic Resonance Spectroscopy (EPR)	155
x. Rietveld analysis	156
xi. References.....	158

Table of Figures

Fig.1.1 Evolution of industrial usage of energy carriers.....	2
Fig.1.2 Different hydrogen storage technologies and their operating conditions.....	5
Fig.2.1 Flow chart borohydride synthesis procedure using metathesis reaction.	16
Fig.2.2 Schematic of $\text{Mg}(\text{BH}_4)_2$ synthesis procedure using MgBr_2 and NaBH_4 thru ball milling.	22
Fig.2.3 Schematic of $\text{Mg}(\text{BH}_4)_2$ synthesis procedure using MgBr_2 and NaBH_4 thru wet mixing in round bottom flask.	23
Fig.2.4 Schematic of $\text{Mg}(\text{BH}_4)_2$ synthesis procedure using MgCl_2 and NaBH_4 thru wet mixing in autoclave.	25
Fig.2.5 Schematic of setup which is used for purification of $\text{Mg}(\text{BH}_4)_2$	26
Fig.2.6 XRPD pattern mixture of MgCl_2 and NaBH_4 in 1:2.5 ratio (NaBH_4 in excess) annealed at 270 °C for 24 h.....	28
Fig.2.7 XRPD pattern of MgCl_2 and NaBH_4 in 1:2.5 ratio (a) ball milled for 24 h (b) ball milled for 24 h and heat treated at 270 °C for 24 h.....	29
Fig.2.8 XRPD pattern of MgBr_2 and NaBH_4 in 1:2 ratio (a) ball milled for 6 h (b) ball milled for 24 h.....	30
Fig.2.9 XRPD pattern of MgBr_2 and NaBH_4 in 1:2.25 ratio (a) ball milled for 6 h (b) ball milled for 24 h.....	31
Fig.2.10 XRPD pattern of purified mixture of MgBr_2 and NaBH_4 in 1:2.25 ratio (a) ball milled for 6 h (b) ball milled for 24 h.	31
Fig.2.11 XRPD pattern of MgBr_2 and NaBH_4 in 1:2.5 ratio (a) ball milled for 6 h (b) ball milled for 24 h.....	32
Fig.2.12 XRPD pattern of purified mixture of MgBr_2 and NaBH_4 in 1:2.5 ratio (a) ball milled for 6 h (b) ball milled for 24 h.	33
Fig.2.13 Raman spectra of $\alpha\text{-Mg}(\text{BH}_4)_2$, mixture at 1:2.5 ratio milled for 6 h, NaBH_4 and ball milled NaBH_4 for 6 h.	34
Fig.2.14 XRPD pattern of MgBr_2 and NaBH_4 in 1:2 and 1:3 ratios not-milled and pre-milled and mixed for 24 hours in round bottom flask	36

Fig.2.15 a) ATR-FTIR spectrum of mixture of MgCl_2 and NaBH_4 in 1:2.5, 1:3 and 1:4 ratios mixed for 6 and 24 h at 100 °C in Autoclave b) Raman spectra of mixture in 1:2.5 ratio mixed for 6 h at 100 °C in Autoclave and as received Aldrich $\alpha\text{-Mg(BH}_4)_2$.	39
Fig.2.16 XRPD pattern of (a) crystalline $\text{Mg(BH}_4)_2 \cdot n\text{Et}_2\text{O}$ heat treated up to 180 °C (b) amorphous $\text{Mg(BH}_4)_2 \cdot m\text{Et}_2\text{O}$ heat treated up to 280 °C.	40
Fig.3.1 Relation between enthalpy of formation $[\text{M(BH}_4)_n]$ and Pauling electronegativity, X_p .	47
Fig.3.2 XRD pattern of mixture ball milled at 3, 6, 12 and 24 h using 500 rpm with 2:1 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 200 reflection.	50
Fig.3.3 XRD pattern mixture ball milled at 3, 6, 12 and 24 h using 500 rpm with 1:1 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 200 reflection.	51
Fig.3.4 XRD pattern mixture ball milled at 3, 6, 12 and 24 h using 500 rpm with 1:10 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 220 reflection.	52
Fig.3.5 XRD pattern of ball milled mixture using 750, 500 and 250 rpm with 1:3 and 1:6 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 220 reflection.	54
Fig.3.6 ATR-FTIR spectrum of ball milled mixture using 750, 500 and 250 rpm with 1:3 and 1:6 ratio of $\text{NaBH}_4\text{:MgBr}_2$.	55
Fig.3.7 XRD patterns of a) ball milled and b) residue in the thimble after purification mixtures in different $\text{NaBH}_4\text{:MgBr}_2$ ratios using 500 rpm and 24 h milling time.	57
Fig.3.8 XRD patterns of 200 reflection a) ball milled and b) residue in the thimble after purification mixtures in different $\text{NaBH}_4\text{:MgBr}_2$ ratios using 500 rpm and 24 h milling time.	58
Fig.3.9 XRD pattern 200 reflection of ball milled mixture at 250 rpm in different $\text{NaBH}_4\text{:MgBr}_2$ ratios for a) 12 h milling time b) 24 h milling time c) left over sample in the thimble after purification.	60
Fig.3.10 ATR-FTIR Spectrum of different $\text{NaBH}_4\text{:MgBr}_2$ mixtures a) ball milled at 250 rpm for 12 h and 24 h and b) residue in the thimble after purification of milled mixtures in different ratios using 250 rpm and 24 h milling time.	61
Fig.3.11 Sample with $\text{NaBH}_4\text{:MgBr}_2$ ratio of 1:8 a) XRD pattern of 200 reflection for 24 h milled, 24 h milled and heat treated at 200 °C for 12 h and 24 h milled and heat treated at 200 °C for 24 h, b) ATR-FTIR spectrum of the same sample with the same milling and heat treating procedure.	62

Fig.3.12 XRD pattern of 220 reflection for $\text{NaBH}_4\text{:MgBr}_2$ blend in 1:4 ratio mixed in Autoclave for 3 h, 6h, 12 h, 24 h at 100 °C.....	64
Fig.3.13 ATR-FTIR spectrum of $\text{NaBH}_4\text{:MgBr}_2$ blend in 1:4 ratio mixed in Autoclave for 3 h, 6h, 12 h, 24 h at 100 °C.	64
Fig.3.14 XRD pattern of 220 reflection for $\text{NaBH}_4\text{:MgBr}_2$ blend in 1:4 ratio mixed in autoclave for 6 h at temperatures of 100 °C and 150 °C.....	65
Fig.3.15 ATR-FTIR spectrum of $\text{NaBH}_4\text{:MgBr}_2$ blend in 1:4 ratio mixed in autoclave for 6 h at temperatures of 100 °C and 150 °C.	65
Fig.3.16 XRD pattern of $\text{NaBH}_4\text{:MgBr}_2$ blend mixed in Autoclave for 34 h at 100 °C in 1:2.5 and 1:4 ratios.....	66
Fig.3.17 ATR-FTIR spectrum of $\text{NaBH}_4\text{:MgBr}_2$ blend mixed in Autoclave for 24 h at 100 °C in 1:2.5 and 1:4 ratios.....	67
Fig.4.1 schematic of two routes for thermodynamically modifying metal borohydride, (a) destabilization of $\text{M}(\text{BH}_4)_n$ (b) stabilization of dehydrogenated products.....	74
Fig.4.2 Hydridic-Protic interaction schematic.....	77
Fig.4.3 II-shaped Pyrex glassware and purification setup for extracting $\text{Mg}(\text{NH}_2)_2$	79
Fig.4.4 PXRD patterns of a) ball milled (BM) and heat treated mixture of $\text{NaNH}_2 + \text{Mg}(\text{BH}_4)_2$ b) after purification of the mixture produced by ball milling, $\text{Mg}(\text{NH}_2)_2$ pattern is given as reference..	80
Fig.4.5 (a) TG (b) MS (c) DSC (d) bigger reprint of MS result with magnified gas desorbed region (inset) for NaNH_2	82
Fig.4.6 (a) TG (b) MS (c) DSC (d) bigger reprint of MS result with magnified gas desorbed region (inset) for $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ mixture.....	84
Fig.4.7 PXRD pattern of 1:1 ratio $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ after hand mill and after decomposing at 155 °C, 320 °C, 420 °C, and 600°C.....	85
Fig.4.8 ATR-FTIR spectra for the mixture $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ after hand mill and after decomposing at 155 °C, 320 °C, 420 °C, and 600 °C.	87
Fig.4.9 (a) TG (b) MS (c) DSC (d) LiNH_2 (TG and MS) results for $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ mixture.....	89
Fig.4.10 PXRD pattern of 1:1 ratio $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ after hand mill and after decomposing at 255 °C, 285 °C, 320 °C, and 600 °C.....	89

Fig.4.11 ATR-FTIR spectra for the mixture $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ after hand mill and after hand mill and after decomposing at 255 °C, 285 °C, 320 °C, and 600 °C.	90
Fig.4.12 (a) TG (b) MS (c) DSC results of $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ mixture.	92
Fig.4.13 PXRD pattern of $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ in 1:1 ratio after hand mill and after hand mill and after decomposing at 110 °C, 160 °C, 220 °C, 380 °C and 600 °C.	93
Fig.4.14 ATR-FTIR spectra for the mixture $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$	94
Fig.4.15 (a) TG spectra of synthesized $\beta\text{-Mg}(\text{BH}_4)_2$ with 6h (red) and 18h (black) b) and MS spectra of it with 6h (red) and 18h (black) with heating rate 10 K/min under Ar flow.	97
Fig 5.1 Meissner effect.	3
Fig 5.2 (a) Type-I, (b) Type-II superconductor behavior.	4
Fig 5.3 Vortices (dark regions) in a type-II superconductor.	5
Fig 5.4 (a) Crystal structure of MgB_2 (b) MgB_2 structure through a and c views.	7
Fig 6.1 PXRD patterns of bulk and nanosized MgB_2 synthesized with the reactant powders boron 95 (red) and nanoboron (black), respectively. Diffractions from MgO and Mg in boron 95 (bulk) sample are indicated by the symbols # and +, respectively.	116
Fig 6.2 SEM images of (a) as received nanoboron, (b) as recieved Mg, (c) mauully ginded mixture of boron 95 and Mg, (d) manually grinded mixture of nanoboron and Mg.	117
Fig 6.3 SEM images of (a) nanosized and (b) bulk MgB_2 powders. TEM images of (c) nanosized MgB_2 and (d) bulk MgB_2 powders. Nanosized and bulk powders were synthesized from nanoboron and boron 95, respectively.	118
Fig 6.4 (a) Comparative EPR spectra of elemental Mg and nanoboron. (b) Definition of symmetry parameter (A/B), peak-to-peak intensity and the linewidth (ΔB_{pp}) in terms of Dysonian EPR signal. (c) Comparative EPR spectra of MgB_2 obtained from boron 95 and nanoboron.	120
Fig.7. 1 (a) PXRD patterns, (b) c/a ratio and lattice parameters a and c (inset), which were obtained from a Rietveld refinement analysis of set1 samples (set1) with 0, 0.1, 1, 5, 10, 30 wt % of MA. 6	
Fig.7.2 Raman spectra of samples (set1) with (a) 0 wt% (b) 0.1 wt% and (c) 10 wt% of MA..	132
Fig.7. 3 (a) Room-temperature EPR spectra (first derivatives with respect to B_0) of undoped MgB_2 and doped MgB_2 with various MA doping levels. (b) Electron g -factors of MgB_2 both for doped and undoped case determined from the inflection points of the spectra. The corresponding regions for C related and vacancy related centers are indicated.	134

Fig.7. 4 Low-temperature EPR measurements (a) for undoped and (b) for nominally 1.85 wt % (2 mol %) C-doped MgB ₂ synthesized from set2.....	135
Fig.I.1 Geometrical illustration of the Bragg's law.....	140
Fig.I. 2 Bruker a) D2 PHASER and b) D8 ADVANCE XRD machines.	141
Fig.I.3 Bruker S8 Tiger XRF spectrometer.	143
Fig.I.4 Power compensated and heat flux DSC.....	145
Fig.I. 5 a) DSC NETSZCH b) DTA/TG/MS SII EXSTAR 6300 coupled with Pfeiffer ThermoStar devices.....	146
Fig.I.6 Thermo Scientific iS10 ATR-FTIR instrument.	148
Fig.I.7 RENISHAW inVia Raman microscope and BURKER RFS 100/S FT Raman spectrometer.	150
Fig.I. 8 Zeiss Ultra Plus FE SEM instrument which is used in this thesis.	153
Fig.I.9 CHNS/O configuration with TCD detector	154
Fig.I.10 FLASH 2000 CHNS/O Elemental Analyzer instrument.	154
Fig.I.11 Bruker EMX spectrometer and rectangular TE102 (X-band) resonator.....	156

Table of Tables

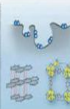
Table 1.1 Technical comparison of hydrogen with other fuels [9].	3
Table 1.2 2009 and 2012 DOE hydrogen storage targets for onboard light duty fuel cell vehicles [17, 18].	4
Table 1.3 List of promising metal borohydrides.	10
Table 2.1 Overview of some known synthesis methods for $\text{Mg}(\text{BH}_4)_2$ and their reaction conditions [18].	19
Table 2.2 Synthesis conditions for metathesis reaction of MgBr_2 and NaBH_4 using ball mill. ...	22
Table 2.3 XRF concentration of as received MgBr_2 and NaBH_4 .	34
Table 2.4 synthesis conditions for reaction using method 2.3.3	37
Table 2.5 Carbon content of $\text{Mg}(\text{BH}_4)_2 \cdot \text{mEt}_2\text{O}$.	40
Table 2.6 Elemental concentration of synthesized and as received using XRF.	41
Table 2.7 N, C, H and S concentrations for as synthesized and as received $\text{Mg}(\text{BH}_4)_2$ getting from CHN.	42
Table 2.8 α - $\text{Mg}(\text{BH}_4)_2$ production yield under different conditions	42
Table 3.1 Absorption bond frequencies for B-H stretching and bending in ball milled mixtures milled for 12 h and 24 h at 250 rpm at NaBH_4 : MgBr_2 ratio of 1:3, 1:6 and 1:8	59
Table 3.2 Absorption bond frequencies for B-H stretching and bending in ball milled and heat treated mixture milled at 250 rpm at NaBH_4 : MgBr_2 ratio of 1:8	62
Table 3.3 Effect of increasing in ball mill time, speed, reactant ratio and annealing on the futures of mixture in the reaction of $(n \text{ MgBr}_2 + m \text{ NaBH}_4)$	63
Table 4.1 Infrared frequencies (in unit of cm^{-1}) for NaNH_2 , $\text{Mg}(\text{BH}_4)_2$ at room temperature and $\text{Mg}(\text{BH}_4)_2$ - NaNH_2 mixture at room temperature, 155, 320, 420 and 600 °C.	88
Table 4.2 Infrared frequencies (in unit of cm^{-1}) for LiNH_2 , $\text{Mg}(\text{BH}_4)_2$ at room temperature and $\text{Mg}(\text{BH}_4)_2$ - LiNH_2 mixture at room temperature, 225, 285, 320, 350 and 600 °C.	92
Table 4.3 Infrared frequencies for $\text{Mg}(\text{NH}_2)_2$, $\text{Mg}(\text{BH}_4)_2$ at room temperature and $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$ mixture at room temperature, 110 °C, 160 °C, 220 °C, 380 °C and 600 °C.	96
Table 4.4 Comparison of all mentioned systems as well as starting materials hydrogen storage properties.	97
Table 7. 1 Sample codes and corresponding wt % values for the doping concentration.	128
Table 7.2 MA, nominal C and real C doping concentrations in MgB_2	131

Aims and scope of this thesis

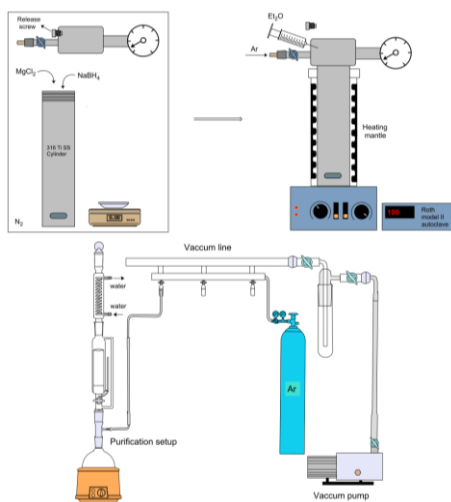
The first part of the present thesis, aims to find a convenient, less expensive and quick synthesis method for production of complex borohydride with a specific focus on magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) as a solid-state hydrogen storage material. Moreover, this thesis intends to investigate the hydrogen storage properties of the amide-borohydride systems with emphasis on $\text{Mg}(\text{BH}_4)_2$ - $\text{M}(\text{NH}_2)_2$ ($\text{M} = \text{Na}, \text{Li}, \text{Mg}$) mixtures, elaborately.

Second part of this thesis is performed in the aim of investigation on synthesis of MgB_2 as a simple structured binary superconductor and more specifically production of nano sized MgB_2 . In addition, understanding the defect structure of bulk, nanosized and carbon doped MgB_2 is another objective of this thesis.

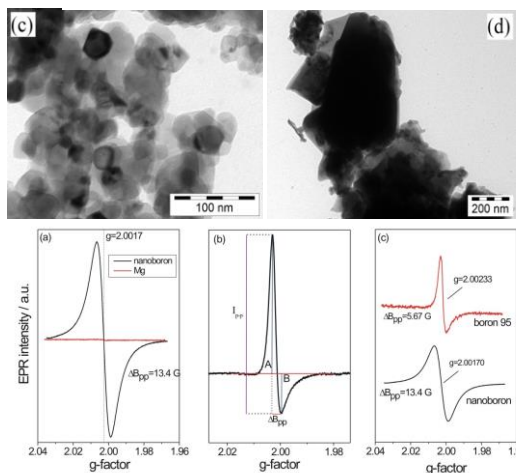
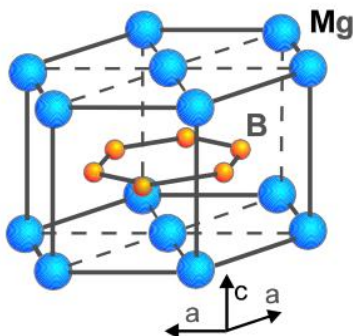
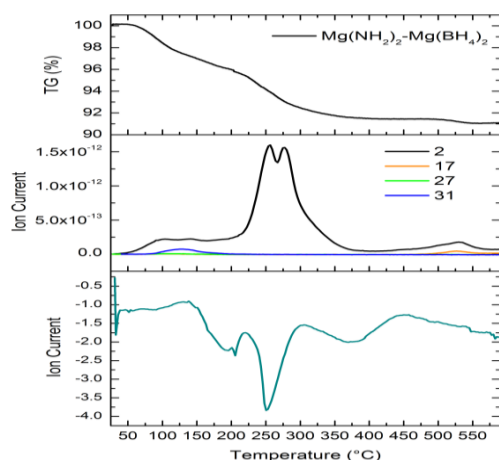
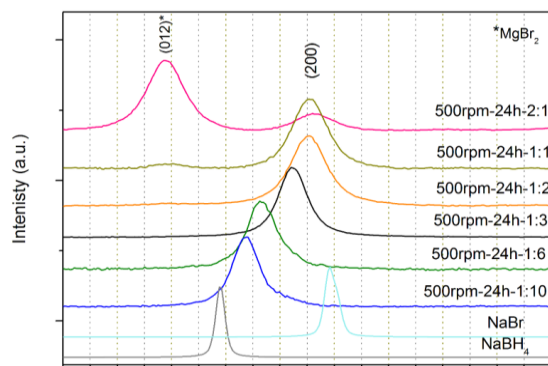
This thesis consists of seven chapters:

						
Liquid hydrogen	Cryo-adsorption	Interstitial metal hydride	Compressed hydrogen	Alane	Salt-like metal hydride	Water
LH_2	Activated carbon	Laves Phase Comp./ $\text{FeTiH}_x/\text{LaNi}_5\text{H}_x$	CGH_2	NaAlH_4	MgH_2	H_2O
100 mat.wt%	6.5 mat.wt%	2 mat.wt%	100 mat.wt%	5.5 mat.wt%	7.5 mat.wt%	11 mat.wt%
Operating temperature						
-253°C	$> -200^\circ\text{C}$	$0 - 30^\circ\text{C}$	25°C	$70 - 170^\circ\text{C}$	330°C	$>> 1000^\circ\text{C}$
Corresponding energy to release hydrogen in MJ per kg H_2						
0.45	3.5	15	n/a	23	37	142

Chapter 1, will compare fossil fuel energy with renewable energies and gives a brief introduction into renewable energies and more specifically hydrogen. It will then introduce different hydrogen storage methods especially for mobile application. Particular emphasis will be given to solid-state hydrogen storage materials.



Chapter 2, five different metathesis synthesis procedures for $\text{Mg}(\text{BH}_4)_2$ using MgX_2 ($\text{X} = \text{Cl}, \text{Br}$) and NaBH_4 are compared and discussed in details. Latterly, a novel and convenient in diethyl ether metathesis reaction of MgCl_2 with NaBH_4 using relatively high pressure and high temperature in an autoclave is introduced.

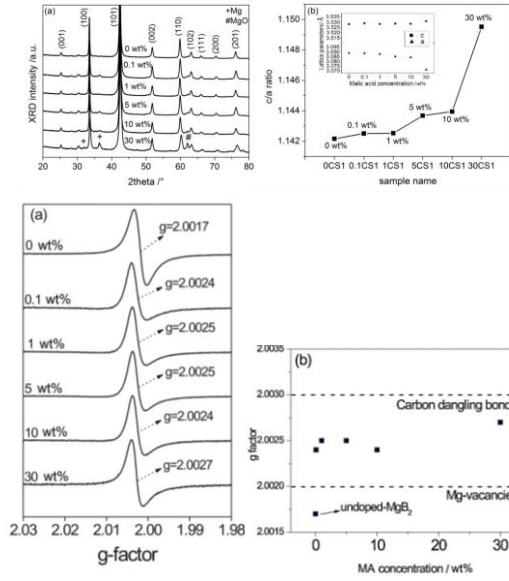


Chapter 3, interesting solid solution formation of $\text{NaBr}_{1-x}(\text{BH}_4)_x$ and/or $\text{Na}(\text{BH}_4)_{1-y}\text{Br}_y$ during synthesis of $\text{Mg}(\text{BH}_4)_2$ using MgBr_2 and NaBH_4 as precursors are shown and the effect of reaction parameters on extend of solid solution formation are argued comprehensively.

Chapter 4, is dealt with investigation into amide-borohydride systems with a focus on hydrogen storage properties of $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ and $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ as well as $\text{Mg}(\text{BH}_4)_2\text{-MgBr}_2$.

Chapter 5, will give a brief introduction to superconductivity and the related terms in this field. Additionally, MgB_2 crystal structure and its superconductive behavior as well as effect of MgO and elemental doping on its superconductive properties are discussed.

Chapter 6, synthesis procedure for MgB_2 bulk and nanosized is introduced and quality of the products are compared regarding MgO amount and particle size and the defect structure of bulk and nanosized MgB_2 and their active role in material properties are investigated.



Chapter 7, Carbon-doped MgB₂ samples in different concentration will be synthesized using doping with malic acid. The microscopic defect structures of carbon-doped MgB₂ will be systematically investigated.

Chapter 1

Introduction

1.1 Non-renewable vs. renewable energy

Since mid-18th which was the start of industrialization, the energy demand has enlarged exponentially and is anticipated to increase by 75% in 2000–2030 period, mostly due to the increasing world population, which might reach 8 billion people until 2030 [1]. As a result, conventional energy sources such as fossil fuels are diminishing rapidly in the world. Moreover, imbalance distribution of natural resources whole around the planet brings some political and economical conflicts between nations. In addition, although they are part of our life they have a negative impact on our planet such as global warming, acid rains, climate change and pollution [2]. For this reason, searching for alternative and sustainable energy sources always attracts too much of interests.

The sustainable energy sources such as solar radiation, wind, hydropower, ocean thermal energy, biomass, geothermal and tidal are plentiful, clean and renewable. The sun is the main sustainable energy source for the earth with 8000 times bigger energy influx than the total energy consumption in the world [1]. However, they are not as convenient as fossil fuels. They are only available at irregular intervals, fluctuate over a time and geography and/or away from consumption centers. They are not storable or transportable, and they cannot be used directly as a fuel for transportation or consumption. They require an energy carrier or an intermediary energy system to connect the primary energy sources and the energy consuming sectors [1, 3, 4].

Currently, electricity is a first choice as an energy carrier, since it is convenient and very efficient at the consumer end. It can be produced from any energy source, including renewable sources. However, it cannot presently be stored efficiently in large amounts and it is not suitable

for long distance transportation, so sources are available intermittently and/or far from consumption centers and balance between production and consumption must be maintained very carefully. It is therefore obvious that electricity cannot be the promising energy carrier of the future [3, 5].

1.2 Hydrogen

Hydrogen is the next promising future energy carrier due to its unique properties. It is the most abundant element in the universe. In addition, it is the lightest fuel in the periodic table and has the richest in energy per unit mass unlike electricity. It can be converted into other forms of energy efficiently and can be transported over long distances without massive losses. On the other hand, tracking an evolution of industrial energy carriers (see Fig.1.1) reveals that usage of more hydrogen rich fuels are emerged by time to avoid CO₂ emission. This shows that hydrogen should be the energy of future [6, 7]:

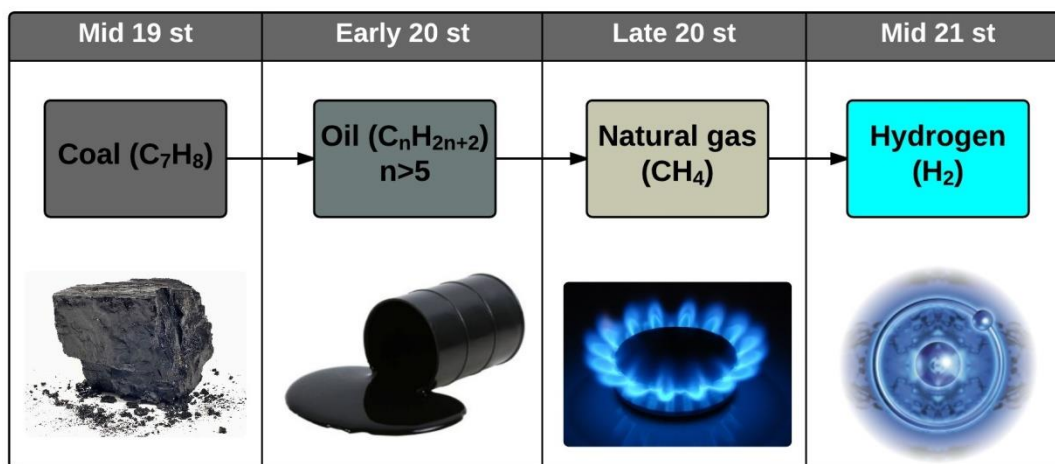


Fig.1.1 Evolution of industrial usage of energy carriers

As it is mentioned, hydrogen gas has the highest energy density of the common fuels on a weight basis, but based on its volume, it has the lowest energy density with 8960 MJ/m³ at ambient conditions in comparison with gasoline with 31170 MJ/m³. Comparison in energy content and properties of different fuels are summarized in Table 1.1.

In spite of unique properties of hydrogen, being expensive due to mainly using non-renewable production methods which are based on turning fossil fuels into hydrogen, as well as not effective storage of hydrogen and highly explosive and flammable in the gas form, preventing the widespread usage of it [2, 4, 7]. The former disadvantage is on the way of overcome by renewable processes for hydrogen production using water and biomass, by means of different kinds of processes such as photolysis, electrolysis, thermochemical, and biochemical [8].

Table 1.1 Technical comparison of hydrogen with other fuels [9].

	Hydrogen	Petroleum	Methanol	Methane	Propane	Ammonia
Boiling point, K	20.3	350-400	337	111.7	230.8	240
Liquid density, kg m ⁻³	71	702	797	425	507	771
Gas density, kg m ⁻³ , s.t.p. ^a	0.08	4.68	-	0.66	1.87	0.69
Heat of vaporization, kJ kg ⁻¹	444	302	1168	577	388	1377
Lower heating value ^b (mass), MJ kg ⁻¹	120.0	44.38	20.1	50.0	46.4	18.6
Lower heating value (liquid) (volume), MJ m ⁻³	8960	31170	16020	21250	23520	14350
Diffusivity in air, cm ² s ⁻¹	0.63	0.08	0.16	0.20	0.10	0.20
Lower flammability limit vol.% (in air)	4	1	7	5	2	15
Upper flammability limit vol.% (in air)	75	6	36	15	10	28
Ignition temperature in air, °C	585	222	385	534	466	651

1.3 Hydrogen storage methods

Effective storage of hydrogen possessing high safety and security especially for transport section is clearly one of the key challenges in hydrogen economy especially in onboard (mobile) applications (e.g. motorized vehicles) [2, 10, 11]. The importance of hydrogen storage materials for onboard application was urged U.S. Department of Energy to launch a target for solid hydrogen storage materials on 2003 [12, 13]. Due to existing challenges in this field, this target was revised down to lower limit many times which the newest targets are shown in Table 1.2.

Existing hydrogen storage technologies can mainly categorize into groups:

- Physically stored hydrogen, such as compressed gas H₂, in a liquid H₂ form, and (Cryo-) absorptions on high surface area materials, e.g. Zeolites, Metal Organic Frameworks)

- Chemically stored hydrogen, like, storage in metal hydrides, in complex metal hydrides, in amine-borane adducts [6, 14-16].

In the first category, there is not any strong chemical bonds between hydrogen and host compound while in the latter case, there is a strong ionic or covalent interaction is valid between hydrogen atoms and other elements in the structure.

Table 1.2 2009 and 2012 DOE hydrogen storage targets for onboard light duty fuel cell vehicles [17, 18].

Storage parameters	units	2009-Technical system		2012-Technical system	
		Target		Target	
		2010	2015	2020	Ultimate
System gravimetric capacity	kWh/kg	1.5	1.8	1.8	2.5
	(wt% H ₂)	(4.5)	(5.5)	(5.5)	(7.5)
System volumetric capacity	kWh/L	0.9	1.3	1.3	2.3
	(g H ₂ /L)	(28)	(40)	(40)	(70)
Operational cycle life	cycles	1000	1500	1500	1500
Min/Max delivery pressure (to FC)	Bar	5/12	5/12	5/12	3/12
Min/Max delivery temperature	°C	-40/85	-40/85	-40/85	-40/85
Cost	\$/gge ^a	3-7	2-4	2-4	2-4

a gge: Gasoline gallon equivalent - is the amount of alternative fuel it takes to equal the energy content of one liquid gallon of gasoline.

Compressed gaseous storage is the simplest way of hydrogen storing at room temperature but the energy density of it is too low. For instance, for light duty onboard application, to be able to drive an automobile about 500 km 5-6 kg H₂ is needed which hydrogen gas should be compressed to fulfill that requirement. For this reason, high-pressure tanks up to 70 Mpa (700 bar) are required. Working on such high pressures, complex structures vessels containing multiple layers with strength and impact resistance should be designed which means additional

cost for high-pressure tanks. For instance, two types of carbon fiber reinforced plastic (CFRP), CFRP III and IV, are currently in use which their prices are 4 times more than DOE target. Furthermore, based on space availability in vehicles and large operating pressure, the tanks must be cylindrical or near-cylindrical in shape and it limits the applications in small vehicles [5, 14-16, 19].

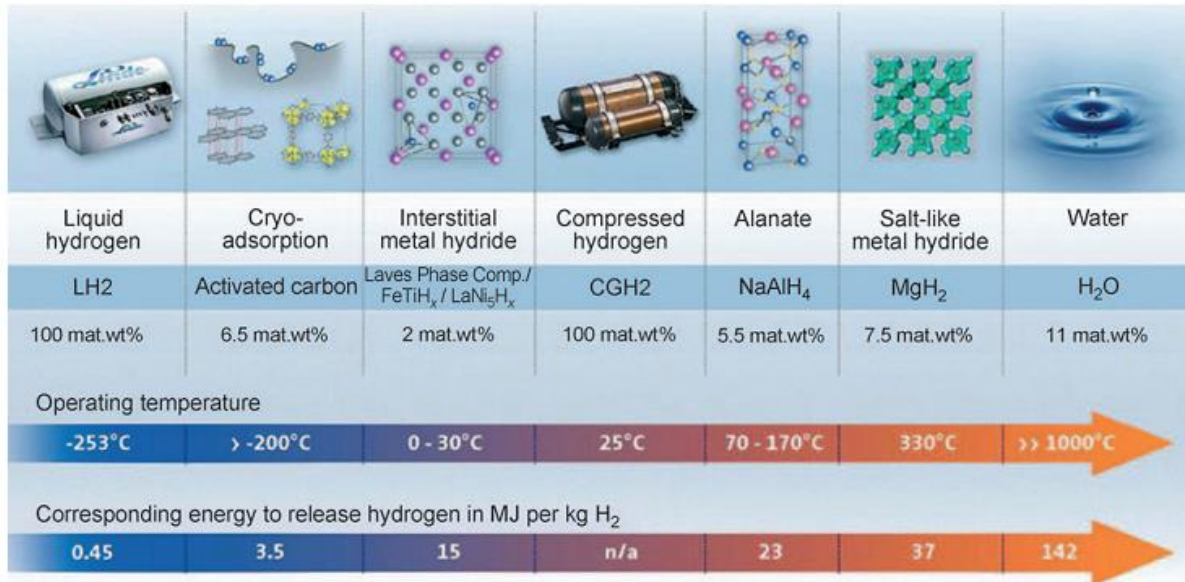


Fig.1.2 Different hydrogen storage technologies and their operating conditions [14].

For storing hydrogen in a liquid form, cool it down to cryogenic temperature (-235 °C) is necessary. This brings a high gravimetric density (100 wt% theoretically) which is the highest among all other storage methods (see Fig.1.2). Nevertheless, for production of LH₂ near to 30-40% of the energy content of fuel is needed which is near to 3 times more energy needed to compress hydrogen to 69 bar [20]. In addition, for any cryogenic tank systems, very efficient multilayer superinsulation consisting of 40 layers of radiation shield foil is required due to boil off losses during dormancy (the period from putting a vehicle into parking mode and venting of hydrogen). As a result, most automobile manufacturer are not seeing any advantage in LH₂ and they have focused on gaseous storage form [2, 14, 15, 19].

Adsorption (physisorption) is the borderline situation between physical and chemical storage. Physisorption is a process in which hydrogen molecules are bound with weak van der Waals forces to the surface of the adsorption material [21]. This technique is more reliable when the storage reversibility is considered, because the adsorbed gas can be released reversibly and safely. Materials with high specific surface such as zeolites, carbon materials, metal organic frameworks (MOF) are suitable candidates for physisorption. The main drawback is weak van der Waals forces between absorbent and non-polar hydrogen molecules. Since the molecular interaction in physisorption process is very weak, storage at ambient condition is too low and it is not practical and major hydrogen adsorption usually take place at only cryogenic temperature. However, compressed cryogenic hydrogen adsorbed on adsorbents, leads to decrease the storage pressure and as a result using less expensive storage tank [5, 14, 19-23].

1.4 Chemical storage of hydrogen

Hydrogen storage in solid materials has the potential to become a safe and efficient way to store energy, both for stationary and mobile applications. They exhibit and impressive volumetric hydrogen density as well as gravimetric density and in many case permits design flexibility in terms of shape and place of the container in the vehicle. This thesis is dealing with solid state hydrogen storage materials.

1.4.1 Metal Hydrides

The simplest and the most studied solid state hydrogen storage materials are metal hydrides (MH_x) which can form by reaction between H_2 and metal or metal alloys. They usually have high volumetric density and simple chemical formula. However, some are suffering from low gravimetric density, and some from either too high or too low enthalpy of formation. [13, 24] For instance, AlH_3 have very high gravimetric density (10 wt%), but due to it low enthalpy of formation (5-7 kJ/mole), it is impossible to recharge it from Al. MgH_2 posses the high volumetric (109 g H_2 /L) and contains 7.7 wt % hydrogen as well as benefits form low cost and limitless availability of magnesium which makes it attractive to use as a solid state hydrogen storage material. However, its unfavorable thermodynamic property (high exothermic enthalpy

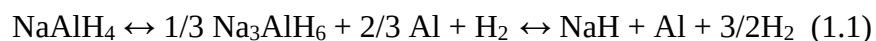
of formation $\Delta H = -75$ kJ/mole) as well as sluggish hydrogen desorption kinetics makes it impractical for onboard usage [1, 10, 25]. On the other hand, usually transition metal and metal alloys, e.g. VH_2 , LaNi_5H_x , possess moderate enthalpy of formation but limited gravimetric densities due to its heavy constituents [13]. Several different approaches were used to improve its thermodynamics and kinetics by nanostructuring using ball mill, alloying with different metals as well as addition of catalysis which are still going on.

1.4.2 Complex Hydrides

Complex hydrides are hydrides composed of cationic alkali or transition metal bonded to an anionic metal /nonmetal–hydrogen complex. Therefore, they can be divided into two groups: (1) group I and II salts of alanates ($[\text{AlH}_4]^-$), amides ($[\text{NH}_2]^-$) and borohydrides ($[\text{BH}_4]^-$) (2) transition metal (TM) complex hydrides that have anionic $(\text{TMH}_x)^-$ complexes such as $[\text{FeH}_6]^{4-}$ attached to a cationic light metal such as Mg^{2+} (Mg_2FeH_6). These complexes have usually mixed ionic-covalent bonding [13, 26].

1.4.2.1 Alanate

Bogdanovic and Schwickardi [27] first proposed the usage of the complex hydrides as hydrogen storage material in 1997 when they investigated the Ti doped sodium aluminum hydride, NaAlH_4 . Hydrogenation and dehydrogenation of NaAlH_4 take place in two steps with 5.6 wt % reversible hydrogen capacity (see Eq.1.1) at 260 °C. Reversibility is proved can be occurred at pressure between 60-150 bar with cyclic instability.



2 mole% TiN addition is proved to increase cycling stability up to 17 times with 5 wt% H_2 at pressure between 115-140 bar [28]. It is also shown that ball milled mixture of single wall carbon nanotubes (SWNTs) and or activated carbon with Ti/Zr catalyzed NaAlH_4 , can be recyclable at 160 °C and 35 bar for 200 cycles [29]. Recently, huge improvement is reported in hydrogen release and reversibility of NaAlH_4 by confining in Ti-functionalized metal organic framework (MOF). Confining within MOF pores can remove stable Na_3AlH_6 due to alternating

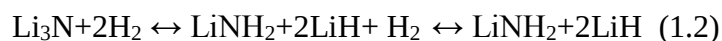
decomposition pathway. The onset of hydrogen release is decrease significantly to 50 °C. however, reversible hydrogen capacity was ~ 4 wt% with limited cyclic behavior [30].

LiAlH₄ has theoretically 10.5 wt% hydrogen content which higher than NaAlH₄. Nonetheless, it is also decomposing in two steps to LiH with intermediate compound of Li₃AlH₆ and total 7.9 wt% of hydrogen desorbing up to 220 °C [31-33] TiCl₃ addition to the system of LiAlH₄/Li₃AlH₆ is proved can improve dehydriding/rehydriding reactions over the temperature range 25-250 °C [32]. Milled MgH₂ and LiAlH₄ mixture showed a 5 wt% reversible H₂ at temperature around 350 °C and pressure of 80 bar with moderate kinetics [31]. Addition of SWCNTs is also investigated in hydrogen storage properties of LiAlH₄. It is reported that, 5 wt% hydrogen can release up to 145 °C with 3.3 wt% reversible capacity at 200 °C and 40 bar [34]. The direct synthesis of LiAlH₄ from LiH and Al powders in the presence of TiCl₃ and Me₂O (as a solvent) and hydrogenation of mixture in MeO₂ at 100 bar has been achieved recently. This study reported, 6.4 wt % of reversible H₂ in 3 cycles with dehydrogenation temperature of 80 °C [35].

However, for NaAlH₄ and LiAlH₄ in order to reach to their maximum capacity, the last step includes decomposition of NaH and LiH at about 430 °C and 680 °C, respectively. Thus, slow kinetics, reversibility and high absorption/desorption keeps them far from being feasible [10, 33].

1.4.2.2 Amides/imides

Since Chen et al.[36] is reported two stepped H₂ desorption (1.2) with being able to be reversible many studies have done around the Li-N-H system.



However, enthalpy of formation for step 1 is too high (148 kJ/mole H₂) to be practically reversible. Soon after, it is also found that there is an intermediate step in hydrogenation/dehydrogenation with the release of NH₃ [37]. Similar case is also reported in Mg(NH₂)₂ although it has more favorable dehydrogenation temperature. In order to tailor hydrogen storage properties, cyclability of amides and remove NH₃, Li based ternary nitrite/amide systems, such as Li-Mg-N-H, Li-Ca-N-H, Li-Na-N-H systems are widely studied up to now [20, 38-41].

1.4.2.3 Borohydrides

Borohydrides belong to a class of materials with the highest gravimetric and volumetric hydrogen storage capacity. There are many types of borohydrides depending on the composition of M, B and H, e.g. $M(BH_4)_n$, $M(B_3H_8)_n$, $M(B_6H_6)_n$, $M(B_9H_9)_n$ and $M(B_{12}H_{12})_n$ [42]. In this thesis, the only $M(BH_4)_n$, tetrahydridoborate/tetrahydroborate will be discussed. $M(BH_4)_n$ electronic structure show that they are nonmetallic with a fairly large band gap (1.8-6.8 eV). B atom surrounded by four H atoms connected with them by covalent bond to form $[BH_4]^-$ anion. It is proved that charge transfer from the metal cation to anions is a major aspect in determining stability of $M(BH_4)_n$ [1, 43, 44]. The structure of borohydrides differ from ionic to framework structure (such as $Mg(BH_4)_2$ and $Ca(BH_4)_2$) and molecular structure (such as $Al(BH_4)_3$ and $Zr(BH_4)_4$) indicating increase in degree of directionality and covalence in the bonding [1]. It is confirmed that, all metal borohydrides structurally are related to oxides, probably due the fact that the ions $[BH_4]^-$ and O^{2-} are isoelectronic, e.g., $Ca(BH_4)_2$ and $Mg(BH_4)_2$ are related to TiO_2 and SiO_2 , respectively [1, 45].

Based on the hydrogen energy density values in Table 1.3, $Be(BH_4)_2$ seems to be the first candidate among the metal borohydrides, as having low onset hydrogen release (123 °C) and low enthalpy of formation (27 KJ/mole). However, all beryllium compounds are toxic and therefore not suitable for hydrogen storage [44, 46]. $LiBH_4$, is the second candidate of choice with a theoretical hydrogen density of 21.8 wt% but practically it can release only 13.8 wt% hydrogen. The reason is that the thermal decomposition is not complete and yielding LiH and B as final products with decomposition temperature above 680 °C [10]. Moreover, $LiBH_4$ has a moderate heat of formation of 75 KJ/mole and extreme conditions in reversibility (600 °C, 350 bar in 12 h or 827 °C, 150 bar in 10 h) [43]. With 16.9 wt% hydrogen content, $Al(BH_4)_3$ is the third promising candidate. It has a very low enthalpy of formation (5.5 KJ/mole) and comparatively low hydrogen release temperature (150 °C). However, it is liquid at room temperature and pyrophoric [46].

Table 1.3 List of promising metal borohydrides.

Metal Borohydride	Dehydrogenated form	H ₂ Density (wt%)		H ₂ Density (kg/m ³)		Enthalpy of formation	Ref.
		Theo.	Exp.	Theo.	Exp.		
Be(BH ₄) ₂	Be+2B	20.8	20.8	146	146	27	[43]
LiBH ₄	LiH+B	18.5	13.8	122	93	75	[43, 46]
Al(BH ₄) ₂	Al+3B	16.9	16.9	133	133	6	[46]
Mg(BH ₄) ₂	Mg+2B	14.9	14.9	147	147	40	[46]
Ca(BH ₄) ₂	2/3CaH ₂ +1/3CaB ₆	11.6	9.7	124	104	75.5	[43, 46]
NaBH ₄	NaH+B	10.7	7.9	114.5	85	90	[43, 46]

Compared to Al(BH₄)₃, the title compound Mg(BH₄)₂ has slightly lower hydrogen content (14.9 wt%) but relatively low density (0.989 g/cm³), higher volumetric density (147 kg/m³) and a low enthalpy of formation (40 KJ/mole). With these properties, it has a high potential to become one of the most important hydrogen storage materials. Mg(BH₄)₂ is tetra morph (α , β , γ (2.5% physically hydrogen storage) and δ (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 MgB₂ [43, 44, 47, 48]. Synthesis routes and decomposition pathway(s) of Mg(BH₄)₂ will be discussed in detail in following chapters.

Reversibility of most of borohydrides is usually problematic due to evolution of diborane (B₂H₆) which leads to storage capacity loss. Its toxicity is also a major issue and it can damage fuel cell in operation. In addition, most of borohydrides are decomposing stepwise with formation of amorphous intermediate M(B₁₂H₁₂)_n which is very stable due to strong B-B bond in icosahedral boron cage in [B₁₂H₁₂]²⁻ anion. These hindrances turn borohydride into a challenging compound to be reversible practically [25, 49-52].

1.5 References

1. Ley, M.B., et al., *Complex hydrides for hydrogen storage – new perspectives*. Materials Today, 2014. **17**(3): p. 122-128.
2. Jain, I.P., P. Jain, and A. Jain, *Novel hydrogen storage materials: A review of lightweight complex hydrides*. Journal of Alloys and Compounds, 2010. **503**(2): p. 303-339.

3. Acar, S., *Sodium Amide – Sodium Tetrahydridoborate System as a Potential Hydrogen Storage Material*, in *Material Science and Engineering*. 2007, Koç University.
4. Martinez, G.A.L., *Development of Hydrogen Storage systems using sodium alanate*. 2010, Technischen Universität Hamburg.
5. Felderhoff, M., et al., *Hydrogen storage: the remaining scientific and technological challenges*. *Phys Chem Chem Phys*, 2007. **9**(21): p. 2643-53.
6. Züttel, A., *Hydrogen storage methods*. *Naturwissenschaften*, 2004. **91**(4): p. 157-72.
7. Escobar, D., *Investigation of ZrNi, ZrMn₂ and Zn(BH₄)₂ metal/complex hydrides for hydrogen storage*. 2007, University of South Florida.
8. Turner, J., et al., *Renewable hydrogen production*. *International Journal of Energy Research*, 2008. **32**(5): p. 379-407.
9. Sequeira, C.A.C., *Hydrogen, the ultimate clean fuel*. *Ciência & Tecnologia dos Materiais*, 2009. **21**.
10. Sakintuna, B., F. Lamaridarkrim, and M. Hirscher, *Metal hydride materials for solid hydrogen storage: A review*. *International Journal of Hydrogen Energy*, 2007. **32**(9): p. 1121-1140.
11. George, L. and S.K. Saxena, *Structural stability of metal hydrides, alanates and borohydrides of alkali and alkali- earth elements: A review*. *International Journal of Hydrogen Energy*, 2010. **35**(11): p. 5454-5470.
12. Klebanoff, L.E. and J.O. Keller, *5 Years of hydrogen storage research in the U.S. DOE Metal Hydride Center of Excellence (MHCoe)*. *International Journal of Hydrogen Energy*, 2013. **38**(11): p. 4533-4576.
13. Yang, J., et al., *High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery*. *Chem Soc Rev*, 2010. **39**(2): p. 656-75.
14. Eberle, U., M. Felderhoff, and F. Schuth, *Chemical and physical solutions for hydrogen storage*. *Angew Chem Int Ed Engl*, 2009. **48**(36): p. 6608-30.
15. Cipriani, G., et al., *Perspective on hydrogen energy carrier and its automotive applications*. *International Journal of Hydrogen Energy*, 2014. **39**(16): p. 8482-8494.
16. Mahlia, T.M.I., et al., *A review of available methods and development on energy storage; technology update*. *Renewable and Sustainable Energy Reviews*, 2014. **33**: p. 532-545.
17. http://energy.gov/sites/prod/files/2015/01/f19/fcto_myrrd_table_onboard_h2_storage_systems_doe_targets_ldv.pdf.
18. http://energy.gov/sites/prod/files/2014/03/f11/targets_onboard_hydro_storage_explanation.pdf.
19. Riis, T., et al., *Hydrogen Storage–Gaps and Priorities*. HIA HCG Storage paper, 2005. **11**.
20. Durbin, D.J. and C. Malardier-Jugroot, *Review of hydrogen storage techniques for on board vehicle applications*. *International Journal of Hydrogen Energy*, 2013. **38**(34): p. 14595-14617.
21. Carrier, H.a.a.F.E. 2008: Wiley-VCH: Weinheim.
22. Lim, K.L., et al., *Solid-state Materials and Methods for Hydrogen Storage: A Critical Review*. *Chemical Engineering & Technology*, 2010. **33**(2): p. 213-226.
23. van den Berg, A.W.C. and C.O. Areán, *Materials for hydrogen storage: current research trends and perspectives*. *Chemical Communications*, 2008(6): p. 668.
24. Bhuiya, M.M.H., A. Kumar, and K.J. Kim, *Metal hydrides in engineering systems, processes, and devices: A review of non-storage applications*. *International Journal of Hydrogen Energy*, 2015. **40**(5): p. 2231-2247.
25. Broom, D.P., *Hydrogen Storage Materials The Characterization of their storage properties*. 2011: Springer.

26. Robert A.Varin, T.C., Zbigniew S. Wronski, *Nanomaterials for Solid State Hydrogen Storage*. 2009: Springer.
27. Borislav Bogdanovic , M.S., *Ti-doped alkali metal aluminium hydrides as potential novel reversible*. Journal of Alloys and Compounds, 1997. **253**: p. 1-9.
28. Bogdanović, B., et al., *Improved Hydrogen Storage Properties of Ti-Doped Sodium Alanate Using Titanium Nanoparticles as Doping Agents*. Advanced Materials, 2003. **15**(12): p. 1012-1015.
29. Dehouche, Z., et al., *The catalytic effect of single-wall carbon nanotubes on the hydrogen sorption properties of sodium alanates*. Nanotechnology, 2005. **16**(4): p. 402-409.
30. Vitalie Stavila, R.K.B., Todd M. Alam, Eric H. Majzoub, and Mark D. Allendorf, *Reversible Hydrogen Storage by NaAlH₄ Confined within a Titanium-Functionalized MOF-74(Mg) Nanoreactor*. ACS Nano, 2012. **6**: p. 9807–9817.
31. Resan, M., et al., *Effect of Ti_xAl_y catalysts on hydrogen storage properties of LiAlH₄ and NaAlH₄*. International journal of hydrogen energy, 2005. **30**(13): p. 1417-1421.
32. Chen, J., et al., *Reversible hydrogen storage via titanium-catalyzed LiAlH₄ and Li₃AlH₆*. The Journal of Physical Chemistry B, 2001. **105**(45): p. 11214-11220.
33. Vittetoe, A.W., et al., *Destabilization of LiAlH₄ by nanocrystalline MgH₂*. International Journal of Hydrogen Energy, 2009. **34**(5): p. 2333-2339.
34. MOHAMMAD ISMAIL, Y.Z., Xuebin Yu, Shi Xue Dou, *Improved Hydrogen Storage Property of LiAlH₄ by Milling with Carbon Based Additives*. International Journal of Electroactive Materials, 2013. **1**: p. 13-22.
35. Liu, X., et al., *Ti-doped LiAlH₄ for hydrogen storage: synthesis, catalyst loading and cycling performance*. J Am Chem Soc, 2011. **133**(39): p. 15593-7.
36. Ping Chen, Z.X., Jizhong Luo, Jianyi Lin & Kuang Lee Tan, *Interaction of hydrogen with metal nitrides and imides*. Nature, 2002. **420**: p. 302-303.
37. Ruckenstein, Y.H.H.a.E., *Ultrafast Reaction between LiH and NH₃ during H₂ Storage in Li₃N*. the Journal of physical Chemistry A, 2003. **107**.
38. Bill, R.F., et al., *Effect of the calcium halides, CaCl₂ and CaBr₂, on hydrogen desorption in the Li–Mg–N–H system*. Journal of Alloys and Compounds, 2015. **645**: p. S96-S99.
39. Yuko Nakamori, G.K.A.N.M.A., Tatsuo Noritake, Shin-ichi Towata and Shin-ichi Orimo, *Guidelines for Developing Amide-Based Hydrogen Storage Materials*. Materials Transactions, 2005. **46**: p. 2093-2097.
40. Chu, H., et al., *Improved Dehydrogenation Properties of Calcium Borohydride Combined with Alkaline-Earth Metal Amides*. The Journal of Physical Chemistry C, 2011. **115**(36): p. 18035-18041.
41. Pottmaier, D. and M. Baricco, *Materials for hydrogen storage and the Na-Mg-B-H system*. AIMS Energy, 2015. **3**(1): p. 75-100.
42. *Solid-state hydrogen storage Materials and chemistry*. 2008: Woodhead Publishing Limited and CRC Press LLC.
43. Li, H.-W., et al., *Recent Progress in Metal Borohydrides for Hydrogen Storage*. Energies, 2011. **4**(12): p. 185-214.
44. Rönnebro, E., *Development of group II borohydrides as hydrogen storage materials*. Current Opinion in Solid State and Materials Science, 2011. **15**(2): p. 44-51.
45. Aeberhard, P.C., et al., *High-pressure crystal structure prediction of calcium borohydride using density functional theory*. Physical Review B, 2011. **83**(17): p. 174102.

46. Soloveichik, G.L., *Metal Borohydrides as Hydrogen Storage Materials*. Material Matters, 2007. **11**.
47. Filinchuk, Y., et al., *Porous and dense magnesium borohydride frameworks: synthesis, stability, and reversible absorption of guest species*. Angew Chem Int Ed Engl, 2011. **50**(47): p. 11162-6.
48. Chłopek, K., C. Frommen, and O.Z.a.M.F. Aline Le'on, *Synthesis and Properties of Magnesium Tetrahydroborate, $Mg(BH_4)_2$* . Journal of Materials Chemistry, 2007. **17**(33).
49. Mohtadi, R., et al., *Alanate–borohydride material systems for hydrogen storage applications*. International Journal of Hydrogen Energy, 2012. **37**(3): p. 2388-2396.
50. Son-Jong Hwang, R.C.B., Jr. Joseph W. Reiter, Job Rijssenbeek, Grigori L. Soloveichik, Ji-Cheng Zhao, Houria Kabbour, and Channing C. Ahn, *NMR Confirmation for Formation of $[B_{12}H_{12}]^{2-}$ Complexes during Hydrogen Desorption from Metal Borohydrides*. 2008. **112**: p. 3164-3169.
51. He, L., et al., *Facile Synthesis of Anhydrous Alkaline Earth Metal Dodecaborate $MB_{12}H_{12}$ ($M = Mg, Ca$) from $M(BH_4)_2$* . Dalton Trans., 2015.
52. Yan, Y., et al., *The role of $MgB_{12}H_{12}$ in the hydrogen desorption process of $Mg(BH_4)_2$* . Chem Commun (Camb), 2015. **51**(4): p. 700-2.

Chapter 2

Synthesis of Magnesium Borohydride, Mg(BH₄)₂

In this Chapter, an overview of current synthesis methods existing for Mg(BH₄)₂ have been discussed initially followed by the introduction of five different experimental processes employed for the synthesis of magnesium borohydride in this project. The novel and convenient preparation techniques for Mg(BH₄)₂ are compared with respect to simplicity of the experimental design, yield and purity.

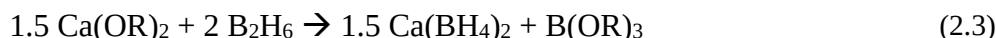
2.1 Introduction

The literature reports five different methods to produce metal borohydrides which are listed below [1-6]:

- Reaction of metal hydride with diborane:



- Reaction of metal alkyls (MR) or metal alkoxides (MOR):



- Reaction of metal hydride with boron compounds:



- High temperature/pressure synthesis from the elements and metal hydride/boride-gas reaction:



- Metathesis reaction of metal halide and metal borohydride:



The Reaction (2.1) is usually used for stable metal hydrides, such as Li, Na and Mg while method (2.2) is more suitable for metals forming unstable or less stable hydrides (such as Be or Al). The production of $\text{Ca}(\text{BH}_4)_2$, $\text{Mn}(\text{BH}_4)_3$ and $\text{V}(\text{BH}_4)_3$ were realized by reaction (2.3) [7, 8]. However, toxicity, low thermal stability and high flammability of B_2H_6 make it less favorable to use. Therefore, diborane is replaced with a boron containing compound, such as trimethylborate (reaction (2.4)) which is known as the Schlesinger process and is used for industrial production of NaBH_4 [2]. Another method is the employment of high temperature and high hydrogen pressure (up to 600 °C and 700 bar) as required in (2.5) and (2.6). In general, premixing of the reactants in a high energy ball mill before annealing is necessary for successful synthesis [3-5]. The most common preparation method for borohydrides is based on metathesis reaction of metal halide with metal borohydride ((2.5)) and can be performed by mechanical milling and/or mixing in solution. In the ball milling case, reaction will proceed with pressure obtained by collision between the balls and vial wall, while temperature and effective mixing are the key factors in solution based methods [3, 9].

If the reaction is performed in a solution, the produced metal halide should be separable from the synthesized metal borohydride. The process is known as precipitation metathesis. Such a reaction occurs usually in a donor solvent in which the metal halide is soluble. Donor solvents have donor atoms with a free electron pair, such O in diethyl ether (Et_2O) and tetrahydrofuran (THF) or N in trimethylamine (TMA), or pyridine. These solvents act as Lewis bases [1, 3, 10, 11].

In mechanical milling, the powder mixtures are mechanically activated to provoke chemical reaction at temperatures much lower than required. Reaction can proceed by the aid of pressure exerting on species in collision between balls and vial [3, 9, 12, 13].

Since metal halides are produced along with metal borohydride, either using solution method or ball milling, a purification step is mandatory to reach pure metal borohydride. Metal cations in metal borohydrides are usually coordinated or complexed by solvent molecules in the solution,

and can form a solvate during the reaction/purification. Subsequently, to obtain pure metal borohydride salt a further desolvation step is needed. which can be done simply by heating the solvate under vacuum [3, 6]. The Flow chart of the borohydride synthesis using metathesis reaction is shown in Fig.2.1.

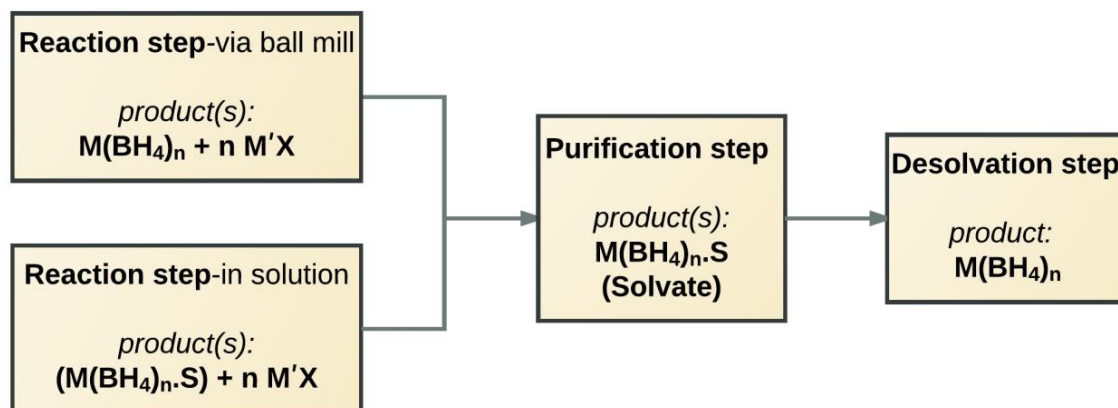


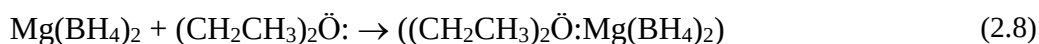
Fig.2.1 Flow chart borohydride synthesis procedure using metathesis reaction.

Synthesis of $\text{Mg}(\text{BH}_4)_2$ was first reported in 1950 by using diborane, similar to the reaction (2.2) [14]. In 1966, J. Plesek and S. Hermanek reported the synthesis of $\text{Mg}(\text{BH}_4)_2$ by the reaction of MgH_2 with diborane (reaction (2.1)) in diethyl ether under pressure [15]. In 1997, Konoplev and Bakulina published for the first time the metathesis of sodium borohydride with magnesium chloride in diethyl ether. The purity of the compound was claimed to be 99 % by weight without mentioning the method of the analysis [16]. Also the PXRD data are too poor for further purity confirmation. A further mechanical milling synthesis using lithium borohydride and magnesium chloride were reported by Nakamori. et. al. in 2006, however, the metal hydride formed ($\text{Mg}(\text{BH}_4)_2$) was not separated from the mixture.

After 2007, several papers were available describing the various synthesis routes of $\text{Mg}(\text{BH}_4)_2$ and its usage as hydrogen storage material [6, 11, 17]. Chlopek et. al. [11] have reported on the wet mixing of NaBH_4 and MgCl_2 in diethyl ether, THF, TMA, TEA, TMEDA and pyridine. Except for diethyl ether, all the other solvents were either too weak to dissolve or possessing a high boiling point and forming a stable adduct. The researchers also investigated the ball milling reaction of MgCl_2 and LiBH_4 which took more than 80 h [11]. In another work, extensive investigations were

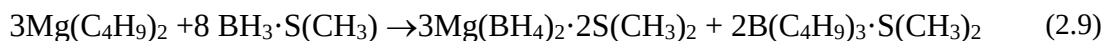
performed to find a more suitable synthesis route. The above mentioned mixing of LiBH_4 with MgCl_2 is usually carried out in diethyl ether overnight, however, the completion of exchange reaction is not achieved for even after 2-3 days mixing. A reaction of NaBH_4 and MgCl_2 in amines over a night was also reported. The MgCl_2 dissolution in amine is highly exothermic yielding an ionic complex and $\text{Mg}(\text{BH}_4)_2$ contaminated with NaCl or NaBH_4 [6].

The main problem in those methods is obtaining solvent-free $\text{Mg}(\text{BH}_4)_2$. During reaction/purification in donor solvents, the dissolved $\text{Mg}(\text{BH}_4)_2$ forms a stable adduct with solvent molecules. In the case of diethyl ether, the adduct formation can be expressed by the equation (2.8):



Once the adduct is formed it is usually difficult to obtain the solvent free salt $\text{Mg}(\text{BH}_4)_2$ requiring laborious thermal treatments under vacuum [10, 17]. In addition, the metathesis reaction using ball mill usually yielding a mixture ($\text{Mg}(\text{BH}_4)_{2-n} \text{X}_n$, $n=0-2$, $\text{X}=\text{halides}$) instead of pure $\text{Mg}(\text{BH}_4)_2$ which is also difficult to separate or even to identify [10].

If $\text{Mg}(\text{BH}_4)_2$ is not soluble in the solvent, filtration will be easier and the yield much higher [10]. To overcome these obstacles, Chlopek et. al. suggested a direct synthesis of $\text{Mg}(\text{BH}_4)_2$ by mixing borane trimethylamine complex (Et_3NBH_3) with pre-milled MgH_2 under Ar atmosphere. They reported that the yield of this reaction is 95% based on MgH_2 with a purity of 98% [11]. Zanella et. al. [10] also proposed two alternative synthesis methods by using $\text{Al}(\text{BH}_4)_3$ and $\text{BH}_3\text{S}(\text{CH}_3)_2$ (equation (2.9)) which act as "BH₄-donor" and $\text{Mg}(\text{C}_4\text{H}_9)_2$ as Mg source, in Toluene/Heptane. As $\text{S}(\text{CH}_3)_2$ is a much softer Lewis base (compared to diethyl ether), a relatively high yield is expected.



Despite the high yield (93%) obtained from these reactions, the method is not convenient enough, not economical and comparatively unsafe due to the following reasons:

- $\text{Mg}(\text{BH}_4)_2$ contains always 5-10% un reacted MgH_2 - after removal of Et_3N - when mixed with pre-milled MgH_2 [3].

- $\text{Al}(\text{BH}_4)_3$ is an instable and highly flammable substance which needs to be synthesized and purified just before use [6].
- There is always some safety issue with borane or borane compounds.
- Elimination of $\text{S}(\text{CH}_3)_2$ is based on reaction (2.9); although performed at moderate temperatures (75 °C), it needs ultra-high vacuum ($\sim 10^{-5}$ mbar) which can be just achievable using turbo molecular pump.
- To prevent the formation of $\text{Mg}[\text{BH}_4\text{-n}(\text{C}_4\text{H}_9)\text{n}]_2$, a huge excess of $\text{BH}_3\text{S}(\text{CH}_3)_2$ is required.
- High price of starting materials.
- Limitation in mass production.

Until now the proposed method by G. L. Soloveichik et. al. [6] is believed to be the most economical and convenient one for production of $\text{Mg}(\text{BH}_4)_2$ on a commercial level. The exchange reaction, using less expensive primary materials, in which MgCl_2 and NaBH_4 are mixed in pipe ball mill for 24 h with a yield up to 77 %. However, a pipe mill should be kept in a glove box equipped for operations with liquids. A pressure release system is also necessary when diethyl ether with comparatively low boiling point of 34 °C is employed as a solvent.

An overview of the reaction conditions for the some important synthesis methods of $\text{Mg}(\text{BH}_4)_2$ are summarized in Table 2.1.

Table 2.1 Overview of some known synthesis methods for Mg(BH₄)₂ and their reaction conditions [18]

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

* with addition of 30 ml n-hexane

** under 10 Mpa H₂ atmosphere

2.2 Experimental Procedure

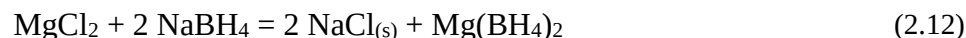
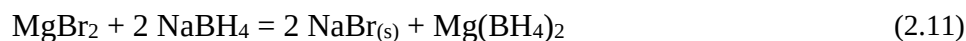
The conventional synthesis methods for $\text{Mg}(\text{BH}_4)_2$ are based on wet-chemistry or solid-state approach, in which metathesis reaction of magnesium halide with metal borohydride takes place followed by solvent extraction with diethyl ether or THF. Based on the literature review in Table 2.1, metathesis reaction of MgCl_2 with LiBH_4 or NaBH_4 at RT is the most reported one while in the present study two alternative metathesis routes are followed in which MgCl_2 with NaBH_4 are reacted at high temperature using furnace and autoclave. Moreover, another three alternative methods for synthesis of $\text{Mg}(\text{BH}_4)_2$ were tested in which MgBr_2 is used instead of MgCl_2 . MgBr_2 has two advantages over MgCl_2 which are (1) being more reactive due to less electronegativity difference ($\Delta\text{EN}_{\text{MgBr}_2} = \text{EN}_{\text{Br}} - \text{EN}_{\text{Mg}} = 2.8 - 1.3 = 1.5$) compared to MgCl_2 ($\Delta\text{EN}_{\text{MgCl}_2} = \text{EN}_{\text{Cl}} - \text{EN}_{\text{Mg}} = 3 - 1.3 = 1.7$). (2) MgBr_2 is soluble in diethyl ether which can reduce reaction time significantly. Furthermore, the more soluble reactants in the solution are expected to give rise to higher yield in the reaction [10]. In the present work, LiBH_4 has not been used as BH_4 source despite of its good solubility in diethyl ether. The reason is that based on (2.10), the reaction between LiBH_4 and MgBr_2 will not proceed as a precipitation metathesis. Since both LiBr and $\text{Mg}(\text{BH}_4)_2$ are soluble in diethyl ether, the separation/purification will be impossible.



The synthesis methods which are used in this study are listed below and the associated metathesis reactions are given in (2.11) and (2.12):

- Method 1)** Solid-state metathesis reaction of MgCl_2 and NaBH_4 using furnace or using ball mill followed by furnace heat treatment.
- Method 2)** Solid-state metathesis reaction of MgBr_2 and NaBH_4 using ball mill.
- Method 3)** Solution based metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether in a round bottom flask.
- Method 4)** Solution based high pressure-high temperature metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether using autoclave.

Method 5) Solution based high pressure-high temperature metathesis reaction of MgCl_2 and NaBH_4 in diethyl ether using autoclave.



It is important to note that, in this work diethyl ether was chosen as a solvent both for extraction and purification. THF needs relatively high desolvation temperature which might lead to the loss of hydrogen and/or leaving carbon impurity in the final product [11].

The reactants, sodium chloride (MgCl_2 , 98% anhydrous), magnesium bromide (MgBr_2 , 98% anhydrous), sodium borohydride (NaBH_4 , granular 98%) were purchased from Aldrich as analytical reagent grade. Diethyl ether (Merck) was used as solvent for purification/reaction medium of the target compound, $\text{Mg}(\text{BH}_4)_2$.

2.2.1 Metathesis reaction of MgCl_2 and NaBH_4 using furnace or using ball mill followed by furnace heat treatment

Two different procedures for $\text{Mg}(\text{BH}_4)_2$ synthesis are used in this method. In the first one, a total of 1 g MgCl_2 and NaBH_4 (molar ratio 1:2.5) were reacted in the furnace for 24 h at 270 °C in a sealed Pyrex tube. This temperature has been carefully selected as it is high enough for an enhanced reaction rate but well below the decomposition temperature of $\text{Mg}(\text{BH}_4)_2$ (290°C). In the second procedure, a mixture of one gram of MgCl_2 and NaBH_4 in 1:2.5 ratio is placed into 80 ml stainless steel vials using 5 mm stainless steel balls and balled milled for 3 h, 12 h and 24 h at 600 rpm. Subsequently, the mixed powders were heat treated at 270 °C for 24 h in a sealed Pyrex tube.

2.2.2 Solid-state metathesis reaction of MgBr_2 and NaBH_4 using ball mill

The mechanochemical synthesis was performed in Fritsch P7 planetary ball mill with 80 ml stainless steel vials using 5 mm stainless steel balls. The mass ratio of ball to powder was fixed to 20:1. Due to moisture sensibility of the Mg compounds, all sample manipulations and powder loading were performed under inert conditions (glove box, N_2 , $\text{O}_2 \leq 1\text{ppm}$, $\text{H}_2\text{O} \leq 1\text{ppm}$). The schematic of the procedure is shown in Fig.2.2. An excess amount of NaBH_4 with respect to the stoichiometric ratio and different reaction times of ball milling (6 and 24 h) were employed to

investigate their effects on the formation of $\text{Mg}(\text{BH}_4)_2$. All synthesis conditions values are summarized in Table 2.2.

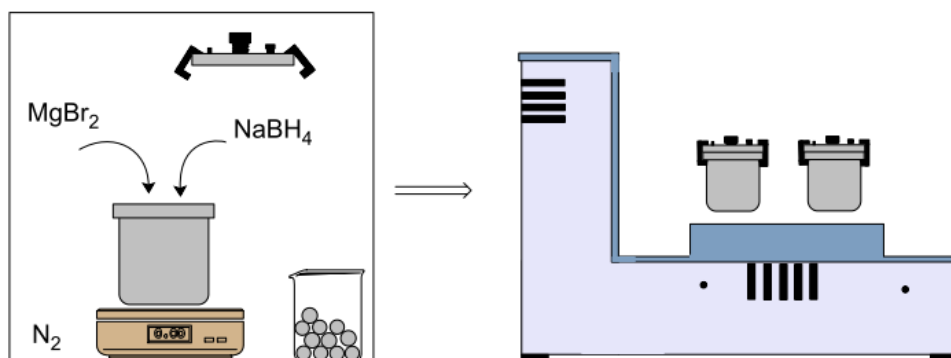


Fig.2.2 Schematic of $\text{Mg}(\text{BH}_4)_2$ synthesis procedure using MgBr_2 and NaBH_4 thru ball milling.

Table 2.2 Synthesis conditions for metathesis reaction of MgBr_2 and NaBH_4 using ball mill.

Series	MgBr_2 (mole)	NaBH_4 (mole)	Ball mill	
			Speed (rpm)	Time (h)
1	1	2	500	6
	1	2		24
2	1	2.25	500	6
	1	2.25		24
3	1	2.5	500	6
	1	2.2		24

2.2.3 Metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether in round bottom flask in ambient condition

In this method, one g mixtures of not-milled and pre-milled MgBr_2 and NaBH_4 (molar ratio: 1:2, 1:3) were measured in a N_2 filled glove box. The reactants were then placed into a two necks round bottom flask equipped with gas inlet adapter with stopcock and sealed using septum. Afterwards, the flask was connected to Schlenk line equipped with condenser in one neck. 100 ml diethyl ether is injected into the flask under Ar purge into. Subsequently, the blends were mixed in diethyl ether at room temperature using magnetic stirrer at 1000 rpm. Diethyl ether was constantly replenish as it was evaporating due to its volatility. Schematic of the synthesis procedure is shown in Fig.2.3.

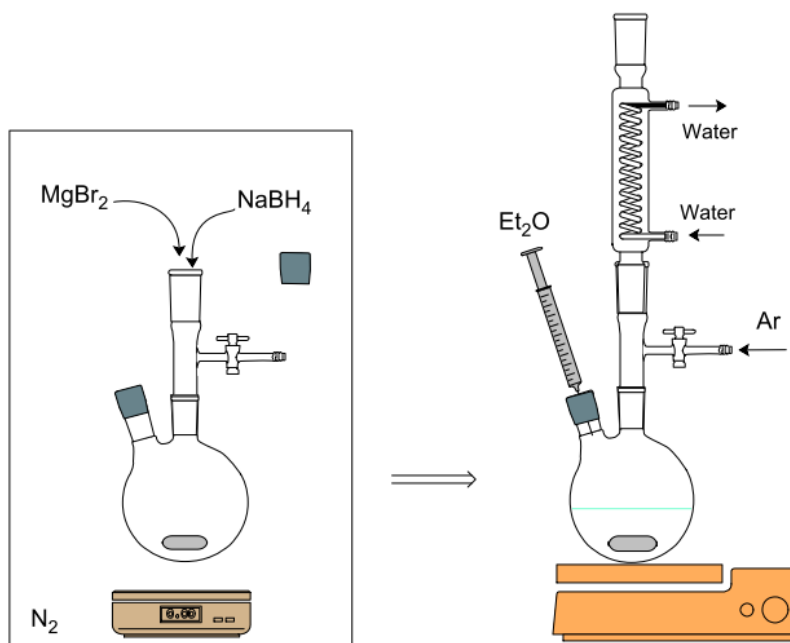


Fig.2.3 Schematic of $\text{Mg}(\text{BH}_4)_2$ synthesis procedure using MgBr_2 and NaBH_4 thru wet mixing in round bottom flask.

2.2.4 High pressure-high temperature metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether using Autoclave

Very low boiling temperature of diethyl ether (34°C) turns it into highly volatile solvent and this is a limiting factor in well proceeding of equation (2.11). In order to perform this reaction in a higher temperature, diethyl ether boiling point should be increased. This increment can be done by increasing system pressure based on Antoine equation.

This synthesis process is performed in a Roth high-pressure laboratory autoclave (Model II) with 250 ml 316Ti stainless steel cylinder, which is designed for max. 200 bar/ 300°C working condition. 1 g mixture of MgBr_2 and NaBH_4 in 1:2.5, 1:3 and 1:4 ratios were placed into autoclave in the N_2 filled glove box and transferred outside while all valves were closed. Diethyl ether is injected into the autoclave through the release screw while Ar was purging into the system. Released screw is closed and pressure of the system is increased to 8, 11 and 18 bar for temperatures 100, 125 and 150°C respectively based on Antoine equation. Stirrer rotation speed

was set to 1000 rpm and mixing for different times. Three sets of samples are prepared in which reactants ratios, reaction temperature and time of reaction are changed.

2.2.5 High pressure-high temperature metathesis reaction of MgCl_2 and NaBH_4 in diethyl ether using Autoclave

A mixture of MgCl_2 and NaBH_4 (total of one g each and molar ratios 1:2.5 and 1:3) was placed in an autoclave in the N_2 filled glove box and stirred in diethyl ether at 100 °C for 6 and 24 h, respectively. The products are processed as described in section 2.2.4. Autoclave device and schematic representation of this procedure is shown in Fig.2.4. Purity of the samples were determined using XRF and C analyzer. The obtained purity grade is discussed in context with commercial (95 %-wt) $\text{Mg}(\text{BH}_4)_2$ powder of Sigma Aldrich.

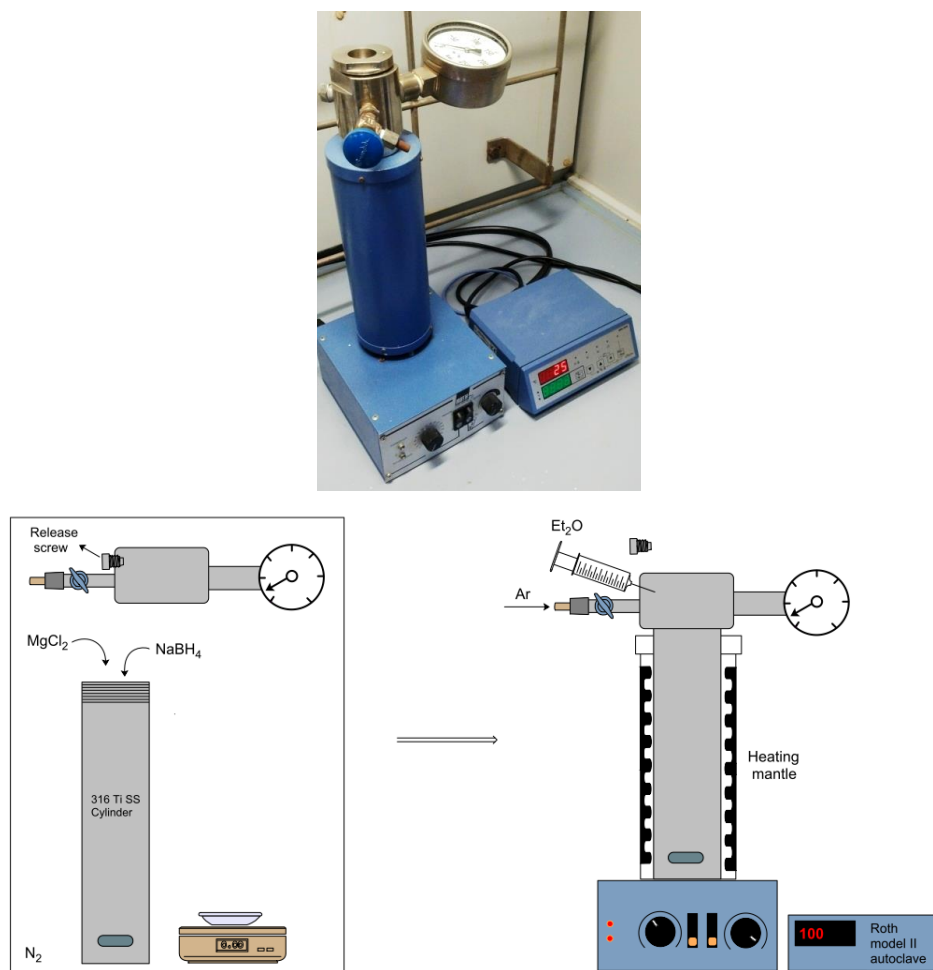


Fig.2.4 Schematic of $\text{Mg}(\text{BH}_4)_2$ synthesis procedure using MgCl_2 and NaBH_4 thru wet mixing in autoclave.

In methods where ball milling is used, a very hygroscopic white raw product was obtained. The powder is transferred into the glove box and placed into a glass thimble and the latter was inserted into a Soxhlet extraction vessel. The extractor was then connected to a Schlenk line and diethyl ether was poured from the top into the vessel under constant Ar flow. In the procedure in which wet mixing was utilized, the solution was transferred into the thimble located in the Soxhlet extraction vessel, by the aid of dropping funnel with bypass while Ar was purging into the system. The coiled condenser was periodically replenished on the top of Soxhlet vessel in order to condense evaporated diethyl ether and provide fresh ether in the Soxhlet vessel. Diethyl ether was

also replenish periodically as condenser was not totally effective to keep all ether in the system. Purification setup is used in this project is shown schematically in Fig.2.5.

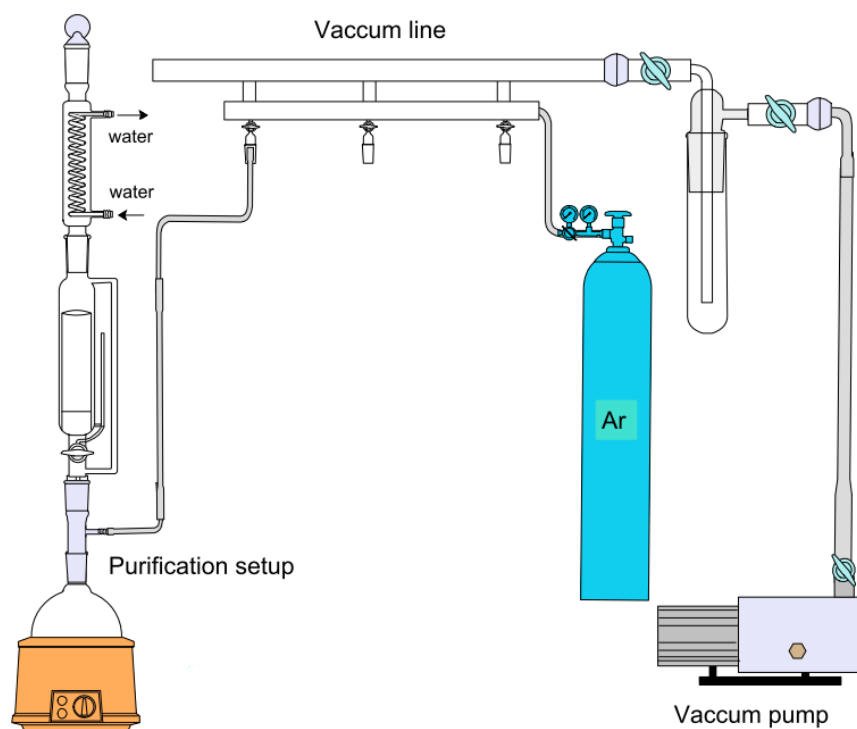


Fig.2.5 Schematic of setup which is used for purification of $\text{Mg}(\text{BH}_4)_2$.

The extraction takes place approximately overnight, after which all $\text{Mg}(\text{BH}_4)_2$ was dissolved in diethyl ether while NaBr/NaCl remained as residue in the thimble. The solvent removal occurred under vacuum (10^{-3} mbar) at room temperature yielding a colorless viscous residue. For completing desolvation, samples are heated under vacuum up to $100\text{ }^\circ\text{C}$ for 2 h and later to $150\text{ }^\circ\text{C}$ for 4 h which turn them into a sticky white powder. The sample is then gathered in the glove box and grinded for 20 min followed by reannealing for 5 h at $180\text{ }^\circ\text{C}$ under vacuum to remove the residual solvent.

The crude material (after ball mill), filtrated reaction product and powders which are remained in the thimble after filtration reaction were analyzed using powder X-ray powder diffraction method (PXRD). PXRDs were done with BRUKER D2 Phaser diffractometer (Cu radiation with LYNXEYETM detector) and BRUKER D8 Phaser diffractometer (Cu radiation with VANTEC-1

detector). The samples were prepared in the glove box and placed into Si/glass holder with Kapton foil cover which 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 ATR-FTIR and Raman Spectroscopy. ATR-FTIR spectroscopy has been done using Thermo Scientific iS10 FT-IR single reflection equipped with diamond ATR in the 650-4000 cm^{-1} with 4 cm^{-1} resolution. Raman spectroscopy measurements were conducted using nearly 5 mg of sample in sealed Pyrex tube ($\varnothing$ = 4 mm) in the range of 2500-1000 cm^{-1} with a BURKER RFS 100/S spectrometer (Nd: YAG-Laser, 1064 nm, 200 mW). Purity of filtrated compounds are investigated using XRF and CHNS/O analyzer. For the elemental, powder specimen was placed in the XRF sample cups (Chemplex Industries Inc.) and measured by “loose-powder method”. Prolene film (4 μm thickness, Chemplex Industries, Inc., Cat.No:426) was used as the thin-film sample support, where typical impurities are reported as Ca, P, Fe, Zn, Cu, Zr, Ti, Al in the ppm level. The measurements were carried out with a Bruker S8 Tiger XRF spectrometer in standardless mode under Helium atmosphere. A 4 KW, Rh anode X-ray tube was used to generate X-rays. For the measurement and calibration method "Best Analysis" and "Elements" were selected respectively. For the analyses of the results, SpectraPlus Eval2 V2.2.454 was used. Carbon, nitrogen and hydrogen (CNH) mass concentration was measured using Thermo scientific Flash 2000 elemental analyzer (CHNS) with He as a carrier gas. For each sample between 2-3 mg sample were measured wrapped into a Tin holder in glove box and transferred with air-tight holder. Calibration was done using 2.5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene (BBOT) standard reference material before starting the measurements.

2.3 Results and discussion

2.3.1 Metathesis reaction of MgCl_2 and NaBH_4 using furnace or using ball mill followed by furnace heat treatment

According to the PXRD result (See Fig.2.6) of the first procedure, heat treatment of the mixture of MgCl_2 and NaBH_4 mixtures (excess NaBH_4 (1:2.5 ratio)) at 270 °C for 24 h was not successful as the starting materials did not react. Based on Fig.2.6 all Bragg reflections come from either MgCl_2 or NaBH_4 and the bump between 15 to 23 degree results from sample holder and krypton foil.

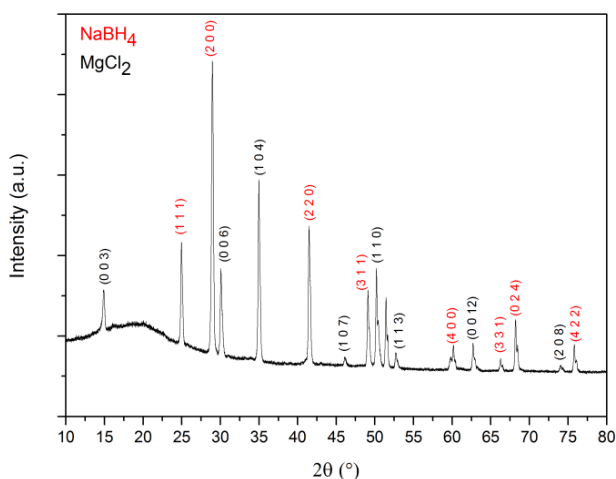


Fig.2.6 PXRD pattern mixture of MgCl_2 and NaBH_4 in 1:2.5 ratio (NaBH_4 in excess) annealed at 270 °C for 24 h.

In order to induce the reaction, an additional step is devised in which reactants were ball milled before heat treatment. All PXRD results of products after ball milling and heat treatment indicate that the reactions were not complete. For instance, PXRD results of 24 h milled mixture as well as 24 h milled and subsequently heat treated one for 24 h at 270 °C are shown in Fig.2.7 a and b, respectively. From Fig.2.7 a, shows that NaBH_4 peaks are clearly present while the broadened peaks of MgCl_2 indicate that compound is semi-amorphous. However, there are no reflections present which can be assigned to the reaction product NaCl . After heat treatment (Fig.2.7 b), the NaCl peaks are clearly emerged while unreacted MgCl_2 and NaBH_4 are also detected in the final product. This proves that the 24 h milling and 24 h heat treatment is not enough to accomplish the

reaction (2.12). In the present case our findings are in the agreement with previous reports that long ball milling/and vigorous wet mixing is necessary to complete the reaction (2.12) [6, 11].

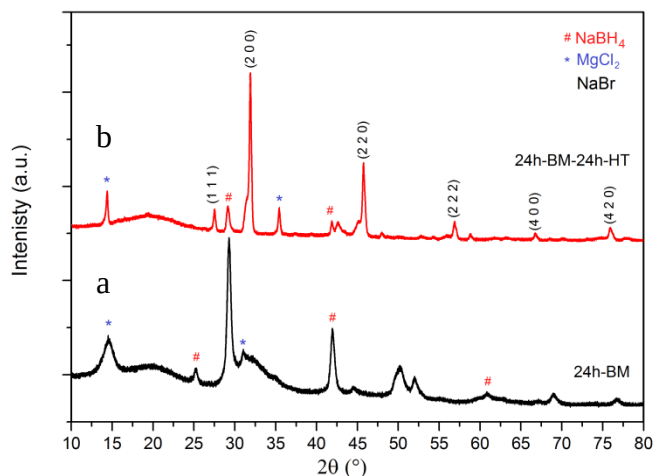


Fig.2.7 PXRD pattern of MgCl_2 and NaBH_4 in 1:2.5 ratio (a) ball milled for 24 h (b) ball milled for 24 h and heat treated at 270 °C for 24 h.

2.3.2 Solid-state metathesis reaction of MgBr_2 and NaBH_4 using ball mill

In the first reaction series, the stoichiometric mixture of $\text{MgBr}_2/\text{NaBH}_4$ (1:2) were ball milled for 6 and 24 h. The PXRD (See Fig.2.8) pattern confirm in both cases an incomplete reaction. After 6 hours of ball mill only precursors were detected, while after 24 hours NaBr with some amount of unreacted MgBr_2 appeared.

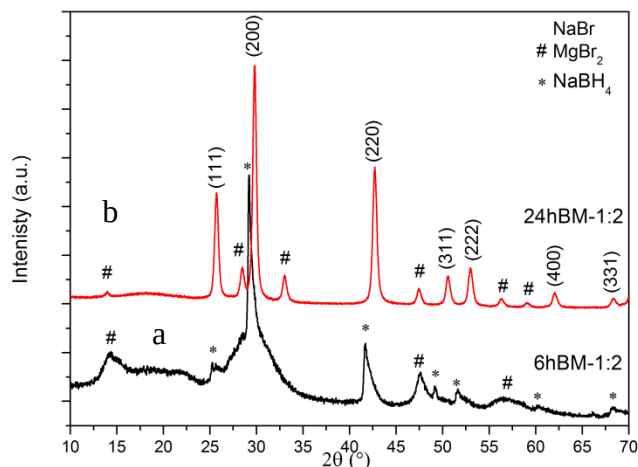


Fig.2.8 PXRD pattern of MgBr_2 and NaBH_4 in 1:2 ratio (a) ball milled for 6 h (b) ball milled for 24 h.

The results of the second reaction series ($\text{MgBr}_2/\text{NaBH}_4$ 1:2.25, 6 and 24 h ball milled) are shown in Fig.2.9. The PXRD patterns reveal in all conditions solely NaBr indicating a complete reaction. As was reported by several authors [19, 20], the absence of $\text{Mg}(\text{BH}_4)_2$ reflections in all reaction products is an indication that the compound formed under this conditions is of an amorphous type. An interesting detail is that for the sample milled for 24 h, the intensity of the bump located in the range of 15 to 20 degree is stronger which is characteristic for more amorphous $\text{Mg}(\text{BH}_4)_2$. The formation of $\text{Mg}(\text{BH}_4)_2$ is further confirmed by ATR-FTIR results (not shown).

After purification and heat treatment of the mixture at 180 °C, MgBr_2 peaks emerged in all powder diagrams. This is because of reduction in crystallinity of MgBr_2 while ball milling and formation of well crystalline NaBr. As NaBr has very intense reflections, those of extremely weak MgBr_2 were not detectable before purification. Moreover, as demonstrated in Fig.2.10, the intensity of the unreacted MgBr_2 decreased significantly by increasing the ball mill time from 6 h to 24 h. $\alpha\text{-Mg}(\text{BH}_4)_2$ also crystallized and became detectable phase in the patterns. It is also the dominant compound in the mixture which is milled for 24 h.

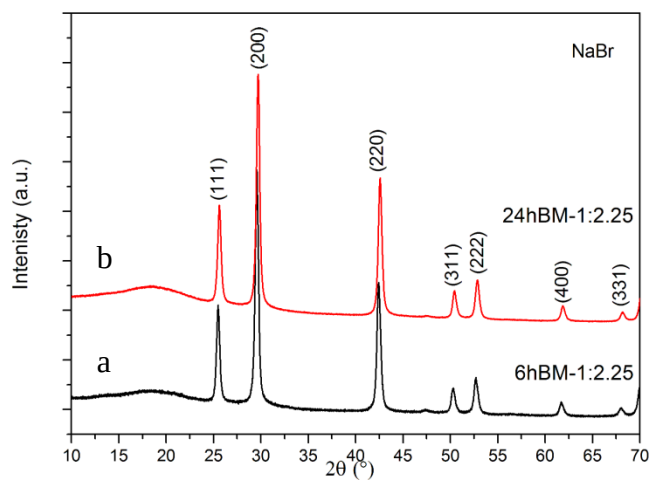


Fig.2.9 XRPD pattern of MgBr_2 and NaBH_4 in 1:2.25 ratio (a) ball milled for 6 h (b) ball milled for 24 h.

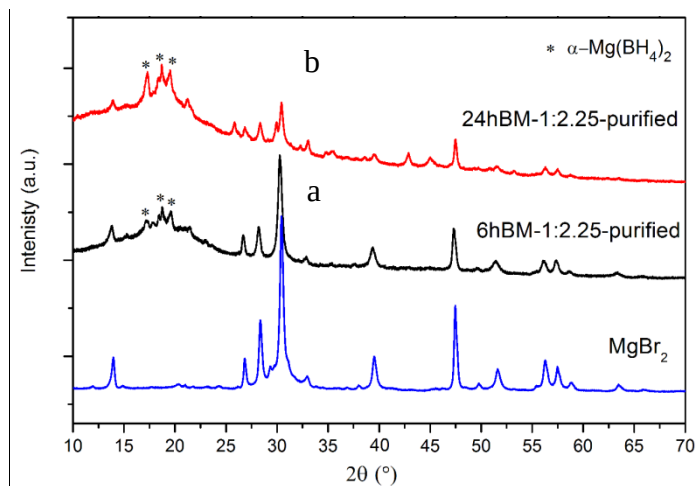


Fig.2.10 PXRD pattern of purified mixture of MgBr_2 and NaBH_4 in 1:2.25 ratio (a) ball milled for 6 h (b) ball milled for 24 h.

PXRD pattern after 6 h and 24 h ball milling for the third reaction series ($\text{MgBr}_2/\text{NaBH}_4$ 1:2.5), is shown in Fig.2.11. It can be seen that in all cases only NaBr forms for both 6 h and 24 h milled mixture without any extra peaks from the recants. However, same as the previous mixture (1:2.25 ratio), $\text{Mg}(\text{BH}_4)_2$ exist in the amorphous form which is proved by ATR-FTIR spectra (not shown). In order to understand the course of the reaction, both mixtures were purified based on the process which was explained beforehand. The PXRD results of the mixtures after purification are shown in Fig.2.12. According to the reference pattern for $\alpha\text{-Mg}(\text{BH}_4)_2$ which is also plotted in Fig.2.12, shows that the final product of both mixtures are solely $\alpha\text{-Mg}(\text{BH}_4)_2$. However, the synthesized $\alpha\text{-Mg}(\text{BH}_4)_2$ has a low crystallinity which leads to poor quality (higher signal to noise ratio) PXRD diagrams.

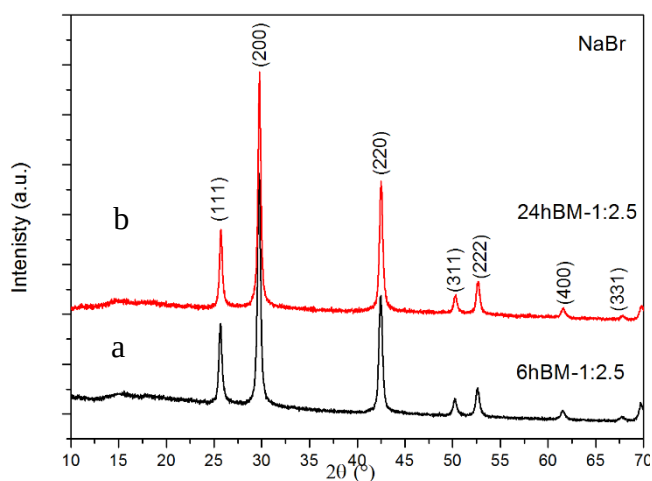


Fig.2.11 PXRD pattern of MgBr_2 and NaBH_4 in 1:2.5 ratio (a) ball milled for 6 h (b) ball milled for 24 h.

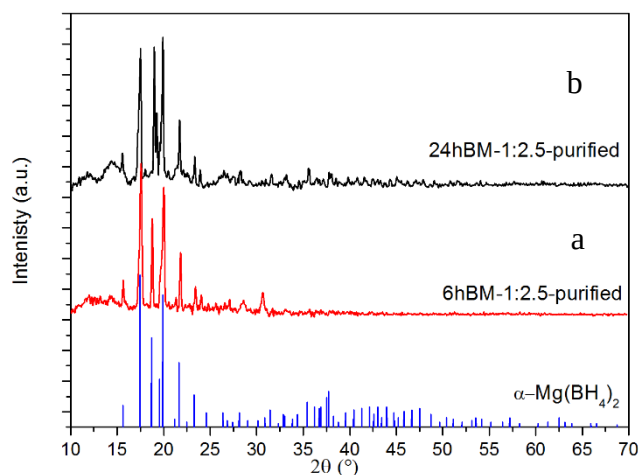


Fig.2.12 PXRD pattern of purified mixture of MgBr_2 and NaBH_4 in 1:2.5 ratio (a) ball milled for 6 h (b) ball milled for 24 h.

In order to investigate the vibrational characteristics of the $[\text{BH}_4]^-$ group in $\text{Mg}(\text{BH}_4)_2$ in context with NaBH_4 , Raman spectroscopy was performed on the both milled and untreated $\alpha\text{-Mg}(\text{BH}_4)_2$ and NaBH_4 which is shown in Fig.2.13. It can be seen that for milled mixture for 6 h the Raman bands are broader and intensities are weaker which is an indication of disorder increment in the periodic arrangement of atoms. Ball milling will increase the defects in the structure, reduce the size of the particles and cause broadening in Raman peaks [21]. However there is a little differences in Raman shifts between milled and pure crystalline $\alpha\text{-Mg}(\text{BH}_4)_2$ which is the indication of identical local structure [22]. Therefore, based on previous studies $[\text{BH}_4]$ group modes in $\text{Mg}(\text{BH}_4)_2$ can be written as follow: B-H symmetric bending mode B-H (ν_4 , 1300 cm^{-1}), B-H asymmetric bending mode (ν_2 , 1575 cm^{-1}), B-H overtone ($2\nu_4$, 2200 cm^{-1}), B-H symmetric and asymmetric stretch (ν_3 , 2305 cm^{-1} and ν_1 , 2331 cm^{-1} , respectively) and combination of ν_2 and ν_4 ($\nu_2+\nu_4$, 2511 cm^{-1}) [23-27]. For NaBH_4 , B-H symmetric bending, ν_2 , is shifted to lower Raman frequencies compared to in $\text{Mg}(\text{BH}_4)_2$ and the symmetric B-H stretch in NaBH_4 reveals also a shift to higher wavenumbers [23]. The Raman modes of NaBH_4 did not show any differences in

crystalline and ball milled form, which is the indication that atomic long range orders are not affected by ball milling.

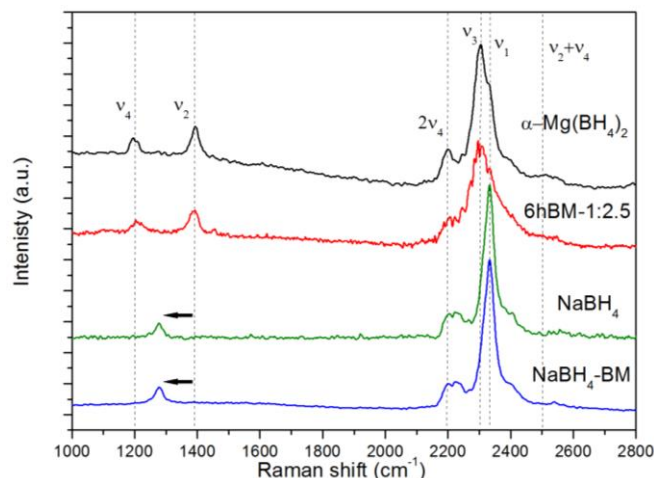


Fig.2.13 Raman spectra of $\alpha\text{-Mg}(\text{BH}_4)_2$, mixture at 1:2.5 ratio milled for 6 h, NaBH_4 and ball milled NaBH_4 for 6 h.

XRF measurement were also done on the purified samples in order to check accuracy of atomic ratio or mass concentration as well as purity of the synthesized $\text{Mg}(\text{BH}_4)_2$. In this case, NaBH_4 (purity 99%), MgBr_2 (purity, 98%) were first measured in order to check the accuracy of the measurement as well as calibration of the instrument. However, the results, summarized in Table 2.3, were not satisfactorily either in purity or mass concentration of as received compounds.

Table 2.3 XRF concentration of as received MgBr_2 and NaBH_4

MgBr_2, 98%	Weight conc. (%)	Theo. weight conc.	NaBH_4, 99%	Weight conc. (%)
Br	90.42	87.5	Na	97.74
Mg	9.52	12.5	Si	1.79
Cl	0.032	-	Al	0.42
Cu	0.011	-	Ca	0.038
Fe	0.009	-		
Ni	0.005	-		

XRF measurements proved that all 1:2.5 purified samples contained bromine. Interestingly, however, no Br related compound (MgBr_2 or NaBr) has been seen in the final product in the PXRD pattern. EDX confirmed also the presence of Br which is not shown here. The existence of Br in the final product can have two different origins, (1) the compound is not well purified and NaBr presents in the purified sample. However, no Na - not even as trace - was detected either in EDX or in XRF. Moreover, NaBr has intense Bragg reflections which should have been observed already in PXRD. (2) Unreacted MgBr_2 . This is likely possible as MgBr_2 is soluble in diethyl ether. However, the employed excess of NaBH_4 should reduce this possibility. Despite surplus Br was detected in all concentrations meaning that Br^- ions were embedded in the structure of $\text{Mg}(\text{BH}_4)_2$. This may happen by partial replacement of BH_4 sites by Br anions and forming a solid solution. This type of substitution has been reported for the ball milled mixture of $\text{Mg}(\text{BH}_4)_2$ and MgBr_2 [28]. However, the substitution is not easily detectable as there is no change in the vibrational frequencies. Furthermore, due to very poor quality PXRD patterns the expected peak shifting for $\text{Mg}(\text{BH}_4)_2$ is hardly to detect.

High energy ball milling synthesis is reported to be able to initiate an anion/cation substitution owing to high impact on the particles [9]. To overcome this problem, wet mixing of the mixture in diethyl ether is performed which is discussed in following section.

2.3.3 Metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether in round bottom flask in an ambient condition

PXRD patterns of the residual products of not-milled and pre-milled mixtures, as well as of filtrate products are illustrated in Fig.2.14, the results are summarized in Table 2.4. The residues after wet mixing and ball milling/wet mixing mainly consist of NaBr , NaBH_4 while the content of MgBr_2 in 1:3 blends is notably lower than that of 1:2 ratio. Moreover, reactions proceeded more rapidly in pre-milled mixtures rather than in not milled ones as can be seen from the increased NaBr formation. The residues contain $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ while filtrate materials are anhydrous MgBr_2 . Based on our experimental observations, MgBr_2 is very hygroscopic and turns to $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ within 15 minutes on exposure to air. $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ can also be converted back to MgBr_2 after heat treatment. Consequently, all filtrates of diethylether treatment contained hydrous MgBr_2 . The

comparison between as received and ball milled MgBr_2 reveals that mechanical milling will reduce the crystallinity (increase of the disorder in the crystal structure) in MgBr_2 . Peaks of MgBr_2 that are seen in milled mixtures are related to “bad crystallized” MgBr_2 after ball milling. PXRD results of filtrates did not show the presence of any crystallized $\text{Mg}(\text{BH}_4)_2$. Thus, $\text{Mg}(\text{BH}_4)_2$ was either not formed or is in an amorphous state.

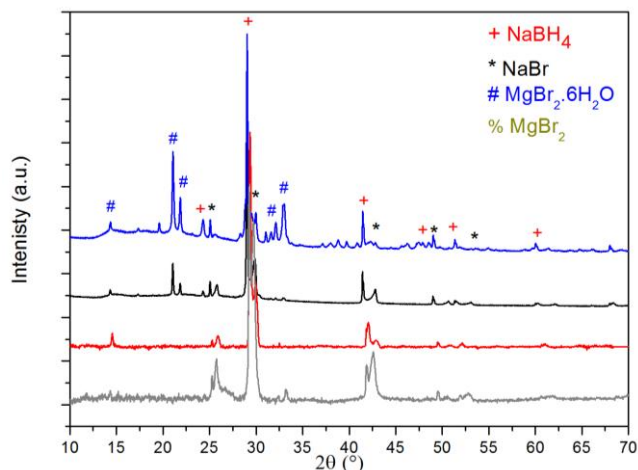


Fig.2.14 PXRD pattern of MgBr_2 and NaBH_4 in 1:2 and 1:3 ratios not-milled and pre-milled and mixed for 24 hours in round bottom flask

ATR-FTIR spectra were taken from the filtrates to confirm the formation of $\text{Mg}(\text{BH}_4)_2$. Based on the spectra, $\text{Mg}(\text{BH}_4)_2$ was formed only in the pre-milled 1:3 ratio mixture. In all filtrates, very intense O-H stretching and bending modes were observed stemming from water as MgBr_2 is very hygroscopic.

Because MgBr_2 is soluble in diethyl ether, if there had been any unreacted MgBr_2 left in reaction products, it should have been extracted by diethyl ether from the residue completely. The existence of MgBr_2 in the residue proves that filtration should have been done either repeatedly or another more suitable method of filtration should be used. Handling air sensitive materials is quite difficult outside of glove box and our glove boxes at KU are not appropriate for liquids especially highly volatile ones like ethers. After some attempts we found that Soxhlet extraction was the most suitable technique for our purpose whose application is described subsequent sections.

Table 2.4 synthesis conditions for reaction using method 2.3.3

MgBr ₂ (mole)	NaBH ₄ (mole)	Mixing method	Time		PXRD Results	
			Ball Mill (h)	Wet mix (h)	Residue	Filtrate
1	2	Magnetic stirring	-	24	NaBr+NaBH ₄ + MgBr ₂ .6H ₂ O	MgBr ₂
1	3	Magnetic stirring	-	24	NaBr+NaBH ₄ + MgBr ₂ .6H ₂ O	MgBr ₂
1	2	Ball Mill- Magnetic stirring	2	24	NaBr+NaBH ₄ +MgBr ₂ .6H ₂ O	MgBr ₂
1	3	Ball Mill- Magnetic stirring	2	24	NaBr+NaBH ₄ +MgBr ₂	MgBr ₂

Another alternative method which is devised to reach completion of the reaction of $\text{MgBr}_2 + \text{NaBH}_4$ and to prevent the anion substitution $\text{Mg}(\text{BH}_4)_2$ was utilizing autoclave at elevated temperatures. The process is discussed in the following section.

2.3.4 High pressure-high temperature metathesis reaction of MgBr_2 and NaBH_4 in diethyl ether using Autoclave

Soloveichik et.al., [6] have reported that wet mixing of the mixture of MgCl_2 and NaBH_4 in the diethyl ether for 32 h at room temperature would not yield any $\text{Mg}(\text{BH}_4)_2$ while using 1:1 mixture of diethyl ether-toluene and increasing reaction temperature to 60 °C will produce $\text{Mg}(\text{BH}_4)_2$ with 15 % yield. We used the idea of higher reaction temperature believing that this measure will affect both the reaction time as well as the product yield in a positive manner. Different stirring time, reaction temperature and reactant ratios were used to investigate how these parameters affect the quality of the final product. Higher NaBH_4 : MgBr_2 ratio (1:4 ratio) was also used to ensure the complete consumption of MgBr_2 and eliminate the risk of contamination of $\text{Mg}(\text{BH}_4)_2$ by MgBr_2 . The reactions proceeded well almost in all series (except for the one stirred for 3 h at 100 °C) however, XRF results showed the presence of Br⁻ in the final products. This shows that the method of synthesis is not affecting the Br⁻ contamination in $\text{Mg}(\text{BH}_4)_2$. Therefore, we moved to the next step which is devised to get purer $\text{Mg}(\text{BH}_4)_2$.

2.3.5 High pressure-high temperature metathesis reaction of MgCl_2 and NaBH_4 in diethyl ether using Autoclave

Summarizing the previous synthesis methods in which ball milling and MgBr_2 were used as a precursor, we can say that it was not possible to obtain pure $\text{Mg}(\text{BH}_4)_2$ free of Br^- contamination. On the other hand, high temperature synthesis introduced for the first time in the present study turned out to be quite successful with respect to both the reaction rate and progress of the process. The question was, what would happen when MgCl_2 was replaced by MgBr_2 ? The ATR-FTIR spectra of the reaction products obtained from the MgCl_2 - NaBH_4 blends with different molar ratios, and duration times are depicted in Figure 2.15 a. First of all, the spectra confirm the formation of α - $\text{Mg}(\text{BH}_4)_2$ in all samples. In addition, samples with increasing reactant ratio the B-H bending shoulder around $\sim 1350\text{ cm}^{-1}$ become more pronounced. This is due to the decrease in tetrahedral symmetry of the $[\text{BH}_4]^-$ anions which in turn causes bending mode to split [29]. However, as the crystallinity is very low, only one big bump can be observed. Raman spectra was also confirming the formation of α - $\text{Mg}(\text{BH}_4)_2$ (e.g. for the sample of 1:2.5 ratio, stirred at 100°C for 6 h) (see Figure 2.15 b).

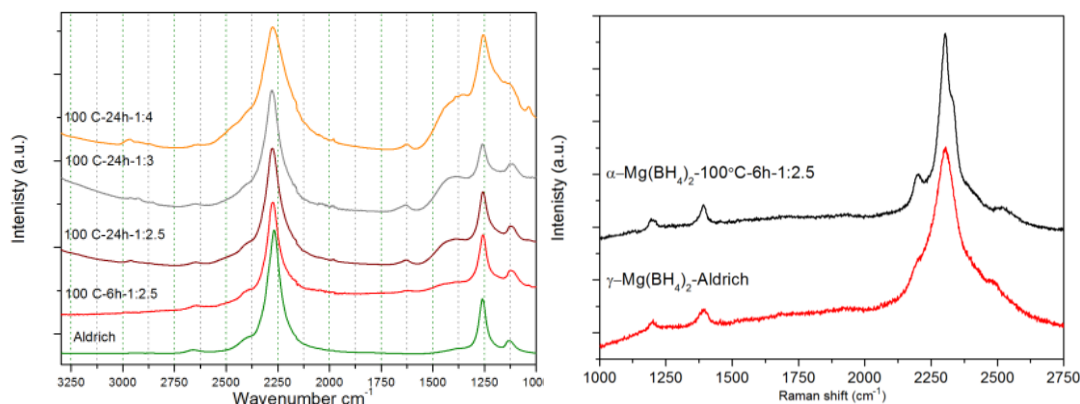


Fig.2.15 a) ATR-FTIR spectrum of mixture of MgCl_2 and NaBH_4 in 1:2.5, 1:3 and 1:4 ratios mixed for 6 and 24 h at 100°C in Autoclave b) Raman spectra of mixture in 1:2.5 ratio mixed for 6 h at 100°C in Autoclave and as received Aldrich α - $\text{Mg}(\text{BH}_4)_2$.

It is found that some mixtures (e.g., the blend 1:2.5, stirred for 6 and 24 h at 100°C) during desolvation process gave crystalline $\text{Mg}(\text{BH}_4)_2$ while others formed an amorphous $\text{Mg}(\text{BH}_4)_2$

adduct. This was also seen in the autoclave synthesis using MgBr_2 as well as ball milled samples. According to our experience, reactant ratio, speed, duration of stirring and temperature of synthesis do not have any effect in amorphization. The amorphization might be related to composition of the $\alpha\text{-Mg}(\text{BH}_4)_2$ adducts which are formed with diethyl ether ($\text{Mg}(\text{BH}_4)_2 \cdot n\text{Et}_2\text{O}$, $n \leq 2$ [6]). In other words, $\alpha\text{-Mg}(\text{BH}_4)_2$ forms a range of complexes with diethyl ether having different compositions which some of them are amorphous and some are crystalline or semi crystalline. Based on the PXRD pattern shown in Fig.2.16 b, no $\alpha\text{-Mg}(\text{BH}_4)_2$ is seen up to $\sim 250^\circ\text{C}$ while after this temperature (at 280°C) a $\beta\text{-Mg}(\text{BH}_4)_2$ phase appears. However, for crystalline adduct (Fig.2.16 a), crystalline “etherated” $\text{Mg}(\text{BH}_4)_2$ is revealed at after vacuuming at room temperature, and $\alpha\text{-Mg}(\text{BH}_4)_2$ phase is emerges after 100°C .

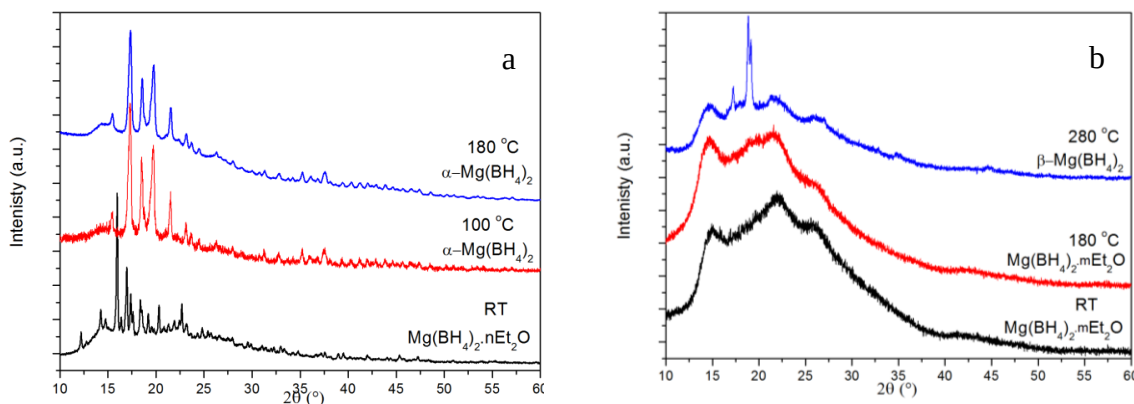


Fig.2.16 PXRD pattern of (a) crystalline $\text{Mg}(\text{BH}_4)_2 \cdot n\text{Et}_2\text{O}$ heat treated up to 180°C (b) amorphous $\text{Mg}(\text{BH}_4)_2 \cdot m\text{Et}_2\text{O}$ heat treated up to 280°C .

In order to track diethyl ether (Carbon) removal from the crystalline $\text{Mg}(\text{BH}_4)_2 \cdot n\text{Et}_2\text{O}$ while desolvation, quantitative carbon analysis was performed using CHN analyzer. The results which are tabulated in Table 2.5 are showing that C concentration in the compound decreased from 29.31 wt % to 1.68 wt % during the desolvation process. We believe that this amount can be reduced further by using higher desolvation temperatures. It should be noted that Aldrich sample which was used as a reference contains also 1.15 wt % carbon.

Table 2.5 Carbon content of $\text{Mg}(\text{BH}_4)_2 \cdot \text{mEt}_2\text{O}$.

Desolvation Temperature (°C)	C amount (wt %)	Physical Appearance
RT	29.31	colorless viscous residue
100	18.10	sticky white powder
150	8.50	sticky white powder
180	1.68	white flaky powder
Aldrich	1.15	white flaky powder

In addition, the XRF results show that the Cl amount is extremely low indicating that highly pure $\text{Mg}(\text{BH}_4)_2$ was successfully synthesized (Table 2.6). The purity of the synthesized $\text{Mg}(\text{BH}_4)_2$ was also compared with the commercial $\text{Mg}(\text{BH}_4)_2$ (purity 95 %) purchased from Sigma Aldrich. According to XRF results both samples contain Cl and Si in trace amounts. While Sigma Aldrich's product is contaminated additionally with Al and S and as synthesized $\text{Mg}(\text{BH}_4)_2$ contains Na and Br. However, since XRF is not the most accurate method for quantification of elements, the results are not 100% reliable. It should be noted that, based on reported information on Sigma Aldrich website, the purity of sample (95 %) is calculated from proton NMR.

Table 2.6 Elemental concentration of synthesized and as received using XRF.

element	$\alpha\text{-Mg}(\text{BH}_4)_2$ this work	$\gamma\text{-Mg}(\text{BH}_4)_2$ Aldrich
	Concentration (wt %)	Concentration (wt %)
Mg	45.52	26.2
Cl	0.857	0.859
S	-	0.41
Na	0.16	-
Al	-	0.056
Si	0.037	0.011
Br	0.012	-

Commonly used method in the literature for the determination of elemental composition are ICP-AES and ICP-OES [6, 10, 11, 30]. Usually all elements can be reliably detected by these methods except halogens (F, Cl and Br) as the ionization of those elements is quite difficult. As a result, ion exchange chromatography is widely used in the literature for halogen determination

specially in the field of hydrogen storage materials [6, 31]. In this work, elemental analysis has been tried using ICP-MS. However, the measurements were not correlatable and repeatable, particularly for the Cl and Br ions. For instance, theoretical Mg/B ratio in $\text{Mg}(\text{BH}_4)_2$ should be 1.124 (based on atomic weights) however, this ratio was 1.236 and 1.197, for Aldrich and as synthesized sample, respectively. This resulted very likely from the differences in the sample preparation.

Moreover, many studies in the field of hydrogen storage materials have been published reporting the purity and elemental composition of synthesized compounds based on the determination of experimental H content - by CHN analyzer - and its comparison with the known theoretical values [6, 11, 32-34]. In this project, we also determine purity of synthesized compound by this method which was 97 % which is shown in the Table 2.7. The results were quite reliable as calibration were done before measurements and results trustability were tested by the commercial compounds, NaBH_4 (99 %) and MgH_2 (98 %).

Table 2.7 N, C, H and S concentrations for as synthesized and as received $\text{Mg}(\text{BH}_4)_2$ getting from CHN.

$\alpha\text{-Mg}(\text{BH}_4)_2$ this work		NaBH_4 -99%	MgH_2 -98%
Element	Avg.	Avg.	Avg.
Nitrogen	0.18877	0.1019	0.1019
Carbon	1.7024	0.1072	0.1072
Hydrogen	14.403	7.3902	7.3902
Sulphur	0	0	0

Yield of production was also investigated in detail as it is shown in Table 2.8. From the information tabulated in table 2.9, amount of starting materials is the most important factor to increase the production yield. For instance, increasing in total amount of MgCl_2 and NaBH_4 in 1:2.5 ratio mixed for 6 h at 100 °C, from 1 g to 5 g, will increase yield of production from 34 % to 63 %. Based on our observation, this significant decrease in yield for lower amount of mixture is mostly correlated with purification method, while high amount of purified and dried powder sticks to the wall of round bottom flask due to static electricity. We believe that yield will increase even more when higher amount of mixture is used. Moreover, time of reaction, mixture ratios and repeating purification are not significantly changing production yield.

Table 2.8 $\alpha\text{-Mg}(\text{BH}_4)_2$ production yield under different conditions

Sample condition	Production yield %			
	Amount of starting materials in total - one time purification		Purification of 5 g mixture	
	1g	5g	One time	Two times
100°C-24h-1:4	37	65	65	69
100°C-24h-1:3	39	-	-	-
100°C-24h-1:2.5	38	-	-	-
100°C-6h-1:2.5	34	63	63	68

2.4 Conclusion

In order to develop a scalable and convenient synthesis method for $\alpha\text{-Mg}(\text{BH}_4)_2$, five different multi steps mechanochemical and wet mixing synthesis – all based on the metathesis reaction of MgX_2 ($\text{X} = \text{Cl}, \text{Br}$) with NaBH_4 – were performed in a planetary ball-mill or in diethyl ether. $\alpha\text{-Mg}(\text{BH}_4)_2$ was separated from the produced halide by Soxhlet extraction method and later is dried using multi steps drying route. Synthesis methods which are used MgBr_2 as a starting material pure $\alpha\text{-Mg}(\text{BH}_4)_2$ could not be synthesized due to Br^- contamination. On the other hand, reaction did not proceed completely in any of heat treating, ball milling and wet mixing methods in a reasonable time while using MgCl_2 as a precursor. A novel and expedient approach was tested and developed at relatively high pressure and high temperature in an autoclave using diethyl ether as solvent. Very short mixing time (6 h) in autoclave at 100 °C was enough to reach to 97 % pure $\alpha\text{-Mg}(\text{BH}_4)_2$ with 63% yield after solvent removal.

2.5 References

1. Soloveichik, G.L., *Metal Borohydrides as Hydrogen Storage Materials*. Material Matters, 2007. **11**.
2. Hirscher, M., *Handbook of Hydrogen Storage: New Materials for Future Energy Storage*. 2010: Wiley-VCH.
3. Cerny, H.H.a.R., *Synthetic approaches to inorganic borohydrides*. Dalton Transactions, 2010. **39**: p. 7.
4. Barkhordarian, G., et al., *Unexpected kinetic effect of MgB_2 in reactive hydride composites containing complex borohydrides*. Journal of Alloys and Compounds, 2007. **440**(1-2): p. L18-L21.
5. Pistidda, C., et al., *Synthesis of amorphous $\text{Mg}(\text{BH}_4)_2$ from MgB_2 and H_2 at room temperature*. Journal of Alloys and Compounds, 2010. **508**(1): p. 212-215.

6. Soloveichik, G.L., et al., *Magnesium borohydride as a hydrogen storage material: Synthesis of unsolvated $\text{Mg}(\text{BH}_4)_2$* . International Journal of Hydrogen Energy, 2009. **34**(5): p. 2144-2152.
7. Egon Wiberg, R.H., *Notizen: Zur Kenntnis von Erdalkaliboranaten $\text{Me}[\text{BH}_4]_2$* . Zeitschrift für Naturforschung B Chemical Science, 1955. **10**: p. 294-295.
8. Wallbridge, B.D.J.a.G.H., *Metal Tetrahydroborates*. Progress in Inorganic Chemistry, 1970. **11**: p. 99-231.
9. Ravnsbæk, D.B., et al., *Powder diffraction methods for studies of borohydride-based energy storage materials*. Zeitschrift für Kristallographie, 2010. **225**(12): p. 557-569.
10. Zanella, P., et al., *Facile high-yield synthesis of pure, crystalline $\text{Mg}(\text{BH}_4)_2$* . Inorganic chemistry, 2007. **46**(22).
11. Chłopek, K., C. Frommen, and O.Z.a.M.F. Aline Le'on, *Synthesis and Properties of Magnesium Tetrahydroborate, $\text{Mg}(\text{BH}_4)_2$* . Journal of Materials Chemistry, 2007. **17**(33).
12. Huot, J., et al., *Mechanochemical synthesis of hydrogen storage materials*. Progress in Materials Science, 2013. **58**(1): p. 30-75.
13. James, S.L., et al., *Mechanochemistry: opportunities for new and cleaner synthesis*. Chem Soc Rev, 2012. **41**(1): p. 413-47.
14. Bauer, E.W.a.R., *Magnesium borohydride, $\text{Mg}(\text{BH}_4)_2$* . Zeitschrift fuer Naturforschung, 1950. **5b**(397).
15. Heřmánek, J.P.a.S., *Chemistry of boranes. IV. On preparation, properties, and behavior towards Lewis bases of magnesium borohydride*. Collection of Czechoslovak Chemical Communications, 1966. **31**: p. 3845-3858.
16. Bakulina, V.N.K.a.V.M., *Some properties of magnesium borohydride*. Bulletin of the Academy of Sciences of the USSR, Division of chemical science, 1971. **20**: p. 136-138.
17. Her, J.H., et al., *Structure of unsolvated magnesium borohydride $\text{Mg}(\text{BH}_4)_2$* . Acta Crystallogr B, 2007. **63**(Pt 4): p. 561-8.
18. Bateni, A., et al., *Novel Approach for Synthesis of Magnesium Borohydride, $\text{Mg}(\text{BH}_4)_2$* . Energy Procedia, 2012. **29**: p. 26-33.
19. Li, H.W., et al., *Effects of ball milling and additives on dehydrogenating behaviors of well-crystallized $\text{Mg}(\text{BH}_4)_2$* . Scripta Materialia, 2007. **57**(8): p. 679-682.
20. Nakamori, Y., et al., *Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiments*. Physical Review B, 2006. **74**(4).
21. Rebecca J. Newhouse, V.S., Son-Jong Hwang, Leonard E. Klebanoff, and J.Z. Zhang, *Reversibility and Improved Hydrogen Release of Magnesium Borohydride*. The Journal of Physical Chemistry C, 2010. **114**: p. 9.
22. Ban, V., et al., *Pressure-Collapsed Amorphous $\text{Mg}(\text{BH}_4)_2$: An Ultradense Complex Hydride Showing a Reversible Transition to the Porous Framework*. The Journal of Physical Chemistry C, 2014. **118**(40): p. 23402-23408.
23. Reed, D. and D. Book, *Recent applications of Raman spectroscopy to the study of complex hydrides for hydrogen storage*. Current Opinion in Solid State and Materials Science, 2011. **15**(2): p. 62-72.
24. Zhang, Z.G., et al., *Thermal decomposition behaviors of magnesium borohydride doped with metal fluoride additives*. Thermochimica Acta, 2013. **560**: p. 82-88.
25. Zavorotynska, O., et al., *Hydrogen cycling in $\gamma\text{-Mg}(\text{BH}_4)_2$ with cobalt-based additives*. J. Mater. Chem. A, 2015. **3**(12): p. 6592-6602.
26. Giannasi, A., et al., *High resolution Raman and neutron investigation of $\text{Mg}(\text{BH}_4)_2$ in an extensive temperature range*. J Phys Chem A, 2010. **114**(8): p. 2788-93.

27. Filinchuk, Y., et al., *Porous and dense magnesium borohydride frameworks: synthesis, stability, and reversible absorption of guest species*. *Angew Chem Int Ed Engl*, 2011. **50**(47): p. 11162-6.
28. Hino, S., et al., *Halide Substitution in Magnesium Borohydride*. *The Journal of Physical Chemistry C*, 2012. **116**(23): p. 12482-12488.
29. D'Anna, V., L.M. Lawson Daku, and H. Hagemann, *Vibrational spectra and structure of borohydrides*. *Journal of Alloys and Compounds*, 2013. **580**: p. S122-S124.
30. Roedern, E. and T.R. Jensen, *Thermal Decomposition of $\text{Mn}(\text{BH}_4)_2$ – $\text{M}(\text{BH}_4)_x$ and $\text{Mn}(\text{BH}_4)_2$ – MH_x Composites with $M = \text{Li}, \text{Na}, \text{Mg}$, and Ca* . *The Journal of Physical Chemistry C*, 2014. **118**(41): p. 23567-23574.
31. Aguey-Zinsou, M.L.C.a.K.-F.-o., *Core–Shell Strategy Leading to High Reversible Hydrogen Storage Capacity for NaBH_4* . *ACS Nano*, 2012. **6**(9): p. 7739-7751.
32. Liu, X., et al., *Decomposition Behavior of Eutectic LiBH_4 – $\text{Mg}(\text{BH}_4)_2$ and Its Confinement Effects in Ordered Nanoporous Carbon*. *The Journal of Physical Chemistry C*, 2014. **118**(47): p. 27265-27271.
33. Hu, J.J., E. Röhm, and M. Fichtner, *Feasibility and performance of the mixture of MgH_2 and LiNH_2 (1:1) as a hydrogen-storage material*. *Acta Materialia*, 2011. **59**(14): p. 5821-5831.
34. Bardají, E.G., et al., *LiBH_4 – $\text{Mg}(\text{BH}_4)_2$: A Physical Mixture of Metal Borohydrides as Hydrogen Storage Material*. *The Journal of Physical Chemistry C*, 2011. **115**(13): p. 6095-6101.

Chapter 3

Solid Solution Formation

In this chapter, solid solution formation possibility is discussed which occurs during synthesizing of $\text{Mg}(\text{BH}_4)_2$. In the Introduction part, the different possibilities of generating mixed anionic solid solutions in borohydrides are explained, followed by experimental procedures using ball milling and autoclave techniques to create them. Effect of changing reactant ratios, milling time and speed are systematically investigated with respect to formation of solid solutions. Moreover, effect of mixing temperature, reactant ratios and time of mixing using autoclave technique is studied systematically.

3.1 Introduction

As mentioned in previous chapters, mechanochemical synthesis (ball milling) has become one of the predominant preparation methods for borohydrides. Metathesis reaction using mechanical milling starts usually from alkali metal borohydride (ABH_4 , $\text{A} = \text{Li, Na, K}$) and metal halide M_nX_m ($\text{M} = \text{mono, di, tri valent metal}$) $\text{X} = \text{Cl, Br}$) forming metal borohydride $\text{M}_n(\text{BH}_4)_m$ and alkali metal halide (AX) as final products [1]. However, while milling process, 1) bimetallic borohydrides (alkaline or alkaline earth and transition metals with a formula of $[\text{M}^{m+}(\text{M}')^{n+}(\text{BH}_4)_{m+n}]$, 2) anion substituted borohydrides $[\text{M}(\text{BH}_4)_{1-x}\text{H}_x]$ and 3) mixed cation-mixed anion borohydrides ($\text{MM}(\text{BH}_4)\text{H}$) can form in different cases [1, 2].

Bimetallic borohydride formation will occur between alkali metal borohydride and metal halide by combination of two reactions, metathesis and addition reactions, which M is typically an alkali metal and M' is a transition metal [1, 3]. $\text{ZnCl}_2\text{-MBH}_4$ ($\text{M}=\text{Li, Na and K}$) system is a good example for formation bimetallic borohydrides. This system is shown that different composition of reactants

can give completely different products. Ball milling $\text{ZnCl}_2\text{:LiBH}_4$ and $\text{ZnCl}_2\text{:NaBH}_4$ with 1:2.5 ratio gives $\text{LiZn}_2(\text{BH}_4)_5$ and $\text{NaZn}_2(\text{BH}_4)_5$, respectively while ball milling $\text{ZnCl}_2\text{:NaBH}_4$ in 1:3 ratio will result in formation of $\text{NaZn}(\text{BH}_4)_3$ [4]. There are many other examples of bimetallic borohydrides such as $\text{MSc}(\text{BH}_4)_4$ ($\text{M}=\text{Li}$ and Na) [5-7], $\text{LiK}(\text{BH}_4)_2$ [8] and $\text{K}_2\text{Mn}(\text{BH}_4)_4$ [9] can be found in the literature. Moreover, structure resemblance in $\text{Mn}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ also causes Mg substitution into $\text{Mn}(\text{BH}_4)_2$ and from a bimetallic compound, $\text{Mg}_x\text{Mn}_{(1-x)}(\text{BH}_4)_2$ ($x=0-0.8$) [2]. Ball milling can also lead to metal halide dissolution in metal borohydride. It is reported that 10 mole% of LiCl can be dissolved in LiBH_4 and form a $\text{Li}(\text{BH}_4)_{1-x}\text{Cl}_x$ compound [10, 11]. This anion substitution can also be seen after ball milling of other metal borohydride-halide systems such as $\text{LiBH}_4\text{-LiX}$ ($\text{X}=\text{Br}$ and I) [12, 13], $\text{CaBH}_4\text{-CaX}$ ($\text{X}=\text{F}$, Cl and I) and $\text{NaBH}_4\text{-NaCl}$ [14, 15]. Mixed cation-mixed anion borohydrides are also reported to form during ball milling. Ball milling mixtures of $\text{ZnCl}_2\text{:KBH}_4$ in 1:1 ratio and $\text{YCl}_3\text{:NaBH}_4$ in 2:1 ratio and combination of ball mill and heat treatment for the mixture of $\text{MCl}_3\text{:LiBH}_4$ ($\text{M}=\text{La}$, Gd and Ce) in 1:3 ratio lead to pure product of $\text{KZn}(\text{BH}_4)\text{Cl}_2$ [16] and $\text{NaY}(\text{BH}_4)_2\text{Cl}_2$ [17, 18] $\text{LiM}(\text{BH}_4)_3\text{Cl}$ ($\text{M}=\text{La}$, Gd and Ce) [19], respectively.

Although substitution at cation and/or anion sites is not favorable to obtain pure borohydrides, formation of complex borohydrides are one of the way of tuning hydrogen storage properties of metal borohydrides which will be discussed in following paragraphs [3, 8, 12-16, 20-22].

The phase stability of metal borohydride $[\text{M}(\text{BH}_4)_n]$ is proved to be related to charge transfer from M^{n+} to $[\text{BH}_4]^-$. Moreover, enthalpy of formation of metal borohydrides is calculated to have a linear relationship with Pauling electronegativity (X_p) (See Fig.3.1.) of M which is closely corresponded with thermal decomposition temperature (T_d). T_d decreases with increasing value of electronegativity [23, 24]. Therefore, development of mixed cation metal borohydride with different Pauling electronegativity is good approach to tuning stability of them. On the other hand, the alkali metal borohydrides (e.g. LiBH_4 , NaBH_4 , KBH_4 , RbBH_4) reveal highly ionic M-BH_4 bonding due to their low electronegativity leads to complete charge transfer from the metal to BH_4 group. This intrinsic property leads to stability of $\text{M}(\text{BH}_4)_2$ and higher thermal decomposition temperatures in this series of borohydrides [1, 8, 24, 25]. In contrast, alkaline earth and transition

metals borohydride exhibit directionality and some degree of covalency in M-BH₄ bonding due to their higher electronegativity. As a result, charge transfer from the metal atom to BH₄ group is less and this leads to destabilization of these units [1]. In bimetallic borohydrides case, introducing alkaline earth and transition metals into alkaline metal borohydride will suppress charge transfer due to higher electronegativity of substituted metal and reduce metal coordination to borohydride and leads to lower decomposition temperature [24]. However, the decomposition temperature for these compounds are almost the average of two component stemming from average electronegativity of MM' in [M^{m+}(M')ⁿ⁺(BH₄)_{m+n}] [1, 8, 21, 23, 24].

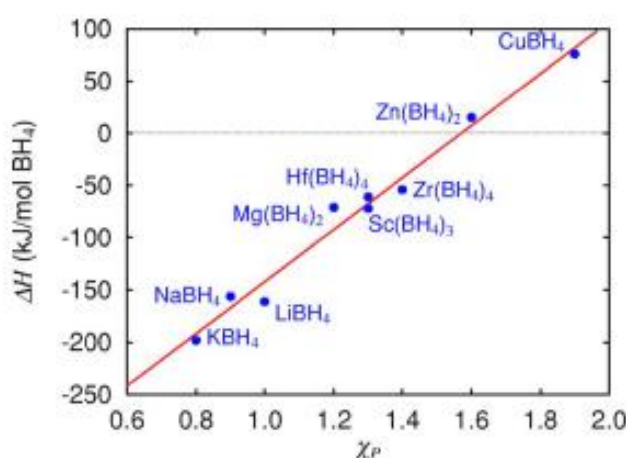


Fig.3.1 Relation between enthalpy of formation [M(BH₄)_n] and Pauling electronegativity, χ_P [23, 26].

Anion substitution is also another pathway to destabilize metal borohydride for solid state hydrogen storage. The idea is came from the work which is reported that stability of Na₃AlH₆ can be reduced by partial substitution of H atoms with F [27]. This might be because of this fact that partial substitution of an element with more electronegative element can change the bond strength of remaining elements and it may decrease T_d [28]. A similar approach has tried for substitution of [BH₄]⁻ with other halides. According to the anion size order, I⁻ (2.20 Å) > BH₄⁻ (2.05 Å) > Br⁻ (1.96 Å) > Cl⁻ (1.81 Å), substitution can tune unit cell volume, internal pressure and physical properties of borohydrides [1, 19, 22, 29]. First anion substitution is reported in the system of LiBH₄-LiCl which borohydride anion is partially replaced with chloride anion after ball milling

and substitution continued readily at higher temperature [10, 11]. Soon thereafter, many anion substitutions have been reported as a result of ball milling following with heat treatment, e.g. $\text{LiBH}_4\text{-LiX}$ ($X = \text{Br, I}$) [12, 13], $\text{NaBH}_4\text{-NaCl}$ [14, 15], $\text{Ca(BH}_4)_2\text{-CaX}$ ($X = \text{F, Cl, Br, I}$) (substitution is only observed with Cl^- and I^-) [30-32] and $\text{Mg(BH}_4)_2\text{-MgX}$ ($X = \text{Cl, Br}$) [28]. The common comment in all above studies, was that anion substitution with halide tends to stabilize the borohydride, leading to hydrogen release at higher temperature. However, rehydrogenation occurs more readily than pure borohydride [22].

Considering these findings, three different categories in the structural chemistry and similarity of metal borohydride-halide can be found to describe anion substitution which are as follow:

- 1) If a compound has a smaller anion than the other material, the former tends to dissolve in latter one while the structure will preserve. As a result, unit cell volume will decrease and lattice energy will increase [19, 22].
- 2) Some polymorphs of metal borohydrides are more prone to anion substitution, especially at higher temperatures such as h-LiBH_4 [11], $\beta\text{-Mg(BH}_4)_2$ [28] and $\beta\text{-Ca(BH}_4)_2$ [32].
- 3) If two compounds are isostructural, such as in the case of NaBH_4 and NaCl(Br) , then the anion substitution will happen at both halide and borohydride sites which leads to two solid solution compound [19, 22]. Systems obeying this rules are $(\text{h-LiBH}_4)\text{-}(\beta\text{-LiI})$, $(\text{h-LiBH}_4)\text{-}(\beta\text{-LiBr})$, $(\beta\text{-Ca(BH}_4)_2)\text{-}(\text{HT-CaCl}_2)$ and $\text{NaBH}_4\text{-NaCl}$.

While synthesizing $\text{Mg(BH}_4)_2$ from NaBH_4 and MgBr_2 or MgCl_2 the ball milled mixtures and left over residues in the thimble, whose peak position in PXRD were clearly shifted with respect to those of pure NaBH_4 or NaBr . For a deeper understanding of this phenomena we decided to investigate these new phase formation while synthesizing $\text{Mg(BH}_4)_2$ more systematically.

3.2 Experimental Procedure

Two main synthesis methods (ball milling and in autoclave mixing) were used to prepare $\text{Mg(BH}_4)_2$, coupled with three different approaches which were chosen to investigate possible formation of $\text{NaBr}_{1-x}(\text{BH}_4)_x$ and/or $\text{Na(BH}_4)_{1-y}\text{Br}_y$ solid solutions. various milling speeds, time and

reactant ratios are used for sample preparations by ball milling and various temperatures, time and reactant ratios for mixtures prepared in Autoclave. Procedures are given below:

➤ **Ball mill**

- 1) *Effect of milling time on solid solution* is investigated based on reaction (2.11). Mixture of $n \text{ MgBr}_2 + m \text{ NaBH}_4$ were milled for 3, 6, 12 and 24 h at 500 rpm using ratios of 2:1, 1:1 and 1:10. The milling took place in P7 planetary ball mill with 80 ml stainless vials using 10 mm stainless steel balls (ball to powder 20:1). The milling process is divided into shorter periods (15min) separated by cooling breaks (15min) to avoid excessive heating.
- 2) *Effect of mill milling speed on solid solution formation* is investigated based on reaction (2.11). Mixture of $n \text{ MgBr}_2 + m \text{ NaBH}_4$ were milled at 250, 500 and 750 rpm using $n:m$ ratios of 1:3 and 1:6 for 24 h. The milling device and characterization is selected as same as previous procedure.
- 3) *Effect of reactant ratios on solid solution* is explored based reaction (2.11). Mixture of $n \text{ MgBr}_2 + m \text{ NaBH}_4$ were ball milled using different $n:m$ ratios (2:1, 1:1, 1:2, 1:3, 1:6, 1:8, 1:10) at for 24h at 500 rpm and for 12 and 24 h at 250 rpm. The milling device and characterization is selected as same as previous procedure.

➤ **Autoclave**

- 1) *Effect of time on anion substitution* is investigated based reaction (2.11). Mixture of $n \text{ MgBr}_2 + m \text{ NaBH}_4$ were mixed for 3, 6, 12 and 24 h using 1:4 ratio in Autoclave at 100 °C using diethyl ether as a mixing medium. The mixing speed was set to 1000 rpm and it is happen under Ar atmosphere.
- 2) *Effect of temperature on anion substitution* is explored based reaction (2.11). Above mixture is mixed for 6 h using 1:4 ratio at 100 and 150 °C. All other parameters (stirring speed, medium and atmosphere) were as above.
- 3) *Effect of reactant ratios on anion substitution* is researched based reaction (2.11). Above blend is mixed for 24 h at 100 °C using 1:4 and 1:2.5 ratios with fixed stirring parameter and environment.

All samples were analyzed by X-ray powder diffraction (XRPD). XRPDs were recorded with a BRUKER D8 Phaser diffractometer (Cu K α radiation with VANTEC-1 detector). ATR-FTIR spectroscopy has done using Thermo Scientific iS10 FT-IR single reflection equipped with diamond ATR in the 650-4000 cm⁻¹ with 4 cm⁻¹ resolution.

3.3 Result and Discussion

3.3.1 Effect of milling time on solid solution

Effect of milling time at different n:m ratios (2:1, 1:1 and 1:10) on changing products and extend of solid solution is investigated at 500 rpm. XRD pattern of mixture with 2:1 ratio (MgBr₂ in excess) is shown in Fig.3.2. Due to excess amount of MgBr₂ the dominant compound in all milling times is MgBr₂. However, MgBr₂ peaks intensity is more pronounced in the sample milled for 3 h and peaks related to NaBr are less intense. Moreover, all reflection related MgBr₂ are broad due to lower crystallinity. In all other mixtures the intensity ratio is almost unchanged. Based on the PXRD pattern in Fig.3.2 b, BH₄⁻ substitution has occurred in NaBr and the mixed phase NaBr_{1-x}(BH₄)_x is formed while the overall composition is maintained for all mixtures.

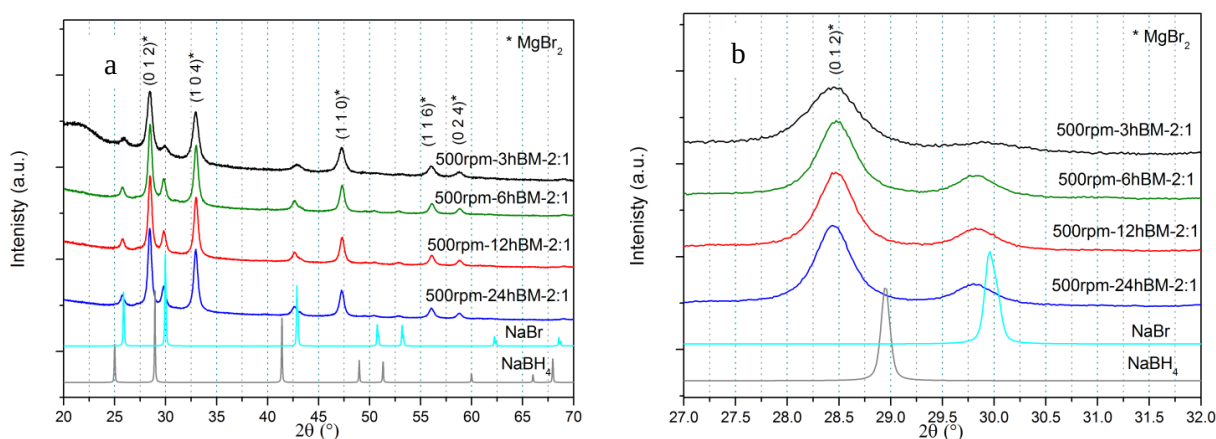


Fig.3.2 XRD pattern of mixture ball milled at 3, 6, 12 and 24 h using 500 rpm with 2:1 ratio of MgBr₂:NaBH₄ a) whole range b) 200 reflection.

For the second series, XRD pattern of the mixture with 1:1 n:m ratio (same ratio of MgBr_2 and NaBH_4) is plotted in Fig.3.3. One can see that MgBr_2 peak intensity has decreased continuously from specimen milled for 3 h down to 24 h which is the sign of progress reaction (2.11). Furthermore, based on Fig.3.3 b the peak position for the (200) reflection did not change along with increasing milling time which is the indication solid solution formation ($\text{NaBr}_{1-x}(\text{BH}_4)_x$) with almost same composition (almost fixed x for all sample).

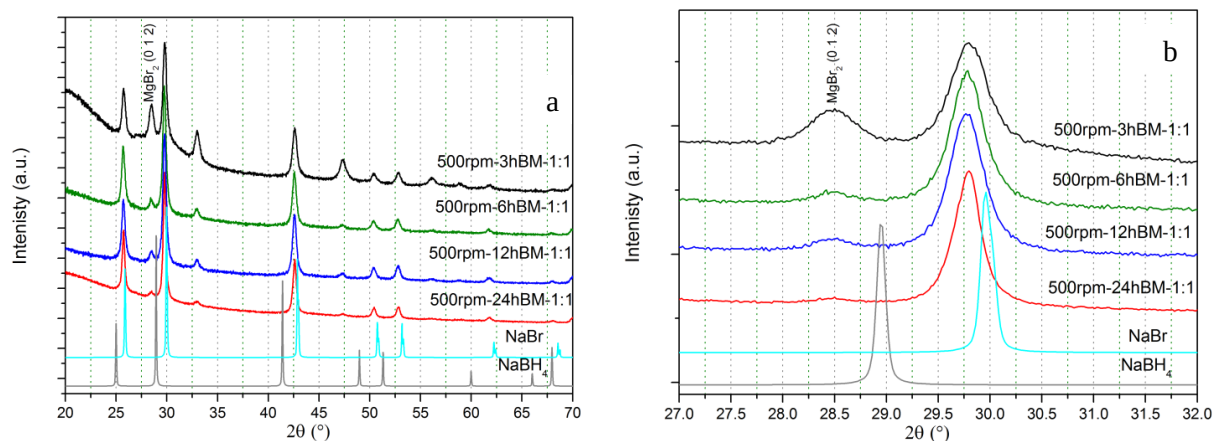


Fig.3.3 XRD pattern mixture ball milled at 3, 6, 12 and 24 h using 500 rpm with 1:1 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 200 reflection

For the third series, XRD pattern of mixture with 1:10 n:m ratio (NaBH_4 in excess) is shown in Fig.3.4. indicating that only reflections related to product of mixture based on reaction (2.11). In addition, the samples reveal beside the main peaks a weak accompanying bump whose intensity is decreasing by increasing milling time. However, although peak positions did not alter by milling time, all peaks are shifted towards NaBH_4 which is a clear evidence for solid solution formation. Moreover, the disappearance of the bump can be interpreted as formation of more uniform solid solution by increasing milling time. This phenomenon can also be seen in other n:m ratios. In other words, the more milling time the more uniform is phase formation and, thus, the narrower the Bragg peaks.

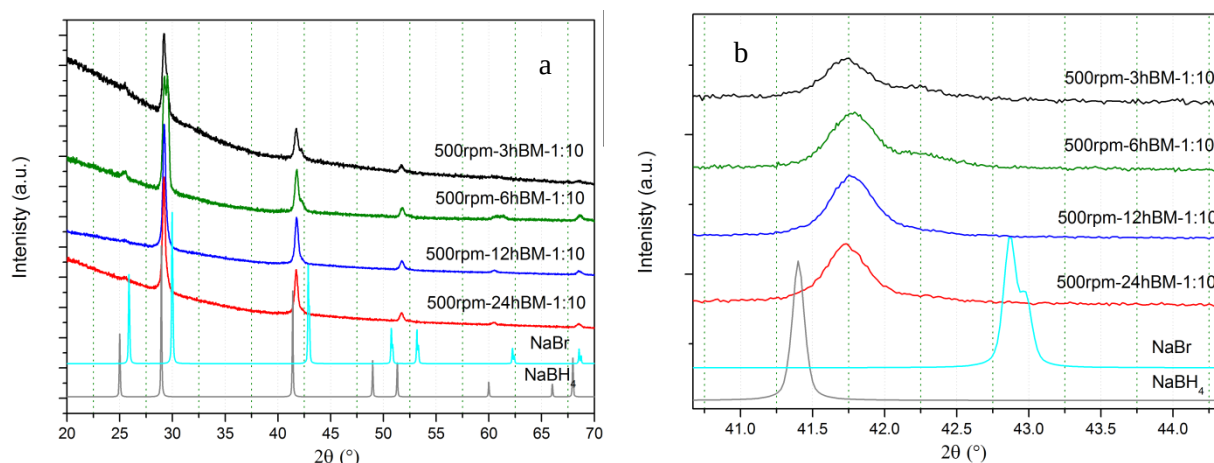


Fig.3.4 XRD pattern mixture ball milled at 3, 6, 12 and 24 h using 500 rpm with 1:10 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 220 reflection.

3.3.2 Effect of ball mill speed on substitution

Effect of milling at different speeds (250, 500 and 750 rpm) on solid solution formation is discussed as follows for n:m ratio of 1:3 and 1:6. XRD pattern in Fig.3.5, demonstrates the quality of XRD pattern as well, as the crystallinity of mixtures milled at 250 rpm are lower than the other two series. It is known that high-energy ball milling causes various defects including cracks, dislocations, pores, new surfaces, grain, vacancies and others. These defects will increase free energy of crystalline phase and demolish crystallinity of the material turning them to semi-crystalline or amorphous material [34, 35]. On the other hand, increasing temperature of milling is easily possible in planetary ball mill which is an important parameter to be considered and which can determine and alter the process and the product. For instance, ball temperature at milling rate of 280 rpm using 100 balls (12.7 mm) were measured to be 110 °C, 150 °C and 180 °C after 5 min, 10 min and 15min, respectively [36]. As a result, lower milling temperature (lower heat generation while milling) will favor amorphization. In this case, nanocrystalline structure will form more rapidly and defect recovery would be less lead all together to an amorphous (or a nanocrystalline) phase [35]. Thus, seeing more broad and diffuse peaks at 250 rpm (Fig.3.5) is based on above-mentioned tribochemical effects. Moreover, seeing sharper peaks in the samples

being milled at 500 rpm and 750 rpm are stemming from the fact that heat generated during the milling was high enough to induce recrystallization.

The other point that can be deduced from Fig.3.5, is that all peaks in all milling speeds are shifted and located between the original peaks of NaBH_4 and NaBr . This shift is more toward lower angles for higher n:m ratio (1:6) in comparison to lower n:m ratio (1:3). The trend can be best explained by solid solution formation. The (220) reflection is shifting towards lower 2 theta angle, clearly indicating of partial substitution of BH_4^- in the NaBr structure. The effective ionic radius of the borohydride anion is only slightly larger (230 pm) than that of bromide (195 pm), giving favor to a mutual substitution of the two species in the respective structures. As a result NaBr is no more a pure compounds but a mixed phase and can be written as $\text{NaBr}_{1-x}(\text{BH}_4)_x$. It is also seen that, amount of shifting is same for specific n:m ratio in different ball mill speeds. This means that ball mill speed will affect neither the chemical composition of the solid solution nor the extend of the anionic substitution. The mixture with 1:3 ratio and milled at 250 rpm (Fig. 3.5) shows an interesting exemption since the XRD peak is very broad and the position is the very close to NaBr . This finding indicates that this peak may not represent only one specific solid solution but containing also NaBr and/or a further solid solution with another composition. Therefore, here having broad peak can be both related to decrease in crystallinity as it is mentioned above and extended degree of substitution [14] or to presence of multiple mixed phases. From Fig.3.5 one can also see that intensity of (111) and (311) reflections are decreasing by increasing NaBH_4 ratio. This shows also the formation of a new phase (solid solution formation) exhibiting different bragg reflection intensities.

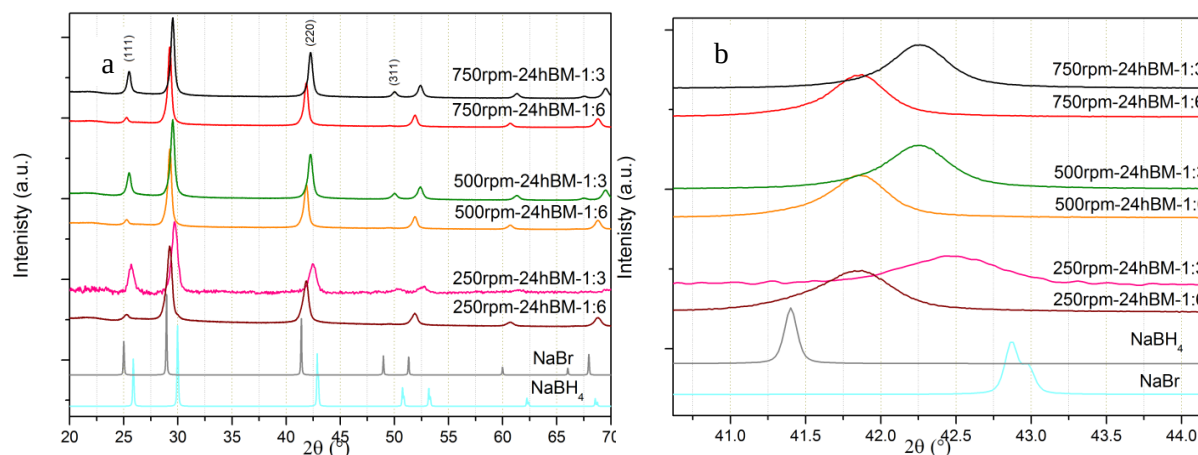


Fig.3.5 XRD pattern of ball milled mixture using 750, 500 and 250 rpm with 1:3 and 1:6 ratio of $\text{MgBr}_2\text{:NaBH}_4$ a) whole range b) 220 reflection.

In order to study the changes in vibrational characteristic of the mixtures, ATR-FTIR spectroscopy was done on all ball milled samples. In idealized case, the free BH_4^- has the tetrahedral symmetry T_d , however in the crystalline state, the free symmetry is generally reduced to a lower “site symmetry” and as a consequence the triple and double degenerate F and E vibrational modes may splitted and all modes became active both in Raman and IR. For BH_4^- symmetric stretching can be observed only in Raman and therefore the peaks detected at 2395, 2283 and 2218 cm^{-1} in the IR spectrum are resulting from antisymmetric (B–H) stretching mode (ν_3) which splits into three bands. (ν_4) bending mode is also IR active and will appear at 1110 cm^{-1} [12, 37, 38]. In general, the symmetry reduction gives rise to an increase number of bands due to above mentioned symmetry effects. However, in $\text{Mg}(\text{BH}_4)_2$, in which the BH_4 groups possess the lowest possible site symmetry (C_1) the IR spectrum shows only one unpatterned (i.e. unsplit) peak which cannot be related to any symmetry effect but to low crystallinity of the compound $\text{Mg}(\text{BH}_4)_2$. Due to dominance of the broad band caused by the poor sample crystallinity all splitting effects are completely obscured.

According to Fig.3.6, two main IR absorption bands for B-H stretching (2400-2200 cm^{-1} range) and B-H bending (between 1300-1000 cm^{-1} range) [13-15, 28] are observed in all mixtures which

show a blue shift with respect to those for NaBH_4 . The shift is less for 1:6 ratio in comparison to 1:3 for regarding that both blends were milled at 750 and 500 rpm. However, in the mixture milled at 250 rpm, the blue shifts are same for both n:m ratios and for 1:6 ratio samples in other mixtures. This indicates that solid solution formed in 250 rpm milled samples has similar structural environment as in pure NaBH_4 . Fig.3.6 is also illustrates that formation of $\text{Mg}(\text{BH}_4)_2$ is taking place in all mixtures with 1:3 ratio as B-H bending mode (ν_4) $\sim 1250 \text{ cm}^{-1}$ is present in all of them. This frequency is almost vanished at 1:6 ratio due to loss of the dominance of NaBH_4 structure. The mentioned shifts originate from Br^- substitution at the BH_4 sites leading to change in the structural environment which restricts the B-H vibration in NaBH_4 . As a result, energy of B-H bonds are increasing and shifting to higher wavenumbers.

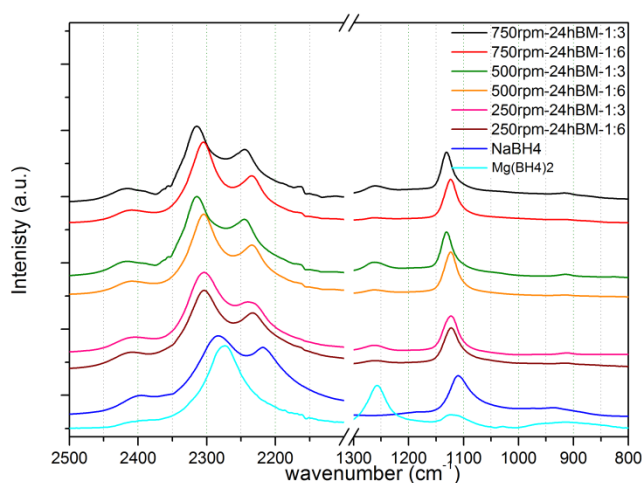


Fig.3.6 ATR-FTIR spectrum of ball milled mixture using 750, 500 and 250 rpm with 1:3 and 1:6 ratio of NaBH_4 : MgBr_2 [36].

3.3.3 Effect of reactant ratio on substitution using ball milling

Effect of starting material ratio (n:m) at ball mill speeds of 250 and 500 rpm and in two different milling times (12 h and 24 h) on anion substitution is investigated using XRD analysis shown in Fig.3.7. Based on Fig.3.7 a the progress of reaction can clearly be followed by increase of n:m ratio. For samples of 2:1, 1:1 and 1:2 ratios MgBr_2 is still present in the pattern while for the rest no MgBr_2 peaks could be detected. Moreover, (111) and (311) reflections show a distinct loss of

in intensity by increasing n:m ratio and are practically disappeared in 1:10 specimen which is consistent with discussion in the section 1.3.3. Furthermore, for the milled mixture 1:8 ratio all Bragg reflections are splitted to duplets which is an indication for the presence of at least two different solid solutions. However, these two compounds are again merged in the 1:10 blend. Fig.3.7 b illustrate XRD pattern of left over material after purification. The trend is similar to milled samples before purification. For the sample 1:8 the peaks are not split like the milled one which is an indication of the merging of the different mixed components under one broad peak. It should be noted that XRD pattern of left over materials (compound left in the thimble after purification) for 2:1 and 1:1 did not shown as MgBr_2 were the dominant compound and Eq.2.8 did not proceed completely.

A close examination of Fig.3.7, shows that the peak positions in XRD undergo a shift towards NaBH_4 by increasing n:m ratio. This phenomenon has also been observed and discussed in the section 1.3.3. XRD pattern of (200) reflection for all mixtures are shown in Fig.3.8 for better visualization of the peak shifting. As was mentioned in section 1.3.3, reflections are shifting toward NaBH_4 for all blends by increasing n:m ratio, the trend is practically the same for both ball milled blend and left over after purification sample. However, the (200) reflection for the left over sample in the thimble for all ratios is shifted less toward NaBH_4 than that in ball milled mixture. This is very like due to the heat treating process is taking place during the purification. While Soxhlet extraction of $\text{Mg}(\text{BH}_4)_2$ with warm diethyl ether, the solid product obtained from the ball milling is continuously washed overnight which may enhance the diffusion of Br^- into NaBH_4 structure and activating the formation of the mixed phase $\text{Na}(\text{BH}_4)_{1-y}\text{Br}_y$. In other words, formation of Br^- -rich solid solutions is favored in the left over mixture after purification. For instance, emergence of pure NaBr 200 reflection in the left over sample at 1:2 ratio would be the witness of this statement.

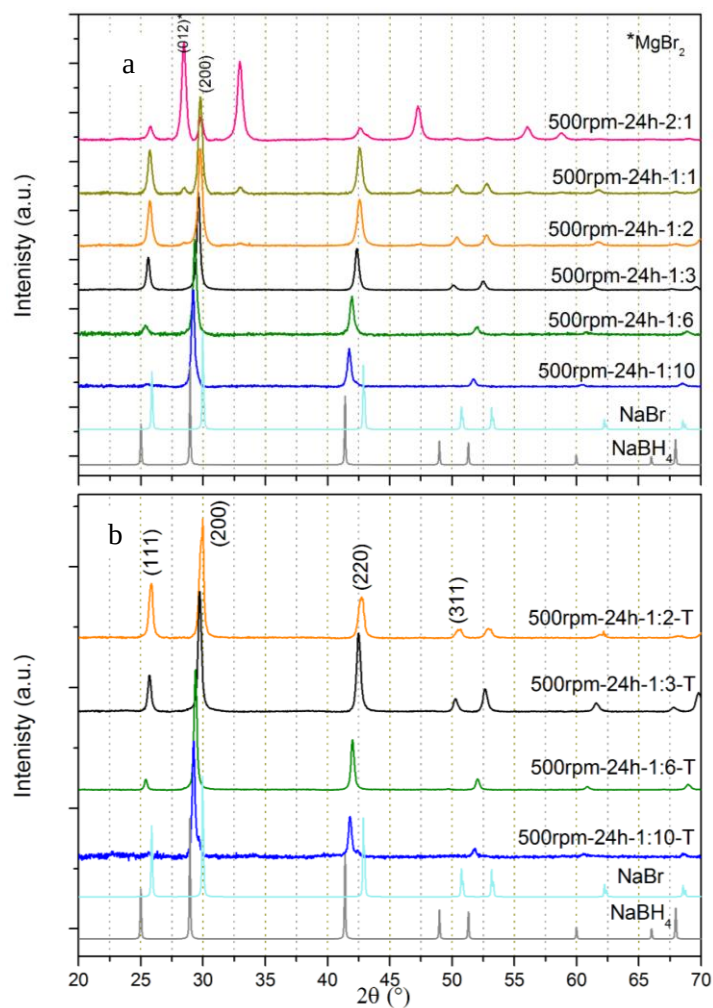


Fig.3.7 XRD patterns of a) ball milled and b) residue in the thimble after purification mixtures in different $\text{NaBH}_4:\text{MgBr}_2$ ratios using 500 rpm and 24 h milling time.

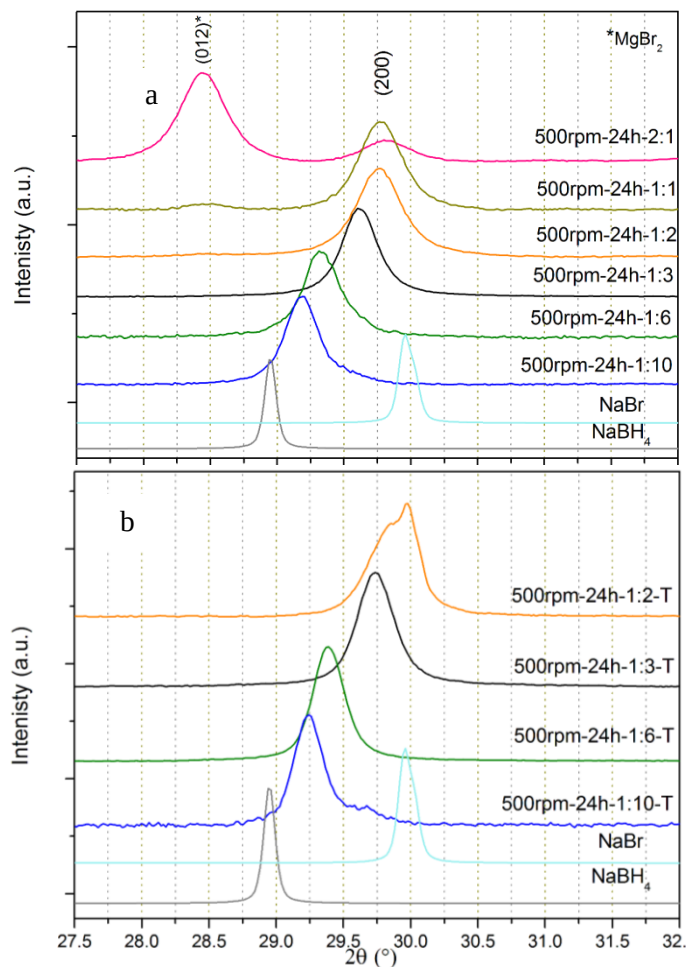


Fig.3.8 XRD patterns of 200 reflection a) ball milled and b) residue in the thimble after purification mixtures in different NaBH₄:MgBr₂ ratios using 500 rpm and 24 h milling time.

For investigating the direction of substitution in NaBH₄ and NaBr, mixtures with different n:m ratios are ball milled using lower milling speed (250 rpm) small time interval (5 min mill 5 min pause) to keep temperature as low as possible to achieve a clear distinction between the effect of milling and heat treating on formation of solid solution. The ball milled sample after 12 and 24 h, as well as left over material in the thimble are examined by XRD and results are plotted in Fig.3.9. The result depicted in Fig.3.9 a is showing the formation of mainly BH₄⁻ doped NaBr for mixture with 1:2 ratio while in all other ratios Br⁻ doped NaBH₄ is formed (Na(BH₄)_{1-y}Br_y). Interestingly,

$\text{Na}(\text{BH}_4)_{1-y}\text{Br}_y$ composition did not change over the range of all n:m ratios. This is also confirmed by the B-H stretches shown in Fig.3.10 and in Table 3.1. For all specimen, the B-H stretching and bending frequencies did not change even after 12 h ball milling time. This means that formation of solid solution contains different reaction/substitution steps and obtaining a more unified solid solution is time a dependent process. This can also be verified by the XRD pattern after 24 h ball milling shown in Fig.3.9 b. Mixtures milled for 24 h showed more unified pattern shifting toward lower degree by increasing NaBH_4 ratio. A trend which was also seen in the previous sections. FTIR-ATR spectra of 24 milled samples are also in consistent with XRD results. The higher the content of NaBH_4 in the mixture, the less blue shift in B-H stretching and bending is observed with respect to pure NaBH_4 . For the samples remained in the thimble after purification (see Fig.3.9 c), formation of Br^- rich mixtures are also occurred as it was seen for specimen milled at 500 rpm.

Table 3.1 Absorption bond frequencies for B-H stretching and bending in ball milled mixtures milled for 12 h and 24 h at 250 rpm at $\text{NaBH}_4\text{:MgBr}_2$ ratio of 1:3, 1:6 and 1:8

Sample	250rpm-12h			250rpm-12h			NaBH_4
ratio	1:3	1:6	1:8	1:3	1:6	1:8	-
B-H AS (ν_3)	2402	2402	2401	2404	2402	2395	2395
B-H AS (ν_3)	2297	2295	2298	2304	2302	2283	2283
B-H AS (ν_3)	2224	2224	2226	2240	2233	2218	2218
B-H B (ν_4)	1117	1119	1117	1125	1122	1110	1110
B-H B (ν_2)	-	-	-	1267	-	-	-

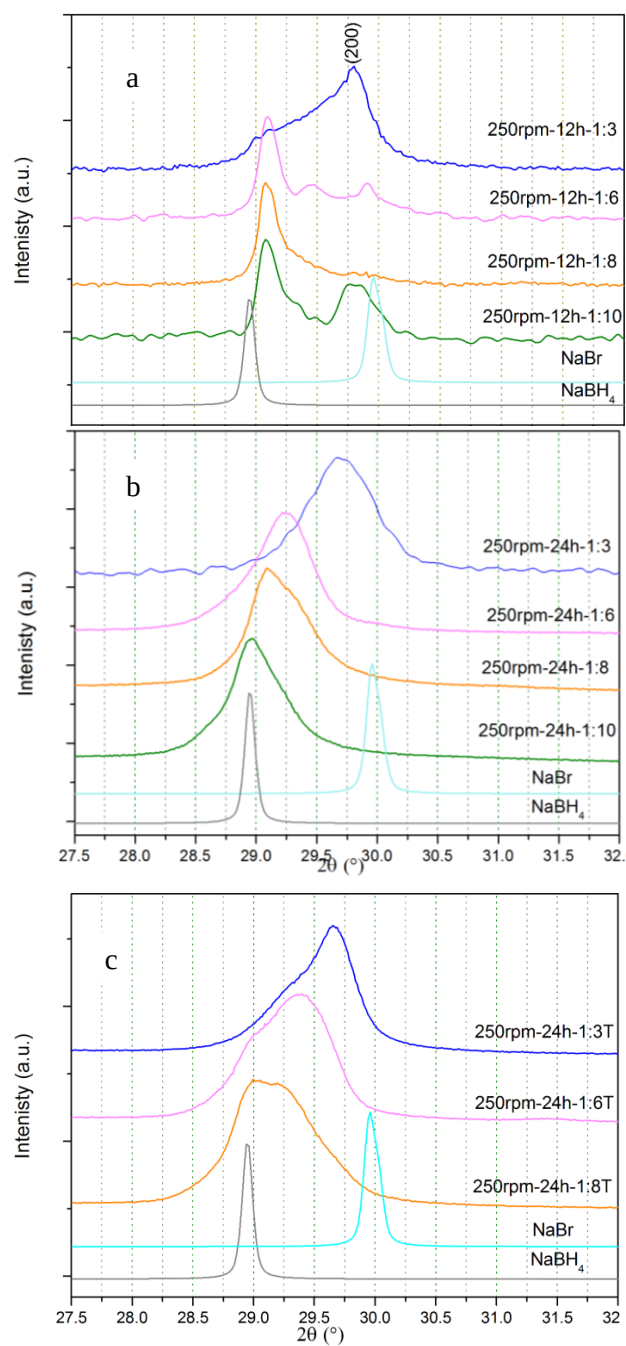


Fig.3.9 XRD pattern 200 reflection of ball milled mixture at 250 rpm in different $\text{NaBH}_4\text{:MgBr}_2$ ratios for a) 12 h milling time b) 24 h milling time c) left over sample in the thimble after purification.

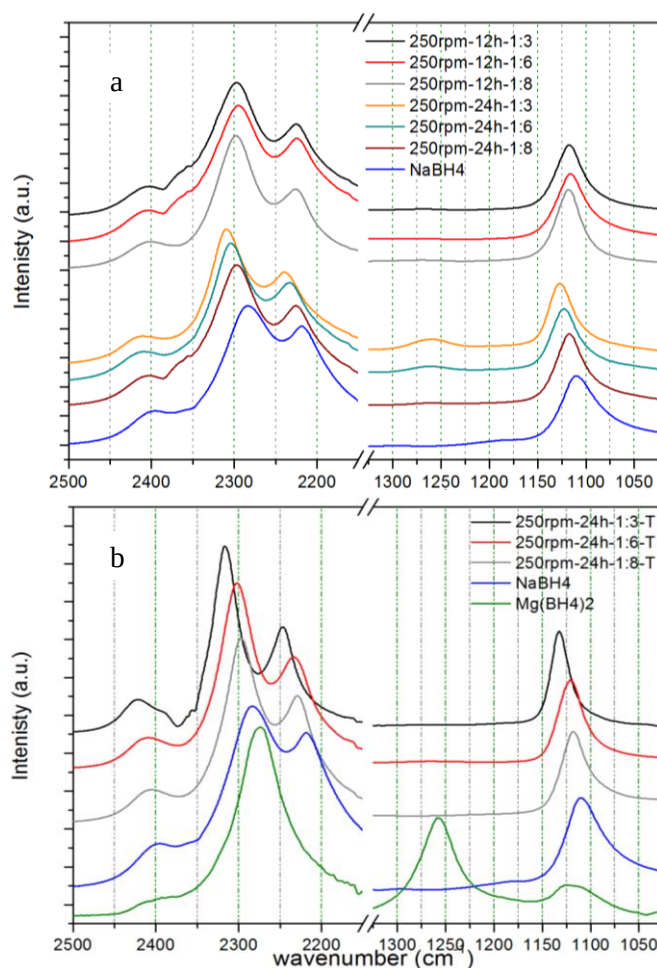


Fig.3.10 ATR-FTIR Spectrum of different $\text{NaBH}_4\text{:MgBr}_2$ mixtures a) ball milled at 250 rpm for 12 h and 24 h and b) residue in the thimble after purification of milled mixtures in different ratios using 250 rpm and 24 h milling time.

In order to investigate effect of heat treatment on the extend of substitution in both NaBH_4 and or NaBr samples which were milled at 250 rpm for 12 and 24 h using n:m ratio of 1:8 and heat treated for 12 and 24 h. The results are depicted in Fig.3.11 showing that peak position for (200) reflection is shifting toward NaBr by increasing heat treating procedure from 12 h to 24 h (Fig. 3.11 a). This finding can confirm the statement of the previous discussion that NaBr rich compositions are preferably forming by heat treatment while ball milling would activate NaBH_4

rich compounds. It can also be seen that the broad peak is getting narrower by increasing time of heating which is compatible with the fact that heat treatment contributes to formation of more unified solid solutions with passing time. Fig.3.11 b and Table 3. are also in consistence with mentioned statement. More Br^- substituted in NaBH_4 (more Br^- are replaced in BH_4^- anion sites) shift absorption bond of B-H toward higher wavenumbers. However, this shifting is only slightly. This can be described by the low symmetry of BH_4^- in pure and Br^- substituted $\text{Na}(\text{BH}_4)_{1-y}\text{Br}_y$ crystal which does not cause a notable change in bond frequencies [39]. All above findings are summarized in the Table 3.3.

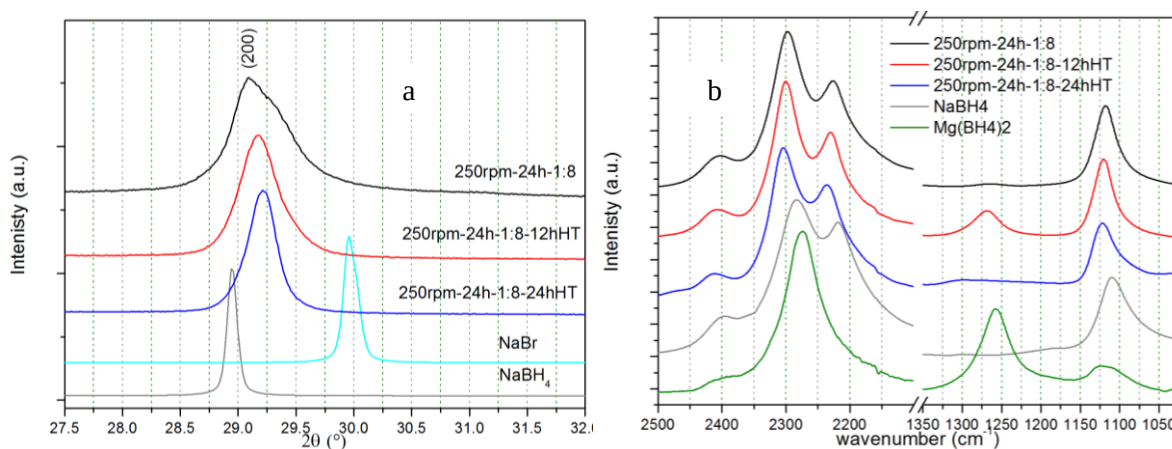


Fig.3.11 Sample with $\text{NaBH}_4\text{:MgBr}_2$ ratio of 1:8 a) XRD pattern of 200 reflection for 24 h milled, 24 h milled and heat treated at 200 °C for 12 h and 24 h milled and heat treated at 200 °C for 24 h, b) ATR-FTIR spectrum of the same sample with the same milling and heat treating procedure.

Table 3.2 Absorption bond frequencies for B-H stretching and bending in ball milled and heat treated mixture milled at 250 rpm at $\text{NaBH}_4\text{:MgBr}_2$ ratio of 1:8

B-H	250rpm-24h-1:8	250rpm-24h-1:8-12hHT	250rpm-24h-1:8-24hHT	NaBH_4
AS (ν_3)	2402	2407	2410	2395
AS (ν_3)	2297	2300	2304	2283
AS (ν_3)	2225	2230	2235	2218
B (ν_2)	1266	1268	-	-
B (ν_4)	1118	1120	1121	1109

Table 3.3 Effect of increasing in ball mill time, speed, reactant ratio and annealing on the futures of mixture in the reaction of ($n \text{ MgBr}_2 + m \text{ NaBH}_4$)

			↑	
	Time	Speed	Reactant ratio (n:m)	Anneal
Progress in Reaction	↑	↑	–	NA
Uniformity in composition	↑	↑	NA	↑
Peak shifting	–	–	(toward NaBH_4)	(toward NaBr)
Crystallinity	NA	↑	–	↑

3.3.4 Effect of time, temperature and reactant ratio on anion substitution using autoclave

Based on experimental procedure in chapter 2, different synthesis routes for $\text{Mg}(\text{BH}_4)_2$ have been tested and tried, among others the autoclave technique. The first precursors used for this technique were NaBH_4 and MgBr_2 with diethyl ether as solvent. The synthesis of pure $\text{Mg}(\text{BH}_4)_2$ was, however, not successful due to contamination with Br^- which is confirmed by using XRF. In all series of reactions, the left over mixture in the thimble after purification ($\text{NaBH}_4 + \text{NaBr}$) was examined using XRD and ATR-FTIR in order to investigate the extend of substitution and solid solution formation.

Effect of mixing time in the Autoclave at specific temperature (100°C) using n:m ratio of 1:4 is studied and XRD result of left over materials is demonstrated in Fig.3.12. This results show after 3 h mixing time, a high amount of NaBH_4 remained unreacted while for other duration of mixing NaBH_4 is mostly consumed and (200) reflection – indicator of NaBr - is revealed. What we observed was shift of this reflection to lower 2theta angels indicating the BH_4^- substitution in NaBr . The Deviation in the position of the original and emerged peaks is pronounced by increasing mixing time. This means that longer mixing time will increase amount of “doped” BH_4^- in NaBr .

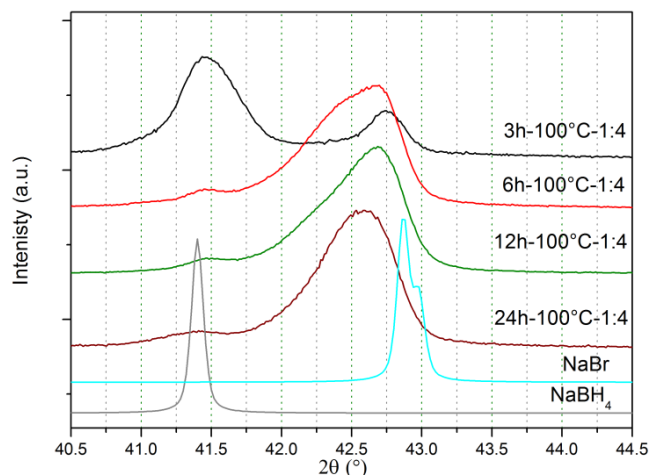


Fig.3.12 XRD pattern of 220 reflection for NaBH₄:MgBr₂ blend in 1:4 ratio mixed in Autoclave for 3 h, 6h, 12 h, 24 h at 100 °C.

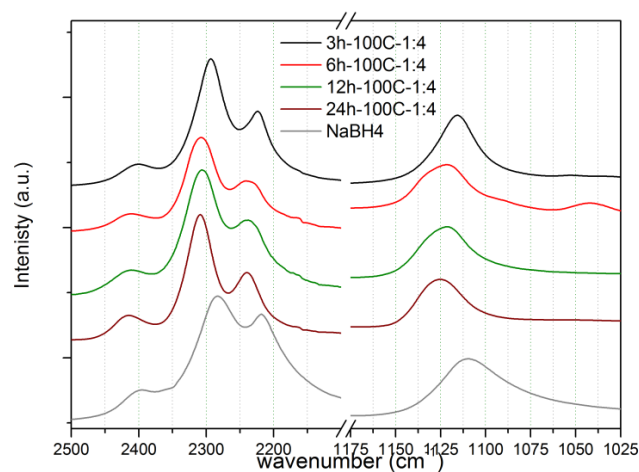


Fig.3.13 ATR-FTIR spectrum of NaBH₄:MgBr₂ blend in 1:4 ratio mixed in Autoclave for 3 h, 6h, 12 h, 24 h at 100 °C.

Based on ATR-FTIR results which is shown in Fig.3.13, B-H stretching and bending frequencies for the sample mixed for 3 h are very close to those for the pure NaBH₄. After 6 h to 24 h of mixing, the wavenumbers show a blue slight shift without changing in peak shape.

Impact of the synthesis temperature is also explored in 1:4 ratio mixing for 6 h in the temperature range of 100 and 150 °C. Based on the XRD diagram for (220) reflection (see

Fig.3.14), an increase in the mixing temperature will create a composition rich in BH_4 and shift the NaBr peak towards lower 2θ .

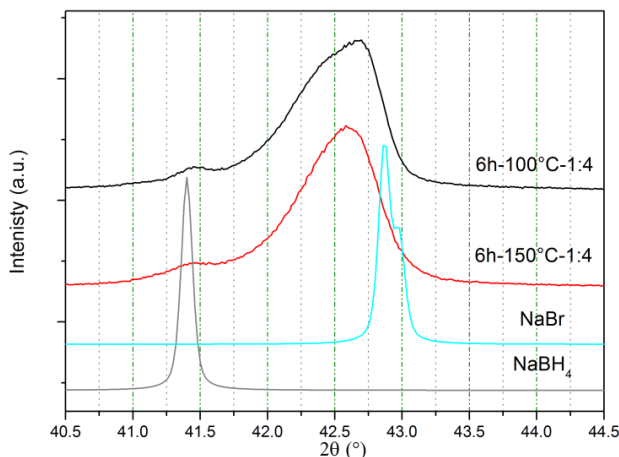


Fig.3.14 XRD pattern of 220 reflection for $\text{NaBH}_4\text{:MgBr}_2$ blend in 1:4 ratio mixed in autoclave for 6 h at temperatures of 100 °C and 150 °C.

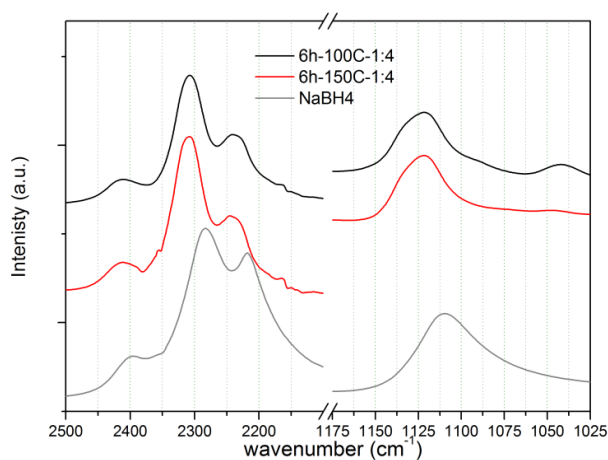


Fig.3.15 ATR-FTIR spectrum of $\text{NaBH}_4\text{:MgBr}_2$ blend in 1:4 ratio mixed in autoclave for 6 h at temperatures of 100 °C and 150 °C.

ATR-FTIR results is also shown in Fig.3.15 according to which the B-H absorptions for both mixtures are undergoing a blue shift compared to those in pure NaBH_4 . However, the observed shift is almost same for both specimens which illustrates that the Br^- substitution is not taking

place when the reaction temperature is raised. This provides a further evidence for the fact that heat treating favors rather the BH_4 substitution in NaBr and not vice versa.

Finally, the effect of the ratio of the educts on the extend of solid solution is investigated for 1:4 and 1:2.5 blends mixed in Autoclave at 100 °C for 24 h. It can be seen from Fig.3.16, that for 1:4 mixture the (220) reflection related to NaBH_4 is present while the main broad peak is shifted slightly towards NaBH_4 . This can be explained by the higher availability of BH_4^- anion which results in halide substitution in NaBr solid solution with a wide range of compositions.

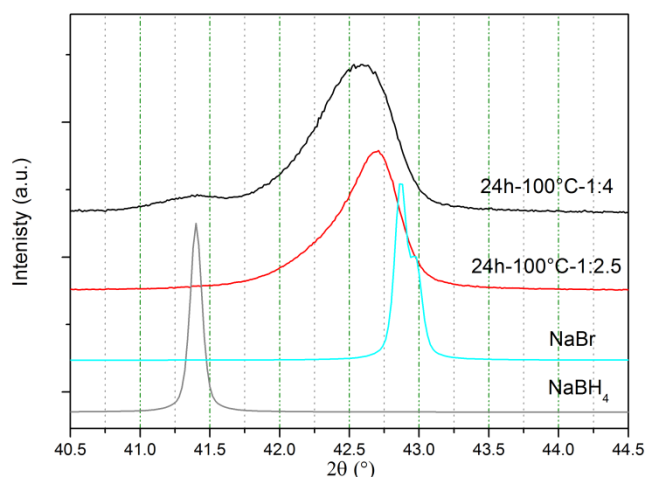


Fig.3.16 XRD pattern of $\text{NaBH}_4\text{:MgBr}_2$ blend mixed in Autoclave for 34 h at 100 °C in 1:2.5 and 1:4 ratios.

ATR-FTIR spectra of the two blends are shown in Fig.3.17. The wavenumbers of the B-H absorption in 1:2.5 sample is slightly more blue shifted than those in 1:4 specimen. The shifting is also related to the dominance of NaBH_4 in 1:4 blend.

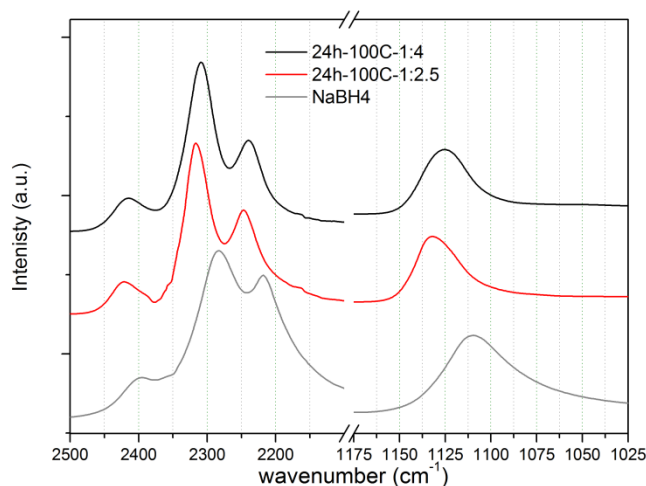


Fig.3.17 ATR-FTIR spectrum of NaBH₄:MgBr₂ blend mixed in Autoclave for 24 h at 100 °C in 1:2.5 and 1:4 ratios.

3.4 Conclusion

Magnesium borohydride which was synthesized by metathesis reaction of MgBr₂ and NaBH₄ is shown an interesting outcome. Results surprisingly were not only in formation of pure Mg(BH₄)₂ and NaBr but yielding also the mixed phases NaBr_{1-x}(BH₄)_x and/or Na(BH₄)_{1-y}Br_y, as consequence of solid solution formation. The effect of milling speeds, time and reactant ratios for sample prepared by ball milling and various temperatures, time and reactant ratios for mixtures prepared in autoclave are investigated in detail with respect to solid solution formation by XRPD and ATR-FTIR. It is found that NaBr_{1-x}(BH₄)_x and Na(BH₄)_{1-y}Br_y can be both activated by ball mill and they both can be presented in the final mixture. However, substitution of Br⁻ into NaBH₄ occurs faster than BH₄⁻ into NaBr. Moreover, increasing in the ball mill time and speed increase uniformity of final composition while only higher speed would responsible for higher crystallinity. Annealing is also beneficial to reach to uniform and well crystalline sample. In the case which Autoclave were used, increasing in time and temperature of mixing leads to more uniform compositions, however, increasing in reactant ratio gives a more complex composition. The most effective character for

peaks shifting was proved to be reactant ratios. Higher NaBH_4 ratios shift all XRPD reflections toward lower 2θ due to higher availability of BH_4^- anion.

3.5 References

1. Ravnsbæk, D.B., et al., *Powder diffraction methods for studies of borohydride-based energy storage materials*. Zeitschrift für Kristallographie, 2010. **225**(12): p. 557-569.
2. Černý, R., et al., *$\text{Mg}_x\text{Mn}(1-x)(\text{BH}_4)_2$ ($x=0-0.8$), a cation solid solution in a bimetallic borohydride*. Acta Materialia, 2011. **59**(13): p. 5171-5180.
3. Ravnsbæk, D.B. and T.R. Jensen, *Mechanism for reversible hydrogen storage in $\text{LiBH}_4\text{-Al}$* . Journal of Applied Physics, 2012. **111**(11): p. 112621.
4. Ravnsbæk, D., et al., *A series of mixed-metal borohydrides*. Angew Chem Int Ed Engl, 2009. **48**(36): p. 6659-63.
5. Hagemann, H., et al., *$\text{LiSc}(\text{BH}_4)_4$: a novel salt of Li^+ and discrete $\text{Sc}(\text{BH}_4)_4^-$ complex anions*. J Phys Chem A, 2008. **112**(33): p. 7551-5.
6. Radovan Cerny, D.B.R., Godwin Severa, Yaroslav Filinchuk, Vincenza D' Anna, Hans Hagemann, and J.S. Dörthe Haase, Craig M. Jensen and Torben R. Jensen, *Structure and Characterization of $\text{KSc}(\text{BH}_4)_4$* . The Journal of Physical Chemistry C, 2010. **114**: p. 19540-19549.
7. Radovan Černý, G.S., Dörthe B. Ravnsbæk, Yaroslav Filinchuk, Vincenza D'Anna, Hans Hagemann, Dörthe Haase, Craig M. Jensen and Torben R. Jensen, *$\text{NaSc}(\text{BH}_4)_4$: A Novel Scandium-Based Borohydride*. 2010. **114**: p. 1357-1364.
8. Nickels, E.A., Jones, M., David, William I. F., Johnson, Simon R., Lowton, Rebecca L., Sommariva, M. and Edwards, Peter P., *Tuning the Decomposition Temperature in Complex Hydrides: Synthesis of a Mixed Alkali Metal Borohydride*. Angew. Chem. Int. Ed., 2008. **47**: p. 2817-2819.
9. Liu, R. and D. Book, *Mn-based borohydride synthesized by ball-milling KBH_4 and MnCl_2 for hydrogen storage*. International Journal of Hydrogen Energy, 2014. **39**(5): p. 2194-2200.
10. Lene Mosegaard, B.M., Jens-Erik Jørgensen, Yaroslav Filinchuk, Yngve Cerenius, Jonathan C. Hanson, Elaine Dimasi, Flemming Besenbacher and Torben R. Jensen, *Reactivity of LiBH_4 : In Situ Synchrotron Radiation Powder X-ray Diffraction Study*. The Journal of Physical Chemistry C, 2008. **112**: p. 1299-1303.
11. Arnbjerg, L.M., et al., *Structure and Dynamics for $\text{LiBH}_4\text{-LiCl}$ Solid Solutions*. Chemistry of Materials, 2009. **21**(24): p. 5772-5782.
12. Rude, L.H., et al., *Bromide substitution in lithium borohydride, $\text{LiBH}_4\text{-LiBr}$* . International Journal of Hydrogen Energy, 2011. **36**(24): p. 15664-15672.
13. Rude, L.H., et al., *Iodide substitution in lithium borohydride, $\text{LiBH}_4\text{-LiI}$* . Journal of Alloys and Compounds, 2011. **509**(33): p. 8299-8305.
14. Ravnsbæk, D.B., L.H. Rude, and T.R. Jensen, *Chloride substitution in sodium borohydride*. Journal of Solid State Chemistry, 2011. **184**(7): p. 1858-1866.
15. Olsen, J.E., M.H. Sørby, and B.C. Hauback, *Chloride-substitution in sodium borohydride*. Journal of Alloys and Compounds, 2011. **509**(24): p. L228-L231.

16. Ravnsbaek, D.B., et al., *Mixed-Anion and Mixed-Cation Borohydride $KZn(BH_4)Cl_2$: Synthesis, Structure and Thermal Decomposition*. European Journal of Inorganic Chemistry, 2010. **2010**(11): p. 1608-1612.
17. Ravnsbæk, D.B., et al., *A mixed-cation mixed-anion borohydride $NaY(BH_4)2Cl_2$* . International Journal of Hydrogen Energy, 2012. **37**(10): p. 8428-8438.
18. Morten B. Ley, D.B.R., Yaroslav Filinchuk, Young-Su Lee, Raphaël Janot, Young Whan Cho, Jørgen Skibsted, and Torben R. Jensen, *$LiCe(BH_4)_3Cl$, a New Lithium-Ion Conductor and Hydrogen Storage Material with Isolated Tetranuclear Anionic Clusters*. Chem. Mater., 2012(24).
19. Huot, J., et al., *Mechanochemical synthesis of hydrogen storage materials*. Progress in Materials Science, 2013. **58**(1): p. 30-75.
20. Tomasz Jaron, P.A.O., Wojciech Wegner, Karol J. Fijałkowski, Piotr J. Leszczyn'ski, and Wojciech Grochala, *Hydrogen Storage Materials: Room-Temperature Wet-Chemistry Approach toward Mixed-Metal Borohydrides*. Angewandte Chemie International Edition, 2015. **54**: p. 1236-1239.
21. Filinchuk, Y., D. Chernyshov, and V. Dmitriev, *Light metal borohydrides: crystal structures and beyond*. Zeitschrift für Kristallographie, 2008. **223**(10): p. 649-659.
22. Ley, M.B., et al., *Complex hydrides for hydrogen storage – new perspectives*. Materials Today, 2014. **17**(3): p. 122-128.
23. Li, H.W., et al., *Materials designing of metal borohydrides: Viewpoints from thermodynamical stabilities*. Journal of Alloys and Compounds, 2007. **446-447**: p. 315-318.
24. Nakamori, Y., et al., *Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiments*. Physical Review B, 2006. **74**(4).
25. *Solid-state hydrogen storage Materials and chemistry*. 2008: Woodhead Publishing Limited and CRC Press LLC.
26. Nakamori, Y., et al., *Thermodynamical stabilities of metal-borohydrides*. Journal of Alloys and Compounds, 2007. **446-447**: p. 296-300.
27. Hendrik W. Brinks, A.F., and Bjørn C. Hauback, *Adjustment of the Stability of Complex Hydrides by Anion Substitution*. J Phys Chem C, 2008. **112**: p. 5658-5661.
28. Hino, S., et al., *Halide Substitution in Magnesium Borohydride*. The Journal of Physical Chemistry C, 2012. **116**(23): p. 12482-12488.
29. Filinchuk, Y. and H. Hagemann, *Structure and Properties of $NaBH_4 \cdot 2H_2O$ and $NaBH_4$* . European Journal of Inorganic Chemistry, 2008. **2008**(20): p. 3127-3133.
30. Rude, L.H., et al., *Anion Substitution in $Ca(BH_4)_2-CaI_2$: Synthesis, Structure and Stability of Three New Compounds*. The Journal of Physical Chemistry C, 2011. **115**(15): p. 7768-7777.
31. Lee, J.Y., et al., *Metal halide doped metal borohydrides for hydrogen storage: The case of $Ca(BH_4)_2-CaX_2$ ($X=F, Cl$) mixture*. Journal of Alloys and Compounds, 2010. **506**(2): p. 721-727.
32. Grove, H., et al., *Halide substitution in $Ca(BH_4)_2$* . RSC Adv., 2014. **4**(9): p. 4736-4742.
33. Llamas-Jansa, I., et al., *Chloride substitution induced by mechano-chemical reactions between $NaBH_4$ and transition metal chlorides*. Journal of Alloys and Compounds, 2012. **530**: p. 186-192.
34. Balema, V.P., *Mechanical Processing in Hydrogen Storage Research and Development*. Material Matters, 2007. **2**(2): p. 16-18.
35. Suryanarayana, C., *Mechanical alloying and milling*. Progress in Materials Science, 2001. **46**: p. 1-184.
36. Takacs, L. and J.S. McHenry, *Temperature of the milling balls in shaker and planetary mills*. Journal of Materials Science, 2006. **41**(16): p. 5246-5249.

37. Somer, M., et al., α - and β - $\text{Na}_2[\text{BH}_4][\text{NH}_2]$: Two modifications of a complex hydride in the system NaNH_2 – NaBH_4 ; syntheses, crystal structures, thermal analyses, mass and vibrational spectra. *Journal of Alloys and Compounds*, 2010. **491**(1-2): p. 98-105.
38. D'Anna, V., L.M. Lawson Daku, and H. Hagemann, *Vibrational spectra and structure of borohydrides*. *Journal of Alloys and Compounds*, 2013. **580**: p. S122-S124.
39. Zavorotynska, O., et al., *Theoretical and Experimental Study of LiBH_4 - LiCl Solid Solution*. *Crystals*, 2012. **2**(4): p. 144-158.

Chapter 4

Hydrogen Desorption Modification of $\text{Mg}(\text{BH}_4)_2$

In this chapter we report on hydrogen dehydrogenation behavior of $\text{Mg}(\text{BH}_4)_2$ in combination different metal amides $\text{M}(\text{NH}_2)_2$ ($\text{M} = \text{Na}, \text{Li}$ and Mg) and MgBr_2 . The chapter starts with literature review on thermodynamically tailored hydrogen storage properties of complex hydrides and borohydrides, followed by synthesis method for $\text{Mg}(\text{NH}_2)_2$, and the preparation procedure for the blends. In the next step, thermal analysis is performed to investigate the thermal behavior of intermediate and final products, as well as to analyze the nature of the evolved gas. Powder X-ray diffraction (PXRD) is used to detect the intermediates and the products of ultimate dehydrogenated. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy is carried out for further characterization in decomposition pathway of the mixtures.

4.1 Introduction

The Gibbs free energy for a hydride desorption reaction is a measure for the stability and can be correlated to temperature of the hydrogen release. However, as the entropy changes (ΔS) corresponds mostly to the change from molecular hydrogen gas to dissolved atomic hydrogen and it is constant for all hydrides ($S^\circ = 130 \text{ JK}^{-1} \text{ mole}^{-1} \text{ H}_2$), the enthalpy change (ΔH) characterize the thermodynamic properties of hydrides. Thus, the stability of M-H bond and the hydrogen release temperature of the hydrides can be correlated with their enthalpy of reaction [1, 2]. Based on the correlation between Pauling electronegativity and enthalpy of formation (see Chapter 3), an increase in the electronegativity of the metal cation will lower the decomposition temperature of metal borohydride [3]



Alkaline and alkaline-earth metal based borohydrides, such as LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, and $\text{Ca}(\text{BH}_4)_2$ have been focus of interest in the recent years because of their high gravimetric and volumetric hydrogen densities. However, the dehydrogenation of these compounds proceeds through several steps with a limitation of the dynamics (their kinetics and mechanisms), therefore tailoring of hydrogen release has been carried out using different approaches. Two possible approaches for improving thermodynamics are (a) reducing the stabilization of $\text{M}(\text{BH}_4)_n$ by producing mixed-metal borohydrides based on alkaline and transition metals ($\text{MM}'(\text{BH}_4)_n$) which was discussed readily in Chapter 3, (Fig.4.1 a), and (b) stabilization of product by the combination of $\text{M}(\text{BH}_4)_n$ with pure elements, metal hydrides and complex hydrides (Fig.4.1 b). These two approaches are schematically shown schematically are shown in Fig.4.1. [1, 4, 5].

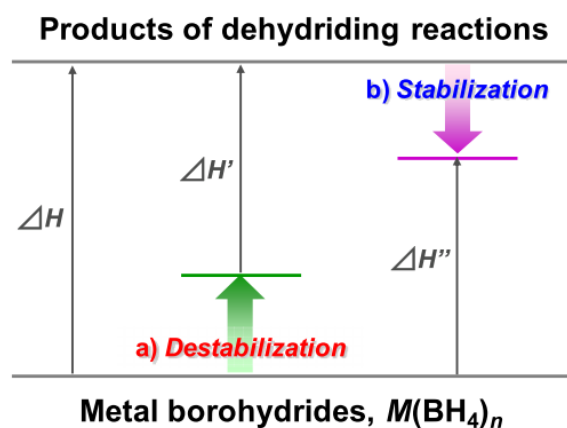


Fig.4.1 schematic of two routes for thermodynamically modifying metal borohydride, (a) destabilization of $\text{M}(\text{BH}_4)_n$ (b) stabilization of dehydrogenated products [1].

It is reported that, addition of elemental Mg and Al to LiBH_4 leads to dropping in dehydrogenation temperatures down to 375 °C and 280 °C [7]. Moreover, $\text{MBH}_4\text{-MH}_x$ systems proved to be a powerful tool for improving the thermodynamic properties because of formation of

stable product (MB_2) with lower enthalpy of formation, *e.g.*, MgB_2 formation in the system of LiBH_4 - MgH_2 [6]. Boride formation instead of elemental boron reduces enthalpy of the reaction by 10-25 kJ/mole H_2 which can lead to decrease in onset temperature release by 150-250 °C [7]. Remarkable destabilization of LiBH_4 was reported due to reaction with LiNH_2 in the LiBH_4 - LiHN_2 system [8].

Inspired by the studies of Aoki, M., *et. all.* [8], a master thesis was started at Koç University focused on the system NaNH_2 - NaBH_4 [9]. Formation of Na_2BNH_6 was detected in two isostoichiometric phases as α -HT and β -LT. Na_2BNH_6 releases hydrogen in the molten state, in the region between 300 °C and 400 °C yielding NaH , Na and a gray amorphous powder which turned out to be elemental boron. The theoretical hydrogen storage capacity was calculated to be 7.6 wt%, in good agreement with the experimental results showing 6–7.7 wt% mass losses due to hydrogen release. Although hydrogen was the dominating species in the gas phase, mass spectra indicates also the presence of NH_3 trace [10]. For decreasing dehydrogenation temperature, effect of adding catalysts was investigated. By adding Pt, Pd, Ni a decrease in the onset of dehydrogenation to ~60 °C was observed. The most significant improvement was achieved in the presence of Pt/Vulcan carbon and Pd/Black Pearls 2000. The dehydrogenation temperature was decreased to ~123 °C with 5.6 wt% Pt/Vulcan carbon and to around 119 °C with 2.9 wt% Pd/Black Pearls 2000 [10].

In 2007 the synthesis of $\text{Mg}(\text{BH}_4)_2$ and its usage of as hydrogen storage material has been reported which lead to an intense research to reduce its hydrogen release onset temperature (250 °C) and improve the reversibility of the process by adding catalysts and/or by combination with suitable complex hydrides. In 2010, LiNH_2 - $\text{Mg}(\text{BH}_4)_2$ system was investigated. The dehydrogenation of the equimolar mixture of the components (1:1), starts at 163 °C and ends with a weight loss of 7.2 wt % at 300 °C. The recorded mass loss and temperature range is a significant improvement compared to the pure $\text{Mg}(\text{BH}_4)_2$ [11]. A year later, a study on the quasi binary system LiBH_4 - $\text{Mg}(\text{BH}_4)_2$ was reported [4]. Although no new phase formation was observed, the

components form a physical mixture ($x\text{LiBH}_4-(1-x)\text{Mg}(\text{BH}_4)_2$) and a eutectic composition existing in the range of $0.5 < x < 0.6$. Melting point of mixture declined to $180\text{ }^\circ\text{C}$ and decomposition temperature is reported to be much lower than that of pure borohydrides. At $270\text{ }^\circ\text{C}$, the $x = 0.5$ composition releases about 7 % of hydrogen gas. Furthermore, some ternary hydride systems such as $\text{LiAlH}_4\text{-MgH}_2\text{-LiBH}_4$ and $\text{LiNH}_2\text{-LiH-Mg}(\text{BH}_4)_2$ were investigated recently which showed a better hydrogen storage properties compared to the pure components (LiNH_2 , LiH , $\text{Mg}(\text{BH}_4)_2$, LiAlH_4 , MgH_2 and LiBH_4) or quasi binary mixtures of them ($\text{LiAlH}_4\text{-MgH}_2$, $\text{LiAlH}_4\text{-LiBH}_4$, and $\text{MgH}_2\text{-LiBH}_4$) [12, 13].

For improving the kinetic behavior and reducing the reaction barriers, appropriate additives with catalytic abilities and the nano-confinement approach were the general methods of choice. A large number of additives from metals, oxides, halides, and carbon-based materials to $\text{M}(\text{BH}_4)_n$ have been examined. The most effective additive for LiBH_4 was found to be the mixture of $0.2\text{ MgCl}_2 + 0.1\text{ TiCl}_3$, in which approximately 5 mass % of hydrogen was released starting from $60\text{ }^\circ\text{C}$ and 4.5 mass % of hydrogen was rehydrogenated at $600\text{ }^\circ\text{C}$ under a hydrogen pressure of 7 MPa [14]. The addition of TiCl_3 was also proved to be effective also for $\text{Mg}(\text{BH}_4)_2$, by reducing the initial dehydrogenation temperature 361 K . Similarly, adding TiF_3 to the $\text{LiAlH}_4\text{-MgH}_2\text{-LiBH}_4$ system leads to hydrogen release at $60\text{ }^\circ\text{C}$ while the dehydrogenation was completed below $400\text{ }^\circ\text{C}$ [12].

In spite of intensive research on this field, none of the current materials can fulfill the requirements of on-board hydrogen storage for fuel cell vehicles; therefore, continuous efforts are required to develop novel materials. The systems of choice in this thesis are the quasi-binary systems-borohydride-amide ($\text{M}(\text{NH}_2)_2$) ($\text{M} = \text{Li, Na, Mg}$) - ($\text{Mg}(\text{BH}_4)_2$).

It is known that, amides usually release hydrogen rapidly and also at lower temperatures when they form complexes with hydrides or borohydrides, such as in $\text{LiNH}_2\text{-Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2/\text{LiNH}_2$ and $\text{Ca}(\text{BH}_4)_2/\text{NaNH}_2$ [11, 15]. This means that existence of BH_4 beside NH_2 reduce onset temperature of hydrogen release and suppress NH_3 evolution, which is poisonous gas

for PEMFC membrane. This is the result of coexistence of oppositely charged hydrogen atoms in these systems [6,12]. Hereby, H atoms in amide are carrier of positive charges, while, H atoms in borohydride are negative. The strong chemical potential for the combination of H^+ and H^- ($\text{H}^{\delta+} + \text{H}^{\delta-} = \text{H}_2$, $\Delta H = -17.73 \text{ eV}$) is the driving forces for releasing hydrogen at lower temperature [15-18]. This mechanism is called hydridic-protic interaction which is schematically shown in Fig.4.2.

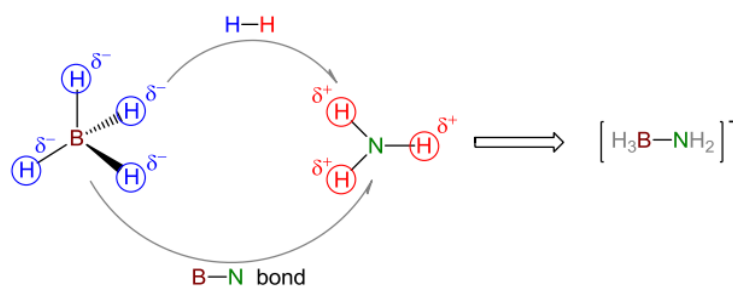


Fig.4.2 Hydridic-Protic interaction schematic.

4.2 Experimental Procedure

4.2.1 $\text{Mg}(\text{NH}_2)_2$ synthesis

In this study, magnesium amide ($\text{Mg}(\text{NH}_2)_2$) is synthesized by two following methods:

Mechanochemical synthesis - Metathesis reaction is performed between magnesium bromide and sodium amide (Eq 4.1) using Fritsch P7 planetary ball mill at 500 rpm with 80 ml stainless steel vials and 5 mm stainless steel balls. The ball-to-powder mass ratio was fixed to 20:1. An excess amount of NaNH_2 with respect to the stoichiometric ratio, is used in ball milling ($\text{MgBr}_2:\text{NaNH}_2 = 1:2.3$).



Furnace reaction - magnesium bromide and sodium amide in 1:2.3 ratio were hand milled in the N_2 filled glove box for 15 min. Afterwards, the mixture transferred to the small steel tube which later synthesized under Ar atmosphere at 240 °C for 24 h.

Unlike NaBr which is good soluble in liquid ammonia, $\text{Mg}(\text{NH}_2)_2$ is practically insoluble in this solvent. By this way, NaBr can be separated from the mixture leaving $\text{Mg}(\text{NH}_2)_2$ as final powder. As a result, in order to extract $\text{Mg}(\text{NH}_2)_2$ form the mixture, The hygroscopic gray residue was transferred into the glove box and was placed into the novel designed Π -shaped Pyrex glassware with two bulbs and Al_2O_3 fused frit located on its arc (See Fig.4.3). Subsequently, a Schlenk tube and high purity ammonia gas are connected to the vacuum line and all the system flushed with Ar for couple of times for ensuring moisture/oxygen free environment. Mixture container bulb is then dipped into liquid nitrogen (LN_2) and kept for couple of minutes ($\sim 196^\circ\text{C}$). Ammonia gas later is introduced into the system and frozen onto the mixture. Pressure of vacuum line was constantly monitored for preventing sudden rise in the pressure of whole system. Lastly, ammonia tube is disconnected from the line and Π -shaped Pyrex was sealed using methane torch, after that. Mixture container bulb is then dipped into cooling bath which is prepared by mixing LN_2 and ethanol to maintain temperature of bulb between melting (freezing temperature $\sim 77^\circ\text{C}$) and boiling point ($\sim 33^\circ\text{C}$) of ammonia. Here, mixture is washed with liquid ammonia and solution containing NaBr is filtered through the frit and transfer to the other bulb. Right after, solution free bulb again was dipped into the prepared cooling bath to produce a pressure difference due to the difference in temperature between two bulbs. Consequently, ammonia was sucking again to the first bulb. This procedure were repeated 3 times for ensuring whole NaBr is solved in the liquid ammonia and pure $\text{Mg}(\text{NH}_2)_2$ is produced.

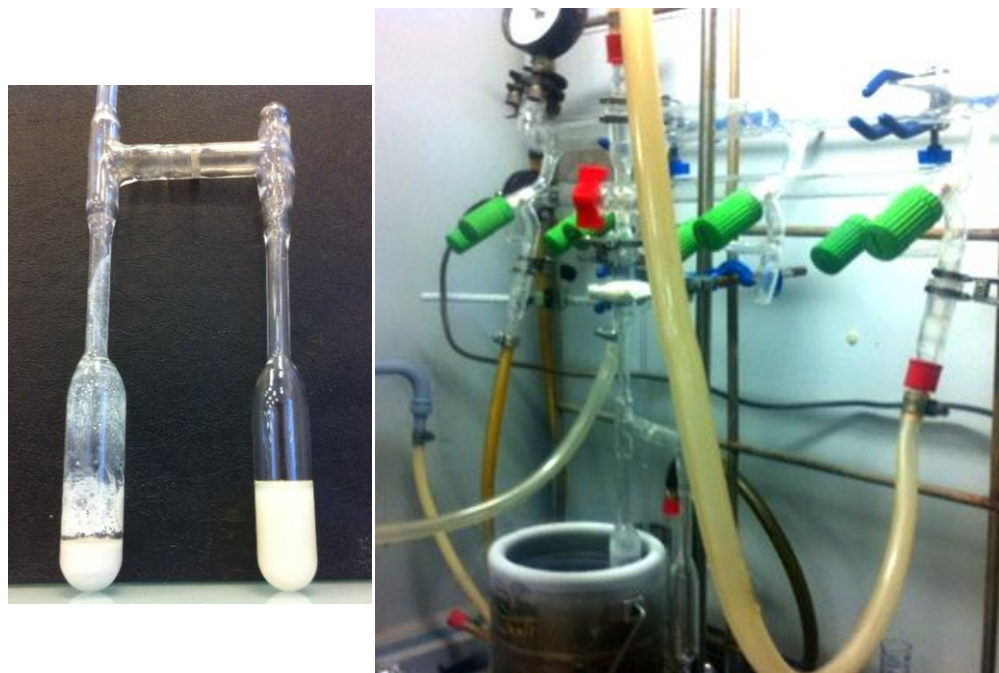


Fig.4.3 Π-shaped Pyrex glassware and purification setup for extracting $\text{Mg}(\text{NH}_2)_2$.

4.2.2 Mixtures preparation for $\text{Mg}(\text{BH}_4)_2$ - $\text{M}(\text{NH}_2)_2$ ($\text{M}=\text{Li}, \text{Na}, \text{Mg}$) system

In this work, $\text{Mg}(\text{BH}_4)_2$ and $\text{Mg}(\text{NH}_2)_2$ were synthesized based on mentioned procedures in this thesis. Lithium amide (LiNH_2 , 95%), sodium amide (NaNH_2 , 95%), sodium borohydride (NaBH_4 , 98%) and magnesium bromide (98% anhydrous) were purchased from Aldrich as analytical reagent grade. $\text{Mg}(\text{BH}_4)_2$ - NaNH_2 , $\text{Mg}(\text{BH}_4)_2$ - LiNH_2 , $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$ mixtures with 1:1 molar ratio were hand milled for 20 minutes in a N_2 filled glove box.

4.2.3 Mixture preparation in $\text{Mg}(\text{BH}_4)_2$ - MgBr_2 system

In this section, the mechanochemical synthesis was performed based on method 2.2.2., The first and second reaction series contained unreacted MgBr_2 and they were used for investigation on the effect of MgBr_2 addition on $\text{Mg}(\text{BH}_4)_2$.

4.3 Results and Discussion

4.3.1 $\text{Mg}(\text{BH}_4)_2\text{-M}(\text{NH}_2)_2$ ($\text{M}=\text{Li, Na, Mg}$) system

PXRD results of products after ball mill, heat treatment as well as purification are depicted in Fig.4.4 a and b. Fig.4.4 a shows that products were exclusively NaBr after ball mill (red pattern) while heat treated mixture (black pattern) consist of both compounds seen in Eq.4.1, NaBr and $\text{Mg}(\text{NH}_2)_2$. The absence of the $\text{Mg}(\text{NH}_2)_2$ reflections and the broad bump around $2\theta \sim 20^\circ$ in the ball milled mixture indicate that amorphous $\text{Mg}(\text{NH}_2)_2$ is formed. Moreover, broadening of all NaBr peaks in the ball milled sample compared to the heat treated one is an indication for reduced crystallite size. However, both methods have shown similar results after purification process of blends. PXRD pattern of purified ball milled mixture is depicted in Fig.4.4 b corresponding to pure $\text{Mg}(\text{NH}_2)_2$. The similar bump around 20° is very likely to presence of amorphous material in the specimen and polymer sample holder. This confirms that NaBr was removed completely and mixture of pure amorphous and crystalline $\text{Mg}(\text{NH}_2)_2$ was obtained.

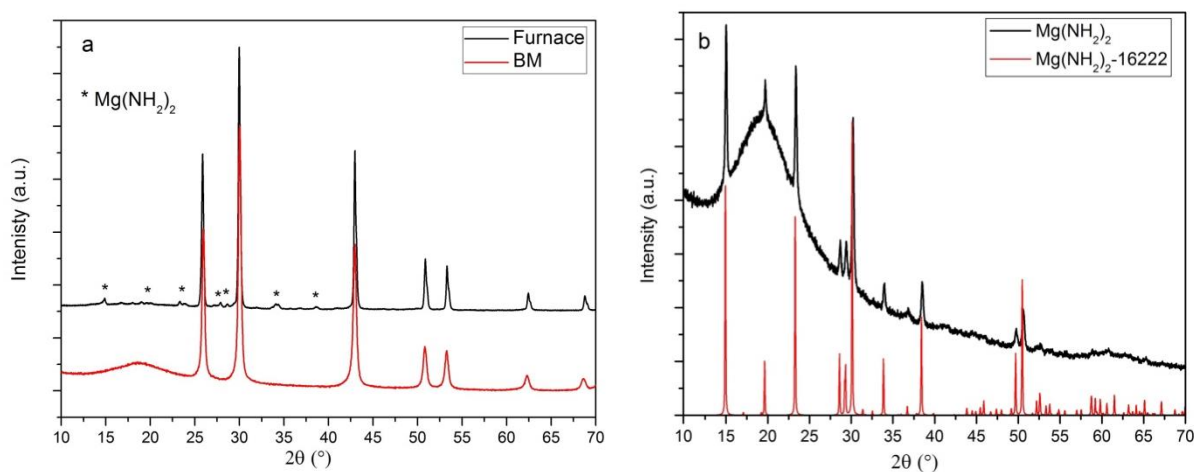


Fig.4.4 PXRD patterns of a) ball milled (BM) and heat treated mixture of $\text{NaNH}_2 + \text{Mg}(\text{BH}_4)_2$ b) after purification of the mixture produced by ball milling, $\text{Mg}(\text{NH}_2)_2$ pattern is given as reference.

In order to investigate the properties of the mixture, TG-MS and DSC studies have been performed on this blend, as well as on the starting components up to 600 °C. For NaNH_2 there are many controversial decomposition pathways and products proposed in the literature [17, 19-21]. To clarify the discrepancies related to the thermolysis process we decided to reinvestigate the thermal behavior of sodium amide and its decomposition steps.

Based on TG-MS results for NaNH_2 (Fig.4.5 a and b) 65 wt% reduction in total weight is observable stemming from NH_3 , N_2 and H_2 release. The decomposed gas is mainly NH_3 along with very little H_2 whose formation starts at 290 °C coupled with a total mass loss of 5.4 wt% up to 465 °C. This amount is in contrast with reported 11.6 wt% loss at 420 °C [20]. The reason might be that all analyses for air-sensitive materials should be done in an inert gas glove box to prevent oxidation and hydrolysis. As a result, one may reach to lower capacity in decomposition as oxidation took place simultaneously. Moreover, according to MS spectra, gas release is started to become maximized at around 465 °C for both of NH_3 and H_2 and keeps continue until 560 °C with 47 wt% loss in weight. In other words, NH_3 and H_2 release following the same trend while amount of NH_3 is substantially higher. In addition, a very small amount of N_2 is

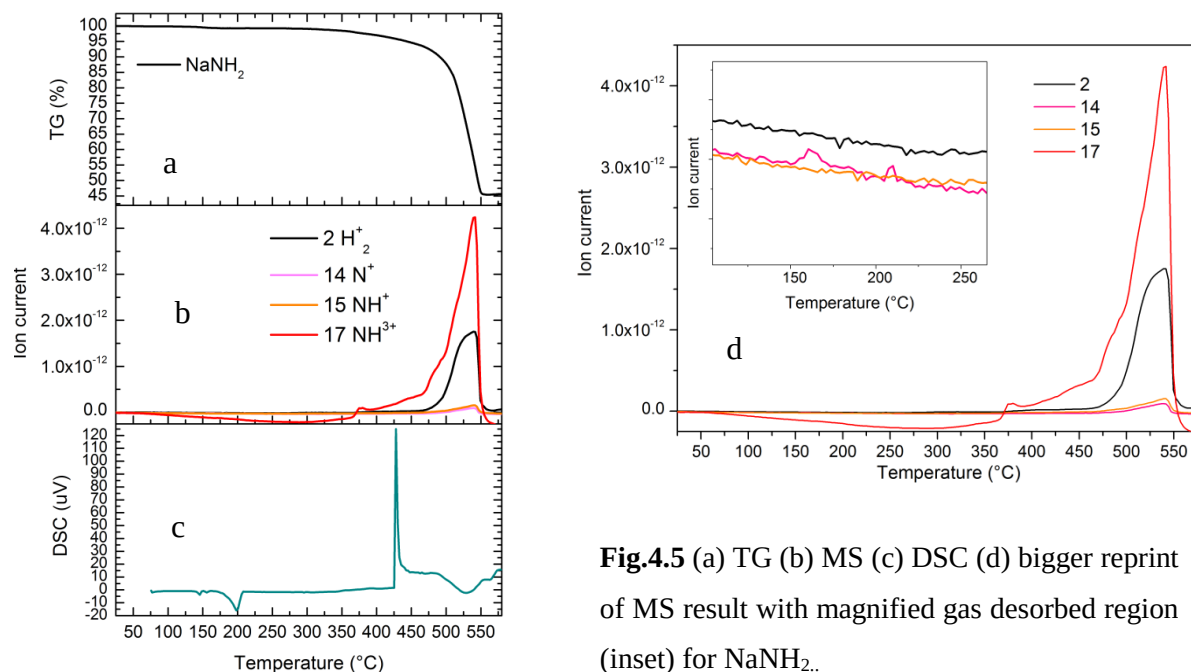
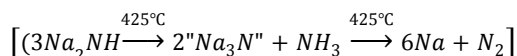
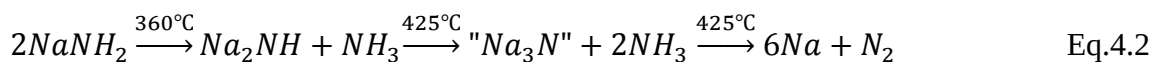


Fig.4.5 (a) TG (b) MS (c) DSC (d) bigger reprint of MS result with magnified gas desorbed region (inset) for NaNH_2 .

released (~ 1 wt%) between 135 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$ which is also seen as two tiny endothermic peaks in DSC curves as shown in Fig.4.5 c. It is reported that this small peak is related to absorbed N_2 from the synthesis of NaNH_2 [22]. These two endothermic peaks were also observed elsewhere but no information was given about their possible origin [17]. Third endothermic peak is related to melting of NaNH_2 ($\sim 200^{\circ}\text{C}$) as it is not associated with any mass loss. A very small change in DSC signal starting at 360 $^{\circ}\text{C}$ with a bump in MS spectra of NH_3 and no/very little decomposition of N_2 and H_2 might be associated with sodium imide formation [17, 19]. A tiny effect in DSC linked to a very intense exothermic peak at 425 $^{\circ}\text{C}$ could be related to formation of sodium nitride (Na_3N) and as this compound is extremely unstable decompose to its elements [19, 21]. Finally, the broad endothermic effect in the region of highest NH_3 , N_2 and H_2 desorption is stemming from the decomposition of NaNH_2 according to Eq. 4.4 [22]. Based on the above findings, the decomposition pathway might be written as in Eq. 4.3 and Eq. 4.4.



TG-MS results for Mg(BH₄)₂-NaNH₂ mixture is shown in Fig.4.6. Based on the MS findings, the weight reduction takes place in four steps. Around 2 wt% mass loss happens in the first stage between RT to 150 °C and can be attributed to Et₂O rest from Mg(BH₄)₂. Nearly 15.4 wt % mass reduction is recorded between 150 °C to 270 °C and related to NH₃ liberation which occurs in three steps based on TG results. Approximately 4.2 wt % mass loss between 270 °C to 350 °C is observed and assigned from the MS data to the release of the H₂ and NH₃ gases. Finally, 2.3 wt% H₂ is liberated up to 520 °C. Increase in mass at higher temperature is generally coupled with the oxidation processes taking place in the decomposed materials. In this mixture, B₂H₆ evolution is completely suppress in comparison to pure Mg(BH₄)₂ and NH₃ release is reduced and shifted to lower temperature range. However, based on intensity in the MS spectra, H₂ release as well as other decomposed gas was 10 times less than in the case of starting materials, NaNH₂ and Mg(BH₄)₂.

DSC results is shown Fig.4.6 c is showing as exothermic peaks around 150 °C which is not associated with any mass change or gas release. This is followed by four endothermic peaks at 293 °C, 361 °C, 390 °C and 482 °C. For understanding the nature of these peaks, as well as for investigation of the decomposition pathway and final products, PXRD plot of the blend is recorded at room temperature, 155 °C, 320 °C, 420 °C, and 600°C are derived from DSC analysis and plotted in Fig.4.7. For the mixture at 155 °C annealing time is extended to 6 hours while for the others the tempering time was only 15 min.

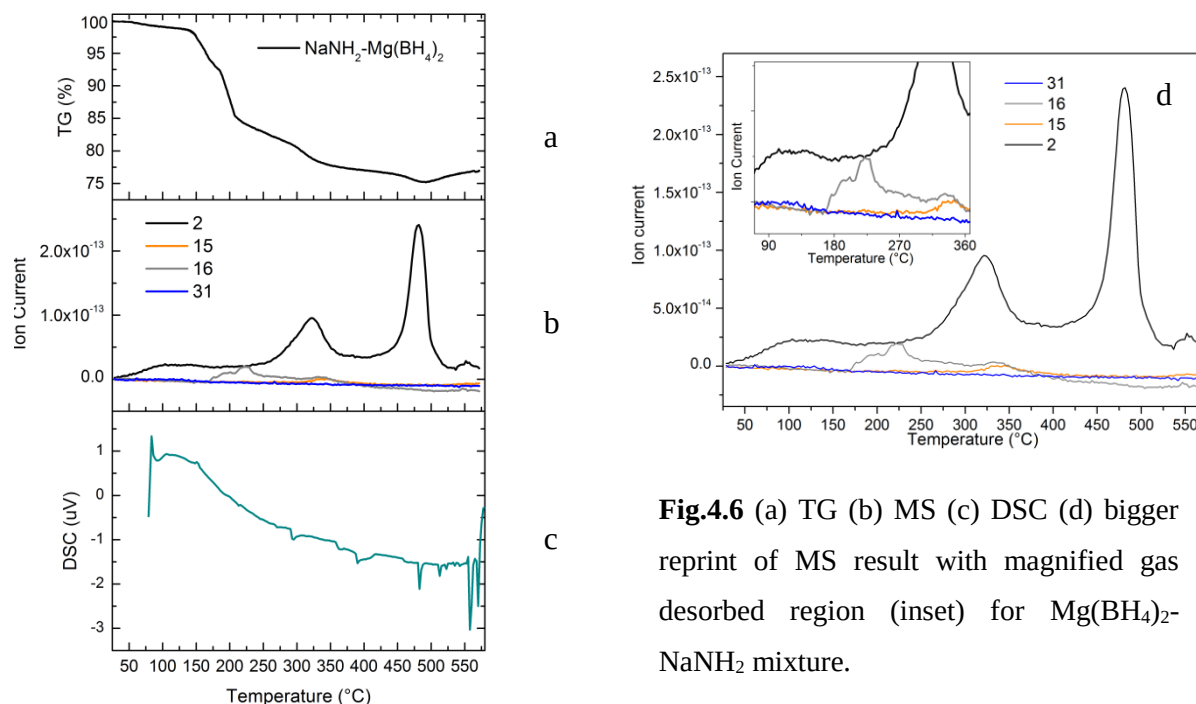


Fig.4.6 (a) TG (b) MS (c) DSC (d) bigger reprint of MS result with magnified gas desorbed region (inset) for $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ mixture.

Interestingly, in the PXRD pattern for the blend at room temperature (25 °C) shown in Fig.4.7, the NaBH_4 formation can be seen just after the hand milling. This formation can be explained employing simple hard acid soft base principles (HASB principle) [23]. Based on this theory, hard acids prefer to bind to the hard bases to give ionic complexes, whereas the soft acids prefer binding to soft bases to give covalent complexes. In this mixture, Na and BH_4 are soft acid and base, respectively due to larger ionic radii and low positive charge in the case of Na, while Mg and NH_2 are hard acid and base, respectively due to smaller ionic radii and high positive charge in the case of Mg. As a result, the formation soft-soft and hard-hard compound is more preferred and thus, NaBH_4 forms.

The PXRD pattern at 155 °C revealed NaBH_4 and NaNH_2 as well as two unidentified peaks. They might be related to formation of Na_2BNH_6 based on finding in Inorganic Chemistry Laboratory at Koç university [10]. According to the PXRD data for the mixture at 320 °C, the

peaks of the unknown compound, as well as of NaNH_2 disappeared and NaBH_4 is solely present. For the mixture heated to 420°C , NaBH_4 peaks vanished while those of MgH_2 are emerged along with MgO . The broad peaks of MgO formed at this temperature result very likely from the reaction between ppm amount of oxygen/humidity present in the chamber [11, 24]. Finally, product after decomposition at 600°C consists of MgO and Na . Based on decomposition pathway of NaNH_2 , formation of Na is following Eq.4.2 while MgB_2 formation is hindered due to formation of MgO .

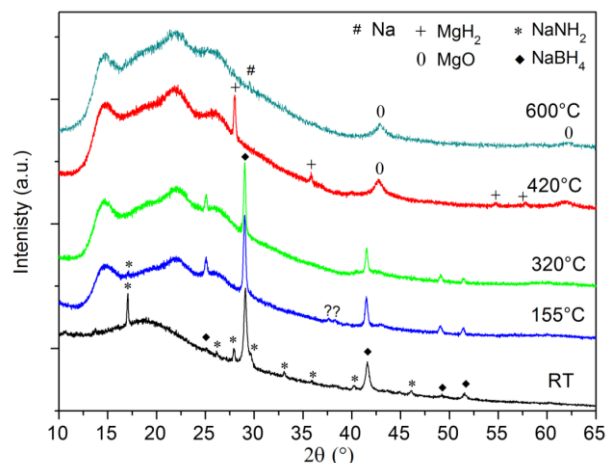


Fig.4.7 PXRD pattern of 1:1 ratio $\text{Mg}(\text{BH}_4)_2$ - NaNH_2 after hand mill and after decomposing at 155°C , 320°C , 420°C , and 600°C .

ATR-FTIR spectra of all starting materials and annealed samples for $\text{Mg}(\text{BH}_4)_2$ - NaNH_2 mixture are illustrated in . B-H stretching band of $\text{Mg}(\text{BH}_4)_2$ appears at 2267 cm^{-1} and B-H bending for $\text{Mg}(\text{BH}_4)_2$ can be also seen at 1259 and 1129 cm^{-1} . The characteristic bands for NaNH_2 are also observed at 3258 (antisymmetric stretch), 3209 (symmetric stretch) and 1529 (bending) cm^{-1} in good agreement with the literature data [25]. The sharp peak at 3635 cm^{-1} is an indication of O-H band in NaOH [26] formed by partial hydrolysis of NaNH_2 . The hydrolysis product is amorphous and thus not detectable in PXRD. For the blend at room temperature, N-H absorption frequencies did not change and one extra IR mode appeared at 3348 cm^{-1} . In addition, the B-H stretching is

slightly splitted into three components. The high frequent peak is shifted to 2296 cm^{-1} with respect to 2267 cm^{-1} in pure $\text{Mg}(\text{BH}_4)_2$. Additionally, the bending mode are shifted to lower values while one band has gained on intensity the other one became weaker. It should be underlined that based on the present experimental results, the B-H stretching in NaBH_4 is quite stable and dominant also in different structural environment, e.g. in e coexistence with $\text{Mg}(\text{BH}_4)_2$.

In the ATR-FTIR spectra (see and Table 4.1) at $155\text{ }^\circ\text{C}$, the B-H stretching absorption band is shifted by 6 cm^{-1} wavenumber to lower values with respect RT. While the B-H bending mode at 1250 cm^{-1} became weaker, the B-H stretching is clearly splitted giving rise to three additional bands. The latter is interpreted as indication for the formation and dominance of NaBH_4 in the mixture at this temperature. Moreover, the stretching modes of N-H are disappearing. The disappearance of the two strong N-H modes in the IR spectrum is a clear evidence for a reaction between $[\text{BH}_4]^-$ and NH_2^- anions in which the latter is consumed according to : $\text{BH}_4^- + \text{NH}_2^- \rightleftharpoons \text{BH}_3 + \text{NH}^- + \text{H}_2$ [11, 13, 17, 27]. On further heating to $320\text{ }^\circ\text{C}$, the B-H bending at 1250 cm^{-1} splits into two small peaks of low intensity. These vanished completely upon heating to $420\text{ }^\circ\text{C}$ and finally to $600\text{ }^\circ\text{C}$, while very intense and sharp peak together with a broad bump emerged at 1363 cm^{-1} and 2474 cm^{-1} , respectively. These peaks might be related to starting oxidation of the mixture to form an amorphous unidentified product. All infrared frequencies for starting materials and mixtures heat treated at related temperatures are listed in Table 4.1.

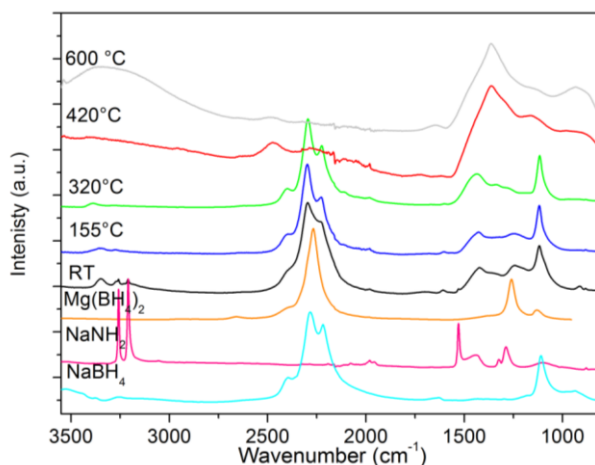


Fig.4.8 ATR-FTIR spectra for the mixture $\text{Mg}(\text{BH}_4)_2$ - NaNH_2 after hand mill and after decomposing at 155 °C, 320 °C, 420 °C, and 600°C.

Table 4.1 Infrared frequencies (in unit of cm^{-1}) for NaNH_2 , $\text{Mg}(\text{BH}_4)_2$ at room temperature and $\text{Mg}(\text{BH}_4)_2$ - NaNH_2 mixture at room temperature, 155, 320, 420 and 600 °C.

Modes	NaNH_2	$\text{Mg}(\text{BH}_4)_2$	NaBH_4	RT	155°C	320°C	420°C	600°C
O-H	3636	3552	3527	3635	3632	3611	3606	3536
N-H				3348	3355	3388		
$\nu(\text{N-H})_{\text{as}}$	3258			3258				
$\nu(\text{N-H})_{\text{s}}$	3209		3254	3209	3272			
		2658						
$\nu(\text{B-H})$			2390		2395	2398	2474	2480
$\nu(\text{B-H})$		2267	2283	2296	2290	2294	2285	
$\nu(\text{B-H})$			2218		2227	2224	2166	2163
							2113	2110
	1980			1980	1980	1979	1980	
$\delta(\text{N-H})$	1529							
N-H	1429			1423	1426	1436		
							1363	1363
$\delta(\text{B-H})$	1288	1259		1243	1250			
$\delta(\text{B-H})$	1101	1129	1109	1118	1118	1116		

Same as for previous mixtures, for exploring the properties of $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ blends, TG-MS and DSC analyses have been performed up to 600 °C shown in Fig.4.9. The TG results coupled with MS spectra show a four-step decomposition. The mass loss up to 7 wt% at 170 °C is attributed to desorption of Et_2O , NH_3 and B_2H_6 while gas released after this temperature is exclusively H_2 . H_2 liberated in three steps in the temperature ranges of 170 °C to 250 °C, 250 °C to 320 °C and 320 °C to 440 °C are accompanied by 5.2 wt %, 1.7 wt % and 2 wt % mass loss, respectively.

DSC curve are depicted in Fig.4.9 c demonstrates three sharp endothermic effects at 213 °C, 259°C, 289°C and one broad peak at 442°C. For understanding the nature of these peaks as well as for exploring the decomposition pathway and final products, PXRD result of the blend is recorded at room temperature, 255 °C, 285 °C, 320 °C, and 600°C, those derived from the DSC analysis and are plotted in Fig.4.10.

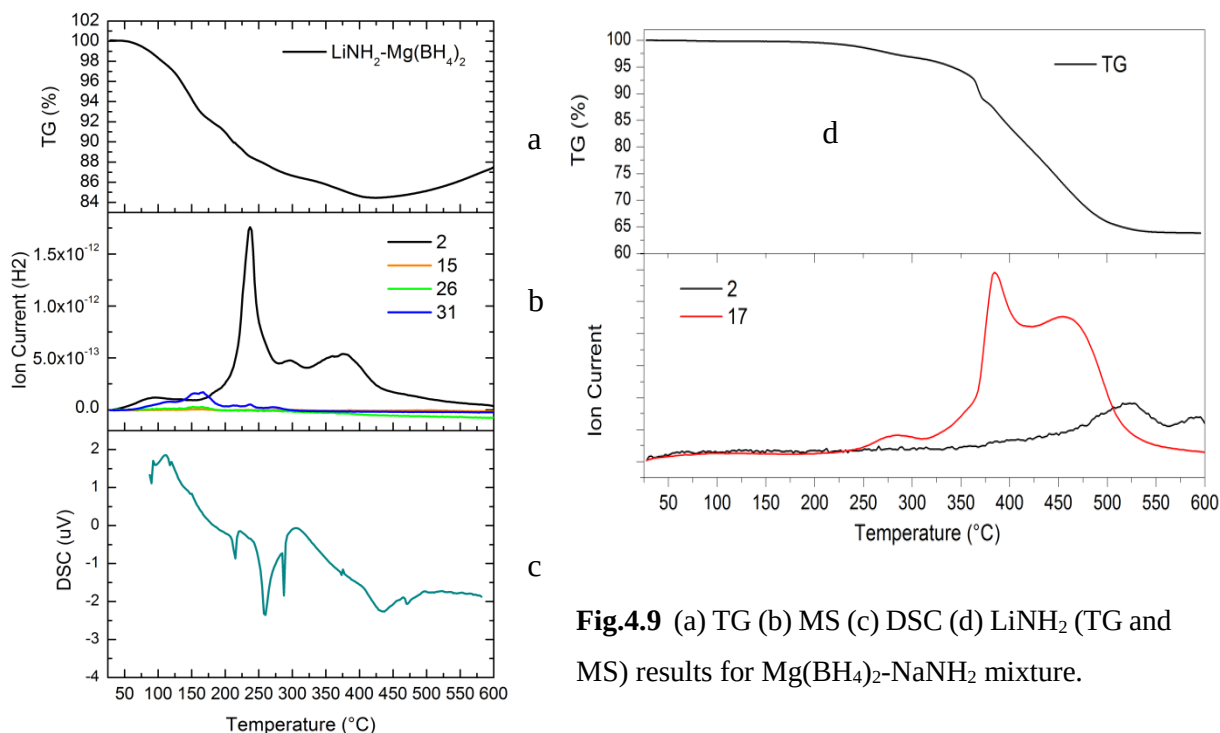


Fig.4.9 (a) TG (b) MS (c) DSC (d) LiNH_2 (TG and MS) results for $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ mixture.

According to the PXRD results of the $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ blend shown in Fig.4.10 at room temperature, only LiNH_2 peaks are detectable while $\text{Mg}(\text{BH}_4)_2$ seems to be in amorphous state (based on ATR-FTIR spectrum in Fig.4.11). For the mixture heated to 225 °C, the LiNH_2 peaks are maintained where as two unknown compounds form. One of the peaks has also been observed in the blend at 285 °C. In addition, LiBH_4 is formed and LiNH_2 are vanished at 285 °C. The formation of LiBH_4 can be interpreted based on HASB principles. The PXRD diagram for the blend at 320 °C indicates that the material is totally amorphous but on heating to 600 °C peaks of to MgO and Mg-Li alloy emerged (see Fig.4.10). It is reported that the reflection position of the Mg-Li is similar to Mg but slightly shifted to higher 2θ [11, 28].

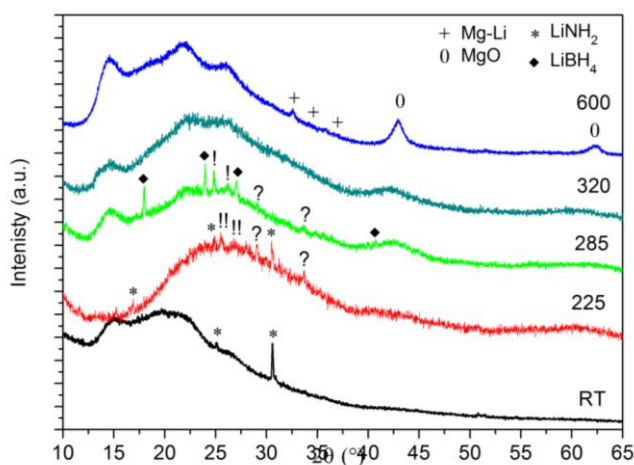


Fig.4.10 PXRD pattern of 1:1 ratio $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ after hand mill and after decomposing at 255 °C, 285 °C, 320 °C, and 600 °C.

In Fig.4.11, ATR-FTIR spectrum of $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$, the B-H stretching of magnesium borohydride is observed at 2267 cm^{-1} while the B-H bending bands are located at 1259 and 1129 cm^{-1} . The modes at 3313 and 3260 cm^{-1} represent the N-H stretching frequencies and the bands at 1441 , 1562 and 1537 cm^{-1} are assigned to N-H bending in LiNH_2 . One can easily see that even for hand milled sample at room temperature all IR frequencies related to N-H bending are disappeared.

A new peak emerges at 1403 cm^{-1} and is later superimposed by a broad peak starting from 1537 cm^{-1} to 1259 cm^{-1} in all other samples heated up to $320\text{ }^\circ\text{C}$. Again the weakening of the N-H band intensities is referred to decrease of the amide ion concentration due to reaction with borohydride groups [11, 27]. In analogy to $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$ system, the B-H bending at 1259 cm^{-1} is vanished for all samples heated up to $320\text{ }^\circ\text{C}$ while the other component becomes more intense and shifts to lower values. For the mixture at $600\text{ }^\circ\text{C}$, a new and intense peak appeared at 1368 cm^{-1} similar to previous blend ($\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$). Surprisingly the peak at 1404 cm^{-1} also reemerged again. The band at 2435 cm^{-1} could not be assigned to any species, yet.

All infrared frequencies for starting materials and $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ mixture heated to respective temperatures are listed in Table 4.2.

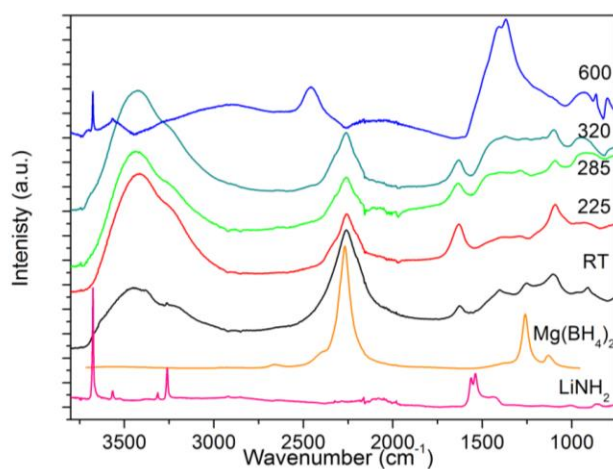


Fig.4.11 ATR-FTIR spectra for the mixture $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ after hand mill and after hand mill and after decomposing at $255\text{ }^\circ\text{C}$, $285\text{ }^\circ\text{C}$, $320\text{ }^\circ\text{C}$, and $600\text{ }^\circ\text{C}$.

Table 4.2 Infrared frequencies (in unit of cm^{-1}) for LiNH_2 , $\text{Mg}(\text{BH}_4)_2$ at room temperature and $\text{Mg}(\text{BH}_4)_2$ - LiNH_2 mixture at room temperature, 225, 285, 320, 350 and 600 °C.

	LiNH_2	$\text{Mg}(\text{BH}_4)_2$	RT	225°C	285°C	320°C	600°C
O-H	3675	3552					3676
O-H	3565						3568
			3450	3415	3443	3425	
$\nu(\text{N-H})_{\text{as}}$	3313						
$\nu(\text{N-H})_{\text{s}}$	3260		3263				
							2453
$\nu(\text{B-H})$		2267	2260	2260	2260	2260	
			1625	1603	1637	1630	
$\delta(\text{N-H})$	1562						
N-H	1537						
N-H	1441			weak	weak	weak	
			1403	weak	weak	weak	1404
							1368
$\delta(\text{B-H})$		1259	1252	1287	1286	-	
$\delta(\text{B-H})$		1129	1104	1092	1092	1097	

Apart from useful storage properties of the amide/borohydride systems, another interesting feature came to the fore which has been first observed in LiBH_4 - LiNH_2 and NaBH_4 - NaNH_2 blends [1, 10]. The ultimate dehydrogenation products in both systems are $\text{Li}_3\text{BN}_2 + \text{H}_2$, $\text{Na}_3\text{BN}_2 + \text{H}_2$ respectively, when stoichiometric ratios (1:2) are employed. The reaction in equimolar ratios yields M_2BNH_6 . The $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$ system is a promising analogous to the above mentioned alkali metal blends in two manners: it comprises the same anion combination and Mg and Li have practical the same ionic radii. Motivated by these facts, we decided to investigate $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$ blends with respect to phase formation, thermal and vibrational behavior.

The thermal properties of the $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$ mixture was investigated by TG-MS and DSC analysis up to 600 °C and depicted in Fig.4.12. Obvious at first sight, is the simplicity of the MS and DSC results. It means also that decomposition pathway in this system is less complicated than the previous ones going only to few steps. The TG and MS results suggest three desorption steps while the first one, ending at 190 °C with 4 wt% mass loss, is related to release of Et_2O , NH_3 and B_2H_6 in analogy to $\text{Mg}(\text{BH}_4)_2$ - LiNH_2 mixture. H_2 is liberated in two steps starting from 190

$^{\circ}\text{C}$ up to $350\text{ }^{\circ}\text{C}$ with 4.3 % reduction in mass. Near to 1 wt% mass reduction is also detected up to $600\text{ }^{\circ}\text{C}$.

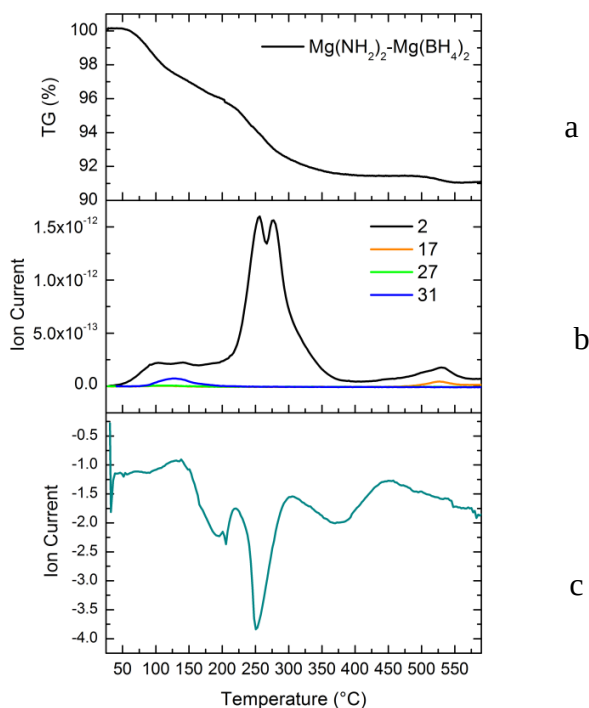


Fig.4.12 (a) TG (b) MS (c) DSC results of $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ mixture.

The DSC curve (Fig.4.12 c), exhibit three endothermic peaks at $190\text{ }^{\circ}\text{C}$, 204°C , 251°C and another broad one at $370\text{ }^{\circ}\text{C}$. There is also very tiny exothermic peak at $152\text{ }^{\circ}\text{C}$ which might be related to formation of Mg_2BNH_6 [29]. For understanding the origin of the thermal effects exploring the decomposition pathway and detection of the final products, the PXRD data of the specimen, obtained at $110\text{ }^{\circ}\text{C}$, $160\text{ }^{\circ}\text{C}$, $220\text{ }^{\circ}\text{C}$, $380\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$ were collected.

PXRD plot of the hand milled samples along with dehydrogenated final product is shown in Fig.4.13. It proves that $\text{Mg}(\text{NH}_2)_2$ and $\text{Mg}(\text{BH}_4)_2$ did not react during hand milling at RT. The only change is the amorphization of $\text{Mg}(\text{BH}_4)_2$ as confirmed by the PXRD and ATR-FTIR (see

Fig.4.14) results. All other mixtures at mentioned temperature were totally amorphous expect for the plot at 600 °C which contained MgO.

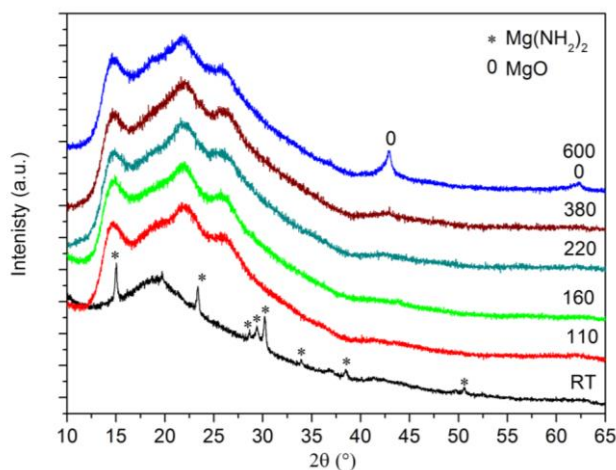


Fig.4.13 PXRD pattern of $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ in 1:1 ratio after hand mill and after hand mill and after decomposing at 110 °C, 160 °C, 220 °C, 380 °C and 600 °C.

For further investigation, the ATR-FTIR spectra of all samples obtained at different temperatures were recorded and are plotted in Fig.4.14. For specimen at room temperature, as well as at 110, the position of the B-H and N-H frequencies did not change and the extra peak at 1389 cm^{-1} is related to B-H in $\text{Mg}(\text{BH}_4)_2$ [23]. Then only difference in the sample at 110 is appearance of peak at 2080 cm^{-1} which is unique among all other specimen. The sample which is heat to 160 °C together with 220 °C the peak around 3200 cm^{-1} related to N-H is intensified extremely while the symmetric and asymmetric N-H peaks are almost disappeared. On the other hand, B-H stretching bond is splitted in to 2 contributions and one bump. The new peak is shifted to higher wavenumber in 220 °C sample rather than 160 °C one. For the sample at 380 °C all N-H stretching bonds were disappeared while B-H bending region is broadened like the sample at 110 °C. For the sample at 600 °C, a new peak is revealed at 2461 cm^{-1} which is also seen in $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$ mixture. Another new and intense peak showed up at 1368 cm^{-1} which is very similar in previous mentioned systems. As all the other mixtures at 600 °C the blend contains MgO due to oxidation.

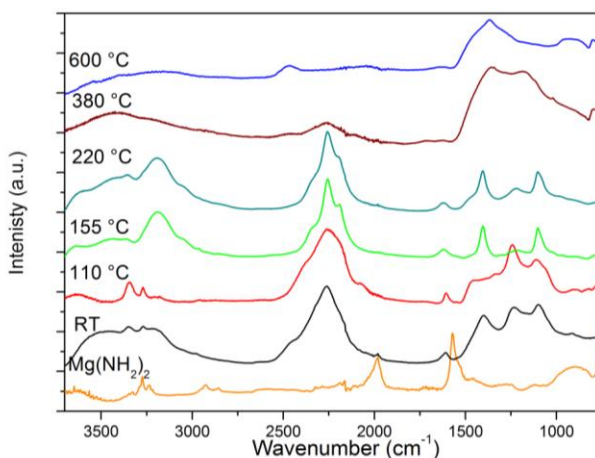


Fig.4.14 ATR-FTIR spectra for the mixture $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$.

Table 4.3 Infrared frequencies for $\text{Mg}(\text{NH}_2)_2$, $\text{Mg}(\text{BH}_4)_2$ at room temperature and $\text{Mg}(\text{BH}_4)_2$ - $\text{Mg}(\text{NH}_2)_2$ mixture at room temperature, 110 °C, 160 °C, 220 °C, 380 °C and 600 °C.

	$\text{Mg}(\text{NH}_2)_2$	$\text{Mg}(\text{BH}_4)_2$	RT	110°C	160°C	220°C	380°C	600°C
O-H		3552			3635			
$\nu(\text{N-H})_{\text{as}}$	3325		3347	3347	3359	3359		3346
$\nu(\text{N-H})_{\text{s}}$	3274		3269	3269				
	3236		3220	3204	3196	3193		
		2658						2461
$\nu(\text{B-H})$		2267	2259	2260	2256	2256	2256	
				2080	2189			
	1980		1980	1980	1980	1979	1978	1986
$\delta(\text{O-H})$			1609	1606	1622	1622		1638
$\delta(\text{N-H})$	1572							
							1358	1368
				1319			1342	
$\delta(\text{B-H})$		1259	1231	1243	1218	1220	1280	
$\delta(\text{B-H})$		1129	1100	1110	1102	1102	1018	

The results obtained from the TG/MS analysis for all $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ are summarized in Table 4.4.

Table 4.4 Comparison of all mentioned systems as well as starting materials hydrogen storage properties.

	$\text{Mg}(\text{BH}_4)_2$	LiNH_2	NaNH_2	$\text{Mg}(\text{NH}_2)_2$	$\text{1LiNH}_2\text{-1Mg}(\text{BH}_4)_2$	$\text{1NaNH}_2\text{-1Mg}(\text{BH}_4)_2$	$\text{1Mg}(\text{NH}_2)_2\text{-1Mg}(\text{BH}_4)_2$
Theoretical hydrogen content %	15	8.7	5	7	11.7	10.7	10.9
H₂ releasing steps	4	2	1	2	3	3	2
H₂ release onset temperature °C	220	320	470	300	170	250	190
Highest peak of H₂ release °C	300	510	530	360	230	480	240-260
Range of mostly H₂ released °C	220-360	-	470-550	-	200-450	450-560	200-350
Gases released except H₂	Et_2O , B_2H_6	NH_3	NH_3	NH_3	NH_3 , Et_2O , B_2H_6	NH_3 , Et_2O , B_2H_6	NH_3 , Et_2O , B_2H_6
B_2H_6 release range °C	130-300	-	-	-	40-180	270-400	60-160
NH_3 release range °C	-	230-530	400-550	300-450	80-160	150-400	60-150

4.3.2 $\text{Mg}(\text{BH}_4)_2\text{-MgBr}_2$ system

Based on methods given in chapter 2 section 2.2.2, $\text{Mg}(\text{BH}_4)_2$ mixed with MgBr_2 while MgBr_2 and NaBH_4 were ball milled in 1:2 and 1:2.15.

As can be seen in Fig.4.15, MS spectra revealed in all cases nearly 11% mass loss on heating to 600 °C. The result show that the exhaust gas is exclusively H_2 . According to figure 3b even small

amounts of MgBr_2 affects both onset temperature of H_2 release and the maximum of the peak for H_2 release. The presence of MgBr_2 shifts H_2 release temperature from 290 °C [24] or 250 °C [30] for pure $\text{Mg}(\text{BH}_4)_2$ to near to 220 °C. Another effect of 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.4.15 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 MgBr_2 ; i.e. from sample with 18 h to 6 h ball milling time. The TG curves of the two samples (Fig.4.15) show beside the above mentioned effects also a slight difference of in the total mass loss (~ 2 wt%) which can be referred to partial hydrolyses of the specimen during the transfer into the measuring cell of the DTA device.

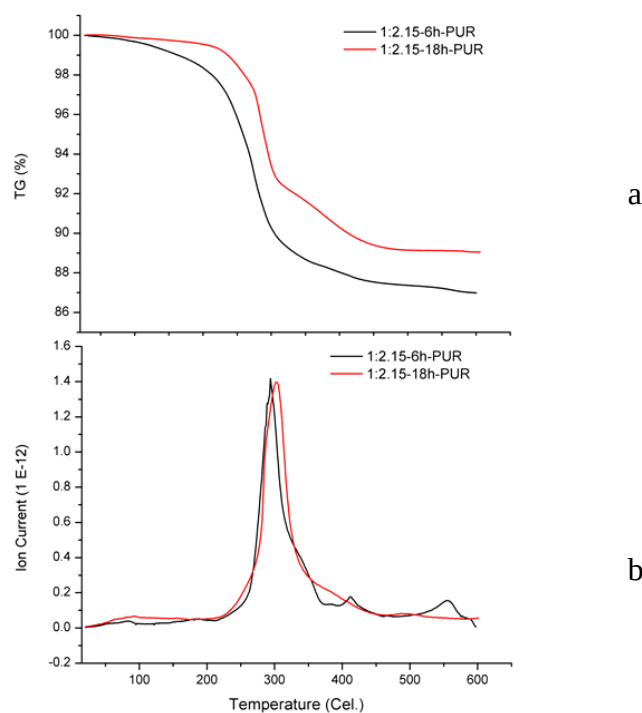


Fig.4.15 a) TG spectra of synthesized $\beta\text{-Mg}(\text{BH}_4)_2$ with 6h (red) and 18h (black) b) and MS spectra of it with 6h (red) and 18h (black) with heating rate 10 K/min under Ar flow.

4.4 Conclusion

For the systems of $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$, the decomposition pathways were predicated using PXRD, DTA-TG-MS, DSC and ATR-FTIR spectroscopy. According to TG/MS results, H_2 onset temperature for $\text{Mg}(\text{BH}_4)_2\text{-NaNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-LiNH}_2$, $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ systems are 250 °C, 170 °C and 190 °C, respectively. These values are significantly lower than those of the starting components. Moreover, NH_3 release in last two systems is highly suppressed and also the release of B_2H_6 in the latter blend is the lowest among the other systems. Interestingly, the dehydrogenation in $\text{Mg}(\text{BH}_4)_2\text{-Mg}(\text{NH}_2)_2$ mixtures occurs in two steps, unlike the other blends and pure $\text{Mg}(\text{BH}_4)_2$ which release their hydrogen in three and four steps, respectively. For the $\text{Mg}(\text{BH}_4)_2\text{-MgBr}_2$ system, MgBr_2 impurity reduces the

onset temperature of hydrogen release from 250 °C to 220 °C. On further increasing of the magnesium bromide content in the samples, the peak maximum of hydrogen release shifts towards lower temperatures.

4.5 References

1. Li, H.-W., et al., *Recent Progress in Metal Borohydrides for Hydrogen Storage*. Energies, 2011. **4**(12): p. 185-214.
2. Robert A. Varin, T.C., Zbigniew S. Wronski, *Nanomaterials for Solid State Hydrogen Storage*. 2009: Springer.
3. Nakamori, Y., et al., *Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativities: First-principles calculations and experiments*. Physical Review B, 2006. **74**(4).
4. Bardají, E.G., et al., *$\text{LiBH}_4\text{--Mg}(\text{BH}_4)_2$: A Physical Mixture of Metal Borohydrides as Hydrogen Storage Material*. The Journal of Physical Chemistry C, 2011. **115**(13): p. 6095-6101.
5. Yang, J., et al., *High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery*. Chem Soc Rev, 2010. **39**(2): p. 656-75.
6. John J. Vajo, S.L.S., Florian Mertens, *Reversible Storage of Hydrogen in Destabilized LiBH_4* . J. Phys. Chem. B, 2005. **109**(9): p. 3719–3722.
7. Soloveichik, G.L., *Metal Borohydrides as Hydrogen Storage Materials*. Material Matters, 2007. **11**.
8. Aoki, M., et al., *Destabilization of LiBH_4 by mixing with LiNH_2* . Applied Physics A, 2005. **80**(7): p. 1409-1412.
9. Acar, S., *Sodium Amide – Sodium Tetrahydridoborate System as a Potential Hydrogen Storage Material*, in *Material Science and Engineering*. 2007, Koç University.
10. Somer, M., et al., *α - and β - $\text{Na}_2[\text{BH}_4][\text{NH}_2]$: Two modifications of a complex hydride in the system $\text{NaNH}_2\text{--NaBH}_4$; syntheses, crystal structures, thermal analyses, mass and vibrational spectra*. Journal of Alloys and Compounds, 2010. **491**(1-2): p. 98-105.
11. X. B. Yu, Y.H.G., D. L. Sun, Z. X. Yang, A. Ranjbar, Z. P. Guo, H. K. Liu, and S. X. Dou, *A Combined Hydrogen Storage System of $\text{Mg}(\text{BH}_4)_2\text{--LiNH}_2$ with Favorable Dehydrogenation*. J. Phys. Chem. C, 2010. **114**: p. 4733–4737.
12. Jianfeng Mao, Z.G., Haiyan Leng, Zhu Wu, Yanhui Guo, Xuebin Yu and Huakun Liu, *Reversible Hydrogen Storage in Destabilized $\text{LiAlH}_4\text{--MgH}_2\text{--LiBH}_4$ Ternary-Hydride System Doped with TiF_3* . J. Phys. Chem. C 2010. **114**: p. 11643–11649.

13. Yang, J., et al., *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**(8): p. 2857-63.
14. Guo, Y.H., et al., *Significantly improved dehydrogenation of LiBH_4 destabilized by TiF_3* . *Energy Environ. Sci.*, 2010. **3**(4): p. 465-470.
15. Poonyayant, N., et al., *An Investigation into the Hydrogen Storage Characteristics of $\text{Ca}(\text{BH}_4)_2/\text{LiNH}_2$ and $\text{Ca}(\text{BH}_4)_2/\text{NaNH}_2$: Evidence of Intramolecular Destabilization*. *The Journal of Physical Chemistry C*, 2014. **118**(27): p. 14759-14769.
16. Vitalie Stavila, W.L., Natchapol Poonyayant, Richard Behrens, Mutlu Kartın, Leonard E. Klebanoff, *Improvement of Hydrogen Storage Properties of Complex Metal Hydrides Through Hydridic-Protic Interactions*, in *WHEC-2012*. 2012: Toronto, Canada
17. Chater, P.A., et al., *Synthesis and characterization of amide-borohydrides: New complex light hydrides for potential hydrogen storage*. *Journal of Alloys and Compounds*, 2007. **446-447**: p. 350-354.
18. Jepsen, L.H., et al., *Boron-nitrogen based hydrides and reactive composites for hydrogen storage*. *Materials Today*, 2014. **17**(3): p. 129-135.
19. Kersting, A.L., *Light Metal Amides and Imides For Hydrogen Storage*, in *The School of Chemistry*. 2011, The University of Birmingham.
20. Wu, C., et al., *Characterizations of composite $\text{NaNH}_2\text{-NaBH}_4$ hydrogen storage materials synthesized via ball milling*. *International Journal of Hydrogen Energy*, 2012. **37**(1): p. 889-893.
21. Eagleson, M., *Concise Encyclopedia Chemistry*. 1993: deGruyter.
22. David, W.I., et al., *Hydrogen production from ammonia using sodium amide*. *J Am Chem Soc*, 2014. **136**(38): p. 13082-5.
23. Pearson, R.G., *Hard and Soft Acids and Bases*. *Journal of the American Chemical Society*, 1963 **85** (22): p. 3533-3539.
24. Chłopek, K., et al., *Synthesis and properties of magnesium tetrahydroborate, $\text{Mg}(\text{BH}_4)_2$* . *Journal of Materials Chemistry*, 2007. **17**(33): p. 3496.
25. Song, A.L.a.Y., *In Situ High-Pressure Study of Sodium Amide by Raman and Infrared Spectroscopies*. *J. Phys. Chem. B*, 2011. **115**: p. 7-13.
26. Busing, W.R., *Infrared Spectra and Structure of NaOH and NaOD* . *The Journal of Chemical Physics*, 1955. **23**(5): p. 933.
27. Chu, H., et al., *Improved dehydrogenation properties of $\text{Ca}(\text{BH}_4)_2\text{-LiNH}_2$ combined system*. *Dalton Trans*, 2010. **39**(44): p. 10585-7.
28. Yu, X.B., D.M. Grant, and G.S. Walker, *A new dehydrogenation mechanism for reversible multicomponent borohydride systems--The role of Li-Mg alloys*. *Chem Commun (Camb)*, 2006(37): p. 3906-8.
29. Noritake, T., et al., *Synthesis and crystal structure analysis of complex hydride $\text{Mg}(\text{BH}_4)(\text{NH}_2)$* . *International Journal of Hydrogen Energy*, 2013. **38**(16): p. 6730-6735.

-
30. Soloveichik, G.L., et al., *Magnesium borohydride as a hydrogen storage material: Synthesis of unsolvated $\text{Mg}(\text{BH}_4)_2$* . International Journal of Hydrogen Energy, 2009. **34**(5): p. 2144-2152.

Chapter 5

Superconductivity and MgB_2

5.1 Superconductivity

There have been noticeable interests on the superconducting materials since 1980s. The main property of these materials is that when they are cooled below a value which is called “critical temperature” they show zero electrical resistance. However, productions of superconductors were quite expensive and complicated. Also, the need for liquefied helium for the cooling process enhances the operational costs. In 1911, this phenomenon was first discovered by the Dutch physicist Heike Kimberling Onnes, during his research on the resistance of metals low temperatures. More than 20 metallic elements and certain semiconductors and many alloys can become superconductors under suitable conditions such as by applying high pressure or, by the specimen in very thin films. A superconductor does not oppose any resistance to the current flow, as if it had no measurable DC electrical resistivity. Superconductivity is a quantum mechanical phenomenon that is characterized by Meissner effect. Until 1950s, there was not any consistent microscopic theory, except the macroscopic theories that allowed you to calculate certain quantities. In 1957, Bardeen, Cooper and Schrieffer described the conceptual and mathematical foundation for superconductivity in the Bardeen-Cooper-Schrieffer (BSC) theory, for which they received the Nobel Prize in 1972 [1].

5.1.1 Critical Temperature (T_c)

Transition to superconducting state occurs abruptly at a critical temperature, T_c , which is a characteristic of the specific metal. Measured critical temperatures range from a few mill degrees Kelvin to over 20 K [2].

5.1.2 Meissner Effect

In 1933, Walter Meissner and Robert Ochsenfeld discovered a magnetic phenomenon showed that all superconductors are diamagnets. This phenomenon can be explained with a thought experiment. Imagine both the ideal conductor and superconductor are above their critical temperature, T_c . Means, they both are in normal conduction state and have electrical resistance. A magnetic field (B_a) is then applied, which results in field penetrating in both materials (Fig 5.1 a). Then both samples are cooled until the ideal conductor have zero resistance. Surprisingly, it is found that while superconductor expels the magnetic field from inside it, the ideal conductor maintains its interior field (Fig 5.1 b). The interesting remark to the point is that; to expel the magnetic field, additional energy is needed by the superconductor. This energy comes from the exothermic superconducting transition. Switching off the field induces currents in the ideal conductor that prevent changes in the magnetic field inside it (Lenz's Law), while the superconductor returns to its initial state that is no magnetic field inside or outside, which proves diamagnetic behavior of superconductors (Fig 5.1c) [2, 3].

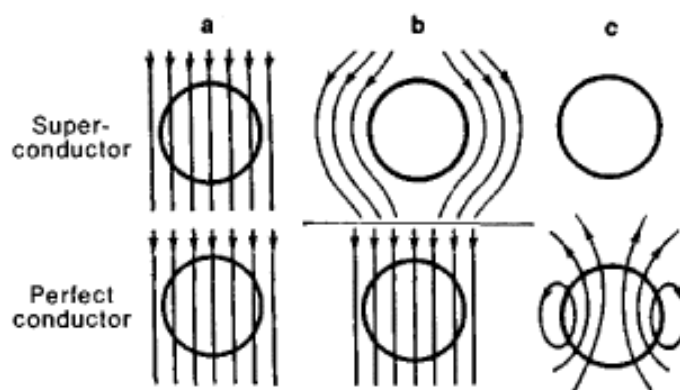


Fig 5.1 Meissner effect [2].

High magnetic fields would destroy superconductivity of a material and restore the normal conducting state. Superconductors that undergo this sudden transition to the normal state above a critical magnetic field are known as *type-I superconductors*. Internal magnetic field strength B_i (H_i), stays at zero till a critical magnetic field, B_c , is reached where an abrupt transition to the normal state occurs (as expected from Meissner effect) (Fig 5.2(a)). Most of the pure elements tend to be type I superconductor. *Type-II* superconductors give a different response to applied magnetic field. An increased applied magnetic field results in two critical field points, B_{c1} (H_{c1}) and B_{c2} (H_{c2}) (Fig 5.2 b). At B_{c1} the superconductor state occurs while the superconductivity vanishes above the second critical point, B_{c2} . Since for the applied fields between B_{c1} and B_{c2} , applied magnetic field partially penetrates into superconductor, this allows superconductor to resist very high magnetic fields. Type-II superconductors find application in technological materials since high second critical field enables high field electromagnets to be made out of superconducting wire. Most of the compounds are type-II superconductor [2].

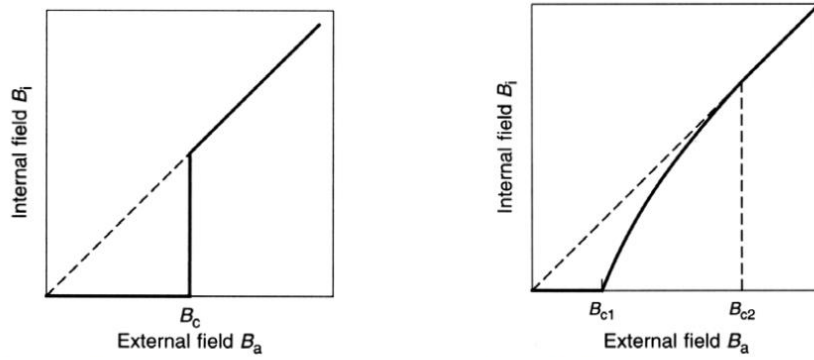


Fig 5.2 (a) Type-I, (b) Type-II superconductor behavior [2].

5.1.3 Vortex states and flux pinning:

A well-known demonstration of the Meissner effect can be demonstrated by cooling a high T_c superconductor ($\text{YBa}_2\text{Cu}_3\text{O}_7$), then placing a small and strong permanent magnet on top of it. This experiment results in levitation of the magnet on the superconductor. Stable and robust levitation only occurs for type-II superconductors, since there is a partial penetration of the magnetic field for them. This partial penetration of the magnetic field is in the form of a regular array of normal conducting regions (Fig 5.3). These regular arrays allow penetration of the magnetic field in the form of thin filaments, named flux lines or vortices. Each vortex of electrical current is associated with its state. Vortex regions are filaments shows non-superconducting property when an external applied magnetic field exceeds the lower critical value, B_{c1} . Then, as the external field strength increases, the number vortex states increase until the field reaches the upper critical value, B_{c2} . After this point, the vortex states gathers and the entire sample turns into normal [2].

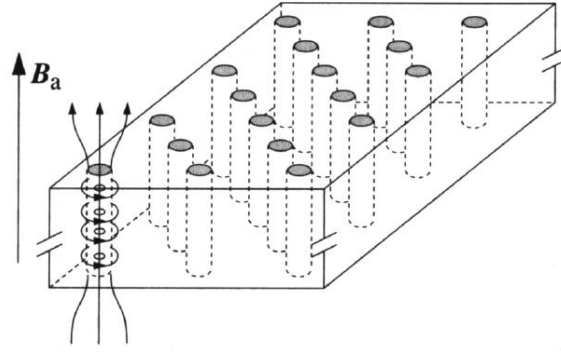


Fig 5.3 Vortices (dark regions) in a type-II superconductor [2].

In practice, materials have defects in their crystal structures. These point defects and grain boundaries stop the motion of the vortices, which is known as flux pinning. This enables stable levitated magnet [2].

5.1.4 BSC Theory

Several scattering mechanisms contribute to the resistivity of normal conductors which includes electron scattering from phonons and scatterings from impurities, surface roughness's and grain boundaries. However, these scatterings do not happen in superconductors. the microscopic theory of this behaviour was explained in BSC theory. The central idea of the BSC theory relies on the assumption that superconductivity forms if the Copper pair interaction dominates over the repulsive Coulomb force. Two electrons in the superconductor are able to form a bound pair called a copper pair if an attractive interaction forms between them, which is contrary to the general rule of repelling force between two like charges. Copper pair is a weak electron-electron bound pair and it can be formed in only very low temperatures. When an electron moving within a crystal lattice, positive ions are attracted to it, which distorts their position by the Coulomb attraction and leave positive charge in the vicinity of its nominal position of ion. Then, the second electron with opposite momentum and spin is attracted to this force. The interaction between a Copper pair is transient, means each electron in the pair continues to form a Copper pair with other electrons. As a result each electron in the solid

attracted to the every other electron and a large network of interaction is developed. This collection of electrons in the solid inhibits any possible collision with the lattice [2, 3].

5.1.5 High- T_c superconductors

The material that is mostly used in laboratory was discovered in 1986 by Bednorz and Müller, which they received Nobel Prize for it. This material is Yttrium-Barium-Copper Oxide, or $\text{YBa}_2\text{Cu}_3\text{O}_7$, which is known as the 1-2-3 superconductor is classified as high temperature (T_c) superconductors. Critical temperatures as high as 135 K have been achieved [3].

5.2 Magnesium diboride (MgB_2)

Magnesium diboride (MgB_2) is a simple binary compound which is its composition and its crystal structure is known since 1953 [4] and followed by other group in 1954 [5]. However, the discovery of its superconducting behavior in 2001 [6] made it an interesting compound in superconducting applications.

MgB_2 has a hexagonal crystal structure (AlB_2 type, space group $P6/mmm$) which is typical among most of diborides and lattice parameters of $a = 3.0849 \text{ \AA}$ and $c = 3.5187 \text{ \AA}$ [7, 8]. In its structure, boron honeycomb sheets are located in between Mg triangular sheets [9]. There are three different types of bonding present in MgB_2 , B-B, Mg-Mg and Mg-B. The two-band nature in MgB_2 arises from B-B bonding [10]. In-plane B-B bonds form 2D graphite-like honeycombed layers due to the strong covalent bonds with localized holes which they give rise to σ band. The out-plane B-B are separated by magnesium atoms which forms quasi 3D bonds with more metallic character having delocalized holes and electrons which makes π bonds [8, 11]. Crystal structure of MgB_2 is shown in Fig 5.4 [8, 12]. For superconductivity, σ -bands are more important as they have the unfilled sites which experience strong interaction with longitudinal vibrations present in the B layers.

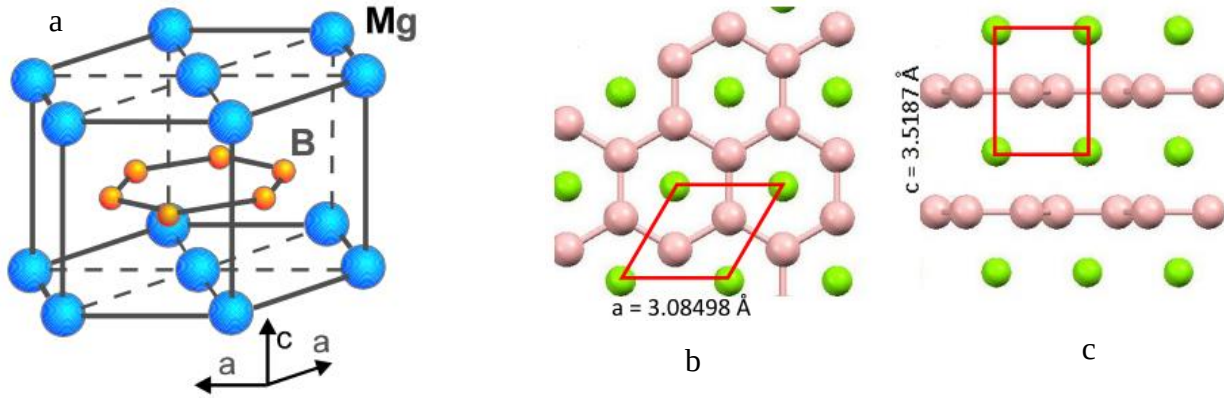


Fig 5.4 (a) Crystal structure of MgB₂ (b) MgB₂ structure through a and c views.

MgB₂ superconductivity is because of metallic nature of 2D boron sheets and mechanism is described as a phonon mediated BCS type mechanism [9]. MgB₂ is a type II superconductor, i.e. increasing magnetic field gradually penetrates through it, gradually vanish, as well It has the lowest normal state electrical resistivity of all known superconductors: $\rho_0 = 0.2 \text{ m}\Omega\text{cm}$. Moreover, MgB₂ has long coherence length (5.23 nm) leads to remove the problem that usually high T_c materials have, which is weak link [13]. MgB₂ also has a low mass density which makes its fabrication convenient [14].

Commercial applications employ, “in situ” and “ex situ” fabrication methods for MgB₂. In the in situ method, starting materials are mixed and form into desire shape (wire, tape or pellet) and being heat-treated under inert atmosphere afterward [15]. In the ex situ production method already synthesized MgB₂ is used to form the sample into wanted shape [16].

Critical current density (J_c), critical magnetic field (H_c) (upper critical field (H_{c2}), irreversibility field (H_{irr})) and T_c are parameters determine the basic superconducting characteristics of any superconductive material. Although MgB₂ benefits from high T_c value it has poor pinning, low critical current density and low H_{c2} at high magnetic fields. In other word, the main practical problem in MgB₂ is that J_c will drop with increasing magnetic field due to poor flux pinning and low upper critical field (H_{c2}) [17, 18].

There are two terms related to superconductive properties of MgB₂ which are ‘intrinsic’ and ‘extrinsic’ properties [19]. Intrinsic properties of polycrystalline MgB₂ are H_{c2} and flux pinning while extrinsic properties includes connectivity and porosity. By enhancing in any of this intrinsic and or/ extrinsic enhancement of MgB₂ superconductor can be achieved [20].

Ex situ MgB₂, usually suffer from poor grain conductivity which has a negative effect on critical current density. It is reported that this can be improved by decreasing MgB₂ grain size, carbon doping and presence of small amount of nanosized-MgO [12, 21, 22]. It is reported that finer grain which are usually produce by high energy planetary ball mill results in higher grain boundaries and will act as pinning centers and leads to higher J_c [23, 24].

5.2.1 MgO role in MgB₂

According to Kim, J.H., et al.[25] report, MgO formation can have two sources : (1) the presence of MgO in the starting powder as Mg could act as an oxygen getter in air with reaction of $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$; and (2) the reaction of melted B₂O₃ at around 450 C with Mg to form MgO, $3\text{Mg(s)} + \text{B}_2\text{O}_3\text{(s)} \rightarrow 3\text{MgO(s)} + 2\text{B(s)}$. Based on their investigation, first reaction has much greater contribution to MgO formation, as sintering in different temperature did not change amount of MgO in final product. This is because Mg is a very active material that is very easy to oxidize in air. In addition, Takahashi, M., et al.[26] mentioned that finer Mg particles leads to larger oxidation surface area and this increase the MgO formation.

Different amount of MgO along with MgB₂ can make a difference in transport and magnetic properties. Singh, D.K., et al.[27] have measure magnetization of MgB₂ sample having near to 40% MgO and MgB₂ sample having around 8% MgO. For MgB₂ with higher amount of MgO broad superconducting transition at around 37.1 K with paramagnetic miser effect is observed and for sample with less MgO sharp diamagnetic transition at 38.8K is seen and magnetization remain almost constant in temperature range of 35-20K. Cui, C., et al., also reported that higher MgO will lead to lower T_c in MgB₂ [28]. They also saw inhomogeneous flux distribution in sample with high MgO. H_{irr} did not change much (6T for pure and 5.5T for not pure) but

magnetization value in pure one was 50 times higher than other one. Moreover, high percentage of MgO made sample too insulation to carry out resistivity measurement. It means that MgO layer is present between MgB₂ grains, which forbid the direct connectivity between MgB₂ grains. Hon, W.M. et al. [29] found from XRD and DTA results that MgO formation is happening before reaction of Mg and B. This newly formed MgO probably acted as nucleation sites for the growth of MgB₂, they attached to the MgB₂ platelets. The presence of MgO would reduce the volume fraction of MgB₂ phases, as a result, downgrading the quality of the superconducting behaviors and suppressing the magnetization loops. Sintering at higher temperature increase particle size and fraction of impurities attached to particles will reduce and will leads to higher T_c and H_c and lager magnetization loop. Perner, O., et al. [30] mentioned that it's very important that avoid weak link behavior at grain boundaries due to non-superconducting surface layer of MgO. Poor connectivity between grains will reduce J_c. Also, Jiang, C.H. et al. [31] reported small amount of nano-MgO (10 nm) (less than 2.5wt%) could increase J_c through enhancing grain connectivity and core density. For 5 wt% MgO sample they have showed the best J_c-B performance at high temperature (20K and 30K) and higher magnetic field which indicate MgO can act as flux pinning centers. Ková, P., et al. [32] also confirmed above statement on role of MgO and they have mentioned that the level of MgO should be optimized as a compromise between inter-grain connectivity and introducing pinning centers.

5.2.2 Doping effect in MgB₂

It is reported that defects in the MgB₂ structure will decrease the mean free path of the normal electrons then decreasing the coherence length ξ and accordingly increasing the H_{c2} values which is a limiting factor in MgB₂. Moreover, defects will introduce pinning centers in order to make the irreversibility line steeper [13]. On the other hand, it has been shown that doping in MgB₂ will decrease T_c. For e.g. superconductivity of Al doped sample would disappear when around half of Mg are replaced by Al. It was mentioned that two different effects lead to a T_c reduction as Al substitution is increasing: a) a positive pressure effect—due to the smaller Al ionic

radius—and b) the increased number of electrons contributed by Al [33, 34]. On the other hand, replacing Mg²⁺ by Al³⁺ will increase the population of the electrons in the two-dimensional (2D) σ -band. Therefore, substitution of Mg by Al will fill the σ -band completely even before a 100% substitution level. In this situation, only the π -band will take part in various physical processes so the system will no longer be a two-band (σ -band and π -band) system [35]. Amount of doping is related to changing in T_c value. It is reported that light doping of C as well as Al (up to 2.5%) will keep T_c unchanged while increase J_c by the factor of 2 [36].

In the carbon doping, the carbon which stays at the grain boundary or at interstitial site can act as a pinning center (extrinsic pinning) and hence helps in enhancing the H_{c2} , H_{irr} , and J_c values. Additionally, the carbon into the structure creates disorder in the sigma band and causes intrinsic pinning to enhance the critical parameters. Therefore, doping carbon causes extrinsic/intrinsic pinning through additions/substitution and enhances the superconducting performance of MgB₂ both ways [37].

5.2.3 Effect of strain and defect in MgB₂

Impurities and defects are known to alter superconductivity properties such as T_c and J_c crucially. In s-wave BCS materials (e.g. MgB₂, electron pair travel together in spherical orbits), London penetration depth, λ , (the distance in which field is decrease to 1/e times of applied field) and coherence length, ζ , (the size of cooper pair which the shortest distance which superconductivity can form in the materials) [38-41]. Serquis et.al.[42] have shown that increasing in lattice strain which is caused by Mg vacancies or MgO existence inside of MgB₂ grains leads to reduction in the T_c [42, 43]. Mg vacancies will be point defect and MgO particles can generate dislocation which are line defects.

5.3 References

1. van Delft, D.K., P., *The discovery of superconductivity*. Phys. Today, 2010. **63**: p. 38–43.
2. Ashcroft, N.W., Mermin N.D., *Solid State Physics*. 1976: Saunders College Publishing.

3. Wesche, R., *The Superconducting State*, in *Physical Properties of High-Temperature Superconductors*. 2015, John Wiley & Sons, Ltd. p. 13-44.
4. V. Russell, R.H., F. A. Kanda and A. J. King, *An X-ray study of the magnesium borides*. Acta Crystallographica, 1953. **6**.
5. M. E. Jones and R. E. Marsh, *Preparation and structure of magnesium boride, MgB_2* . J. Am. Chem. Soc, 1954. **76**: p. 1434–6.
6. Nagamatsu, J., et al., *Superconductivity at 39 K in magnesium diboride*. Nature, 2001. **410**(6824): p. 63-64.
7. Janiche, W.H.a.W., *The structural type of aluminum boride (AlB_2)*. Naturwissenschaften, 1935. **23**.
8. Susner, M.A., *Influences of Crystalline Anisotropy, Doping, Porosity, and Connectivity on the Critical Current Densities of Superconducting Magnesium Diboride Bulks, Wires, and Thin Films in Materials Science and Engineering 2012*, The Ohio State University.
9. Nishibori, E., et al., *Bonding Nature in MgB_2* . Journal of the Physical Society of Japan, 2001. **70**(8): p. 2252-2254.
10. Kortus, J., et al., *Superconductivity of Metallic Boron in MgB_2* . Physical Review Letters, 2001. **86**(20): p. 4656-4659.
11. Xi, X.X., *Two-band superconductor magnesium diboride*. Reports on Progress in Physics, 2008. **71**(11): p. 116501.
12. Buzea, C. and T. Yamashita, *Review of the superconducting properties of MgB_2* . Superconductor Science & Technology, 2001. **14**(11): p. R115-R146.
13. MR Cimberle, M., PManfrinetti and A Palenzona, *Magnetic characterization of sintered MgB_2 samples effect of substitution or 'doping' with Li, Al and Si*. SUPERCONDUCTOR SCIENCE AND TECHNOLOGY, 2002. **15**: p. 43-47.
14. Schmidt, J., et al., *Pulse plasma synthesis and chemical bonding in magnesium diboride*. Solid State Sciences, 2003. **5**(4): p. 535-539.
15. H. Kumakura, A.M., H. Kitaguchi and H. Hatakeyama, *Critical Current Densities of Powder-In-Tube (PIT)-Processed MgB_2 Tapes*. Materials Transactions, 2004. **45**: p. 3056-3059.
16. Kovac, P.H., I.; Meligek, T.; Grivel, Jean-Claude; Pachla, W.; Strbik, V.; Diduszko, R.; Homeyer, J.; Andersen, N.H., *The role of MgO content in ex situ MgB_2 wires*. Superconductor Science & Technology, 2004. **17**: p. L41-L46.
17. Ghorbani, S.R., et al., *Flux pinning mechanism in SiC and nano-C doped MgB_2 : evidence for transformation from δT_{c0} to δI_{pn}* . Superconductor Science and Technology, 2014. **27**(12): p. 125003.
18. Arpita, V., et al., *Superconductivity of the bulk MgB_2 + nano(n)-SiC composite system: a high field magnetization study*. Nanotechnology, 2008. **19**(12): p. 125708.
19. Collings, E.W., et al., *Prospects for improving the intrinsic and extrinsic properties of magnesium diboride superconducting strands*. Superconductor Science and Technology, 2008. **21**(10): p. 103001.
20. Prikhna, T.A., *Properties of MgB_2 bulk*. Condensed Matter - Superconductivity, 2009.
21. Ivanovskii, A.L., *Band structure and properties of superconducting MgB_2 and related compounds (a review)*. Physics of the Solid State, 2003. **45**(10): p. 1829-1859.

22. Yanson, I.K. and Y.G. Naidyuk, *Advances in point-contact spectroscopy: two-band superconductor MgB_2 (Review)*. Low Temperature Physics, 2004. **30**(4): p. 261-274.
23. Varin, R.A. and C. Chiu, *Synthesis of nanocrystalline magnesium diboride (MgB_2) metallic superconductor by mechano-chemical reaction and post-annealing*. Journal of Alloys and Compounds, 2006. **407**(1-2): p. 268-273.
24. A Kario, R.N., W Häßler, C Rodig, C Mickel, W Goldacker, B Holzapfel and L Schultz, *Critical current density enhancement in strongly reactive ex situ MgB_2 bulk and tapes prepared by high energy milling*. Superconductor Science and Technology, 2011. **24**.
25. Kim, J.H., et al., *The effects of sintering temperature on superconductivity in MgB_2/Fe wires*. Superconductor Science and Technology, 2007. **20**(5): p. 448-451.
26. Takahashi, M., et al., *The influence of magnesium grain size and ball milling time on the phase formation of MgB_2 tapes*. Superconductor Science and Technology, 2009. **22**(12): p. 125017.
27. Singh, D.K., et al., *Role of MgO impurity on the superconducting properties of MgB_2* . Physica C: Superconductivity, 2014.
28. Cui, C., et al., *Nanoparticles of the superconductor MgB_2 : structural characterization and in situ study of synthesis kinetics*. Acta Materialia, 2004. **52**(20): p. 5757-5760.
29. Hon, W.M. and D.H.L. Ng, *Relationships between microstructure and superconducting behaviors of MgB_2* . Journal of Applied Physics, 2006. **99**(8): p. 08M502.
30. Perner, O., et al., *Microstructure and impurity dependence in mechanically alloyed nanocrystalline MgB_2 superconductors*. Superconductor Science and Technology, 2004. **17**(10): p. 1148-1153.
31. Jiang, C.H., H. Hatakeyama, and H. Kumakura, *Effect of nanometer MgO addition on the in situ PIT processed MgB_2/Fe tapes*. Physica C: Superconductivity, 2005. **423**(1-2): p. 45-50.
32. Ková, P., et al., *The role of MgO content in ex situ MgB_2 wires*. Superconductor Science and Technology, 2004. **17**(10): p. L41-L46.
33. Profeta, G., A. Continenza, and S. Massidda, *Phonon and electron-phonon renormalization in Al-doped MgB_2* . Physical Review B, 2003. **68**(14).
34. de la Peña, O., A. Aguayo, and R. de Coss, *Effects of Al doping on the structural and electronic properties of $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$* . Physical Review B, 2002. **66**(1).
35. Mudgel, M., et al., *Anomalous thermoelectric power of the $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ system with $x = 0.0-1.0$* . Journal of Physics: Condensed Matter, 2008. **20**(9): p. 095205.
36. Berenov, A., et al., *Enhancement of critical current density in low level Al-doped MgB_2* . Superconductor Science and Technology, 2004. **17**(10): p. 1093-1096.
37. Mudgel, M., et al., *Enhanced critical parameters of nanocarbon doped MgB_2 superconductor*. Journal of Applied Physics, 2009. **106**(3): p. 033904.
38. Alloul, H., et al., *Defects in correlated metals and superconductors*. Reviews of Modern Physics, 2009. **81**(1): p. 45-108.
39. Sharoni, A., I. Felner, and O. Millo, *Tunneling spectroscopy and magnetization measurements of the superconducting properties of MgB_2* . Physical Review B, 2001. **63**(22).
40. Raveau, B., *Defects and Superconductivity in Layered Cuprates*. Physics Today, 1992. **45**(10): p. 53.
41. Xue, Y.Y., et al., *Nonstoichiometry, defects and transport properties in MgB_2* . Physica C- Superconductivity and Its Applications, 2002. **377**(1-2): p. 7-14.

-
42. Serquis, A., et al., *Effect of lattice strain and defects on the superconductivity of MgB_2* . Applied Physics Letters, 2001. **79**(26): p. 4399.
 43. Y. Zhua, L.W., V. Volkova, Q. Lia, G. Gub, A.R. Moodenbaugh, M. Malaca, M. Suenagaa, J. Tranquadab, *Microstructure and structural defects in MgB_2 superconductor*. Physica C: Superconductivity, 2001. **356**: p. 239–253.

Chapter 6

Defect structure of ultrafine MgB₂ Nanoparticles

6.1 Introduction

Current research interest in MgB₂ is motivated by novel wire or coil applications such as magnetic-resonance imaging (MRI) magnets operating at cryogenic temperatures [1-4], maglev transport [5, 6], power transmission lines [7, 8], high-speed, high-sensitivity and low-voltage sensors [9], low-cost and high-efficiency offshore wind turbines for clean energy future [10], and other renewable energy devices such as 2nd generation superconductor wires and coils [8, 11]. Very recently, a world-record electric-current flow (more than 3 MA) from a power converter to magnets has been achieved in CERN's LHC particle accelerator by using MgB₂ transmission cables [12]. MgB₂ is also a promising candidate material for a feedback coil, which is an important component for plasma confinement [13] due to its relatively high critical transition temperature (T_c) about 39 K [14]. These applications exploit the two band superconducting properties of MgB₂, which results relatively high critical current density (J_c) and critical magnetic field (H_c) (at low magnetic field). Details on practical applications of MgB₂-based wires can be found in a recent review article [2].

There are different methods for ex situ synthesizing MgB₂ such as high temperature heat treatment [15] pulse plasma technique [16] and self-propagating high-temperature synthesis (SHS) [17]. One can find more details about the different synthesis techniques of the compound MgB₂ in an outstanding review article [18]. However, the simplest ex situ synthesis method for MgB₂ would be heating treating the mixture of Mg and B at high temperature, up to 850 °C in Ar atmosphere. This high reaction temperature for synthesis of MgB₂ is due to the strong Boron-

Boron bonds in elemental boron ($\Delta H_{B(s) \rightarrow B(g)} = 560 \text{ KJ/mole}$). Typically, there are two main difficulties in MgB₂ synthesis using this method which are tendency of Mg to react with their environment (specially oxygen) at high temperature, and Mg volatility which may cause loss of mass and result in Mg-poor phases such as MgB₄ [19].

Despite the interesting studies over last decades, there are still controversy in various properties and particularly the defect structure of undoped MgB₂. It has been emphasized that the disorderness such as defects strongly changes the properties of the MgB₂ [5]. Another critical issue is the confinement of the crystallite or particle size to the nano-dimension. Although metal ion or recently popular carbon doping and compound morphology play a decisive role to control materials properties, the synthesis method defines an additional, most crucial role that markedly impacts nature and amount of intrinsic defects and/or impurities.

In this work, the defect structure of bulk and nanosized undoped MgB₂ materials and their active role in material properties will be investigated by the aid of electron paramagnetic resonance (EPR) spectroscopy. EPR is well suited for this task since it provides a direct method to monitor different paramagnetic states of vacancies and, thus, complements other experimental techniques such as powder X-ray diffraction (PXRD) and scanning/transmission electron microscopy (SEM/TEM) microscopy. In this sense, EPR does not only work very well on the identification of paramagnetically active intrinsic defects but also one may obtain reliable correlation to the structural and electronic properties of MgB₂. So far very limited works have been presented for investigating the defect structure by the aid of EPR. Most of the works [20-25] have been dealt with the superconducting critical transition temperature or spin susceptibility at low temperatures. Thus the defect structure of the pure MgB₂ at room temperature remained unclear. Things become more complicated and controversial when the crystallite size is scaled to the nano-dimension. Such particles have their size and defect related, special characteristics and may show enhanced functionalities.

6.2 Experimental procedure

Both bulk and nanosized MgB_2 samples were prepared by using well-known solid state synthesis techniques. For the bulk and nano specimen we utilized as starting powders Mg (99.8 %) and amorphous boron 95 (B95-97 %), as well as Mg (99.8 %) and amorphous nanoboron (B > 98.5 %), respectively. All reactant powders were received from the Turkish company Pavezyum Kimya, Istanbul. A typical reaction mixture contained a total of 1 g of Mg and B (molar ratio 1:2) powders which were grinded with a mortar and pestle for 15 min in open air. For both samples, pellets with 13 mm diameter are pressed using hydraulic press by 10 t/cm². The pellets were placed into small metal sample holders and then heated in a tube furnace under Ar flow within 1.5 h to 700 °C, annealed for 2 h and then quenched to room temperature. All products of the heat treatment were analyzed using PXRD method. PXRDs were measured with BRUKER D2 Phaser diffractometer (Cu-K α_1 radiation (0.1540 nm) with LYNXEYETM detector). The lattice parameters of the two MgB_2 samples were refined using Rietveld method. The quantitative phase analyses of the products were performed employing the TOPAS software. SEM images of powders were taken with Zeiss Ultra Plus FE-SEM at 2 kV accelerating voltage. LEO 912 Omega transmission electron microscopy (TEM) instrument were used with an accelerated voltage of 120 kV. TEM samples were prepared by dispersing the powder in dilute ethanol medium under ultrasonic agitation. A drop of the suspension was placed on a carbon coated one mesh copper grid (EMS CF200-Cu). X-band (9.86 GHz) cw-EPR measurements were performed with Bruker EMX spectrometer. We have used cylindrical super-high-quality (SHQ) resonator from Bruker. The offset in the magnetic field and the exact g-factors in X-band measurements were determined with a polycrystalline DPPH (2-diphenyl-1-picrylhydrazyl) reference sample with well-known g-factor ($g = 2.0036$). The EPR spectral analysis has been performed using the WINEPR program from Bruker.

6.3 Results and Discussion

PXRD patterns of both bulk and nanosized MgB_2 are shown in Fig 6.1. In both, MgB_2 and MgO are the final products. Mg deficient borides, such as MgB_4 , MgB_{12} etc. was not present. Only in bulk MgB_2 a small amount of excess Mg was detected. This can be referred to either not sufficient reaction temperature or too short dwell time of heat treatment for Mg and boron 95 to react. From Rietveld analysis the lattice parameters a - and c - for nanosized and bulk MgB_2 were calculated as 3.09036(6) Å and 3.5286(1) Å and 3.08856(5) Å and 3.5267(1) Å respectively. The quantitative Rietveld analysis showed MgB_2 (93.61 %), MgO (4.85 %) and Mg (1.54 %) for bulk) and MgB_2 (96.38 %) and MgO (3.62 %) for nanosized MgB_2 . The analysis also reveals that MgO contamination in nanosized MgB_2 is around 1.3 % less than in the bulk one. It has been reported that the reduction of MgO strongly increases the connectivity in MgB_2 [26]. On the other hand, there are many attempts to remove the EPR inactive MgO from MgB_2 material however these methods only reached success for a certain amount of reduction of MgO [27-29]. Indeed the reduction of MgO amount without any chemical modification, i.e., chemical etching (see ref. [30] and references there in) is very interesting result. By only changing, the starting material to nanoboron and it is observed that the amount of MgO was reduced compared to bulk boron. However, in our preparation route it is also not possible to remove MgO completely by annealing.

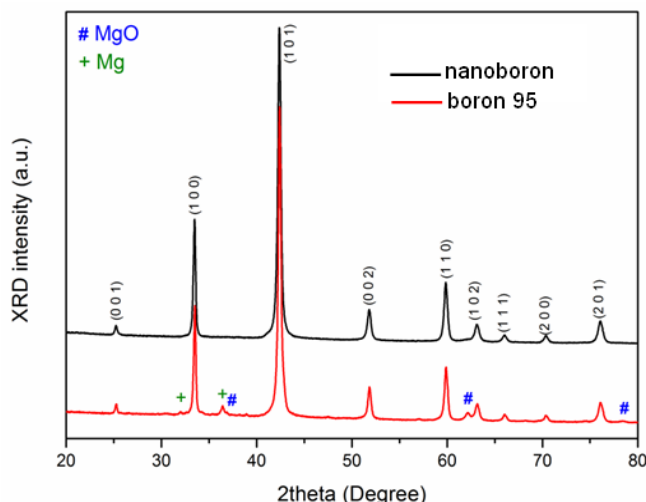


Fig 6.1 PXRD patterns of bulk and nanosized MgB_2 synthesized with the reactant powders boron 95 (red) and nanoboron (black), respectively. Diffractions from MgO and Mg in boron 95 (bulk) sample are indicated by the symbols # and +, respectively.

Fig 6.2 (a-d) is showing the SEM images of nanoboron, Mg powder, manually grinded Mg with boron 95 and nanoboron powders for 15 min. As depicted in Fig 6.2 c the Mg and B particles are spatially separated from each other. Magnified image of one of the Mg particles clearly reveals that Mg is only partially covered with the boron 95. In contrast, Mg particles grinded with nanoboron are almost completely “coated” (Fig 6.2 d). In addition, mixtures containing nanoboron tend to more agglomeration than those with boron 95. The reason might be the ultrafine size and the higher surface energy of the nanoboron particles, spreading more readily and uniformly over the surface of the Mg particles. Moreover, the wetting ability of nanoboron may reduce the diffusion length and enhance the reaction rate. The result is a complete reaction at considerably lower temperatures. Probably, the unreacted Mg detected in bulk- MgB_2 originates from this fact, meaning that 700°C is not sufficient for a complete reaction of Mg with boron 95.

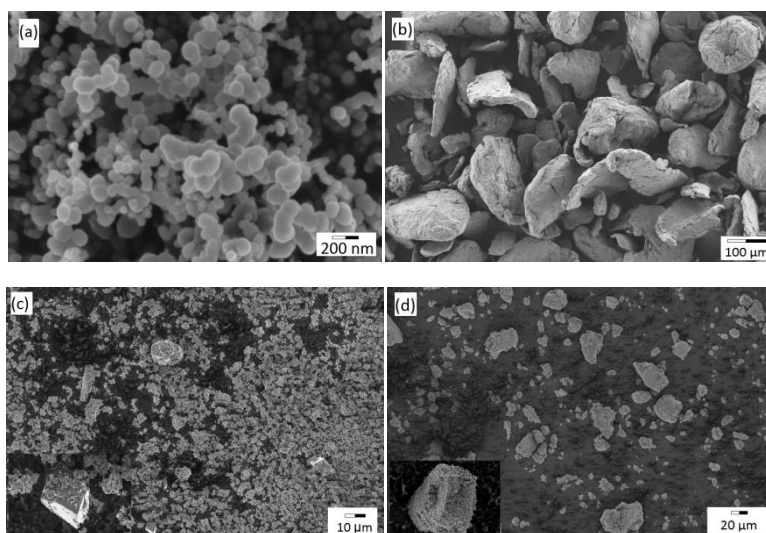


Fig 6.2 SEM images of (a) as received nanoboron, (b) as received Mg, (c) manually grinded mixture of boron 95 and Mg, (d) manually grinded mixture of nanoboron and Mg.

SEM and TEM images of MgB_2 microstructure synthesized from boron 95 and nanoboron powders are shown in Fig 6.3 (a-d). In bulk MgB_2 prismatic and well-shaped hexagonal crystals are clearly seen from the SEM images whose particles sizes using image analysis tools are in the range of 100-400 nm. Plate like and poor crystallized moieties can be well distinguished in nanosized MgB_2 . Low crystallinity might be related to higher amorphous content of the particles with a mean size of 50-250 nm. Furthermore, the Fig 6.3 a and c reveals that the particles of the nanosized MgB_2 are more uniform and smaller compared to those of bulk MgB_2 shown in Fig 6.3 b and d. The reason of the different particle sizes in the two MgB_2 samples is closely related to the material properties of the starting B powders. In nanoboron all particles are < 250 nm (50-250 nm) and has a similar particle size distribution with the starting B powder, while the size range of boron 95 is quite broad and distributed between 0.05-1.5 μm. Most probably, the small crystallites (50-200 nm) observed in Fig 6.3 b and 3d which are stemming from the reaction of boron 95 particles of smaller sizes. So far, the role of the particle size of the starting B powders in the quality and performance of bulk MgB_2 has been investigated by several researchers [31,

32]. Present results are harmonizing very well with those reported in [31] and [32], emphasizing the particle size correlation between the B precursor and the final product MgB_2 . At this point, two additional points are also worth mentioning and should be underlined: i) The average particle size of nanosized MgB_2 is similar, even smaller than in the starting nanoboron powder and ii) the size and morphology of Mg has practically no influence on the MgB_2 particle size.

The reason behind reach to even lower particle size than starting nanoboron, might be mainly due to the fact that boron has a 3D structure and MgB_2 a layer one (2D). The reaction between Mg and boron starts with the diffusion of Mg into boron particles, because of the 2D character of MgB_2 structure, the growth of MgB_2 crystals are, however, restricted only in two directions which may result in a smaller particle size compared to the precursor nanoboron.

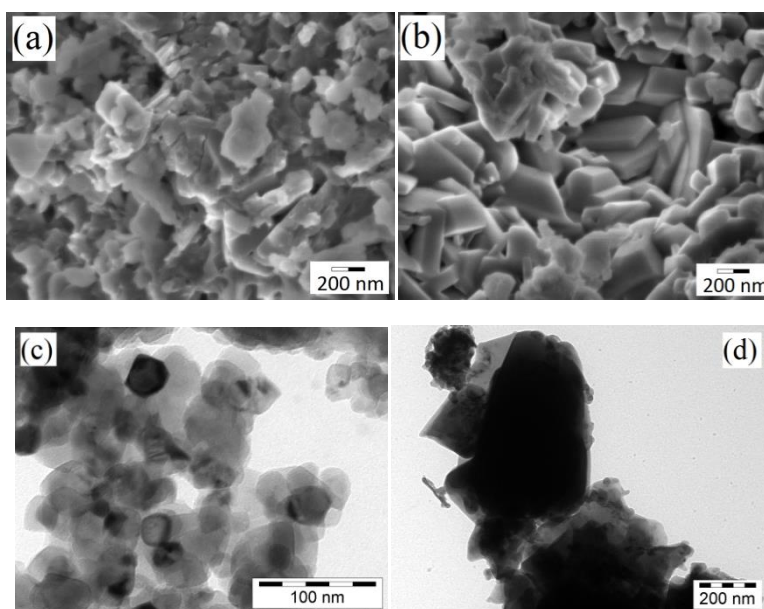


Fig 6.3 SEM images of (a) nanosized and (b) bulk MgB_2 powders. TEM images of (c) nanosized MgB_2 and (d) bulk MgB_2 powders. Nanosized and bulk powders were synthesized from nanoboron and boron 95, respectively.

Fig 6.4 a compares the EPR spectra of the elemental Mg and the MgB_2 obtained from nanoboron samples. This clearly shows that elemental Mg which is used in sample preparation

has no paramagnetic impurities thus EPR inactive. The peak-to-peak intensity (I_{pp}) and linewidth (ΔB_{pp}) and the symmetry coefficients A and B were depicted on the EPR spectra in Fig 6.4 b. The symmetry ratio A/B gives information about the symmetric behavior of each EPR signal defect centers with respect to particle size. From the definition the EPR line is supposed to be symmetric when $A/B = 1$, and it is asymmetric when $A/B \neq 1$. In Fig 6.4 c a single EPR line with different lineshapes were observed for bulk and nanosized MgB₂. Both signal at first shows the extreme purity of the material. There are no contaminations or transition metal ion impurities such as Mn, Fe, Cu or Co which can be easily detected by EPR which is extremely sensitive to any kind of paramagnetic metal-ion impurity, with a detection limit of 10^{10} spins[33]. Nanosized MgB₂ reveals totally symmetric feature. On the contrary, the bulk powder signal shows rather asymmetric behavior. Possible defect centers in pure MgB₂ material could be the Mg vacancies (V_{Mg}), oxygen vacancies (V_O), boron vacancies (V_B) and the interstitials (O_i or B_i). In particular influence of Mg vacancy in MgB₂ on structural and superconducting properties has been discussed controversially [34]. According to their g-factors (close to free-electron g factor: 2.0023) given in Fig 6.4 c such defects can be attributed to V_O in bulk MgB₂ sample either on the grain boundaries or on the surface since MgO is present as a secondary phases. On the other hand dominant contributions from the grains in bulk sample can also increase the asymmetry ratio [24]. That results typical Dysonian lineshape in EPR spectrum which is given in Fig. 4c for the bulk MgB₂. This is characteristic for conductive species [35, 36] and strong indication of enhancing the metallic character and influencing the ionic conductivity property due to structural defects, namely V_O , in bulk MgB₂. The same effect has been reported by the aid of X-ray photoelectron spectroscopy (XPS) and SQUID measurements [37]. In the absence of MgO phase and elemental Mg-excess symmetric line with Lorentzian lineshape were observed for the nanosized MgB₂ implying homogeneous line broadening and also evidencing that the particle size in powder are smaller than the skin depth [38]. The size dependent broadening of linewidth ΔB_{pp} from bulk (5.67 G) to nanosize (13.4 G) can be attributed to the interactions of conduction

electrons with phonons associated with V_{Mg} .

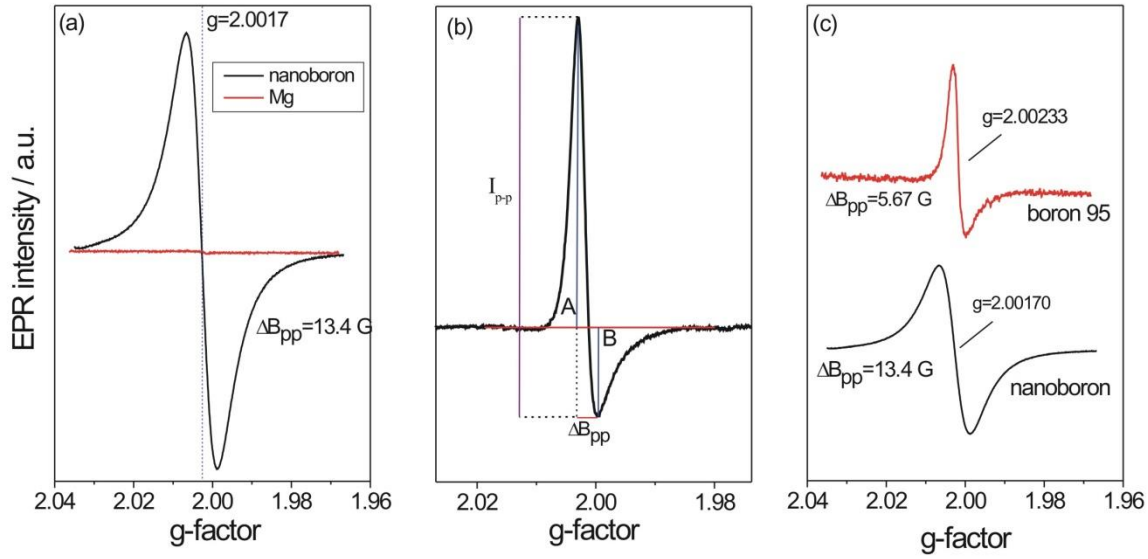


Fig 6.4 (a) Comparative EPR spectra of elemental Mg and nanoboron. (b) Definition of symmetry parameter (A/B), peak-to-peak intensity and the linewidth (ΔB_{pp}) in terms of Dysonian EPR signal. (c) Comparative EPR spectra of MgB_2 obtained from boron 95 and nanoboron.

This is consistent with the inhomogeneously distributed Lorentzian shape of EPR signal which indicates that the unpaired electrons are not isolated at a certain site but rather in an impurity or conduction band probability hopping from one site to another site. Thus it can be concluded that, V_{Mg} dominantly influences the electronic properties of nanosized MgB_2 from nanoboron even it has high purity and crystallinity (c.f. XRD and TEM picture in Fig 6.1 and Fig 6.3 c). In the other word, coexistence of MgO and MgB_2 in the material brings a natural expectation of the existence of O and Mg vacancies due to strain inducing MgO in MgB_2 [39]. However, the interplay between two defect centers is proved by EPR spectroscopy and clearly distinguished O and Mg deficiencies in the material. The question is also confirmed by the structural XRD measurements that nanoboron has less MgO phase which also revealed less amounts of V_{O} and higher V_{Mg} . So that is a clear indication that the origin of V_{O} is the higher

amount of MgO in the bulk sample. The existence of V_O in MgO has been discussed in very good papers in literature as well [40-42]. It is also expected that the non-metallic character of nanosized MgB₂ could enhance the intergrain connectivity [43].

6.4 Conclusion

Nanosized MgB₂ is synthesized by using nanoboron and Mg without using any mechanical energy deposition such as ball-milling. SEM images showed that particle sizes in nanosized MgB₂ were in the range of nanoboron precursor and TEM picture is confirmed that the particle size is at nanoscale. These results showed that size of nanoboron is one of the important factors to control the MgB₂ quality. Moreover, nanoboron presented a good wetting ability and enabled to reduce synthesizing temperature and reaction rate. The present study allows also concluding that the choice of B precursors is of prime importance for the functionality of MgB₂ materials which in turn is governed by the particle size. Indeed, there is a linear size correlation between the particles of the reactant B powders and the final product MgB₂. This means that a significant average particle size reduction for MgB₂ can be achieved only by using B particles of submicron or nano size. An interesting detail is that the average particle size in nanoscale MgB₂ is even smaller than in the starting nanoboron powders. The size and shape of the second reactant Mg powder has practically no influence on the MgB₂ particle diameter. From the point of defect structure, the bulk MgB₂ revealed EPR signal related to V_O, whereas EPR of nanosized sample was dominated by V_{Mg} indicating enhancement of non-metallic conductivity which arise due to the localization of the unpaired electrons. This may give additional functionalities to MgB₂ at nanoscale for the possible use in relevant superconducting technology fields.

6.5 References

1. Chen, S.K., et al., *Reaction method control of impurity scattering in C-doped MgB₂: proving the role of defects besides C substitution level*. Superconductor Science & Technology, 2013. **26**(12): p. 125018.
2. Patel, D., et al., *Rational design of MgB₂ conductors toward practical applications*. Cryogenics, 2014. **63**: p. 160-165.
3. Baig, T., et al., *Conduction cooled magnet design for 1.5T, 3.0T and 7.0T MRI systems*. Superconductor Science & Technology, 2014. **27**(12): p. 125012.
4. Ling, J., et al., *Development of a 0.5-T/240-mm MgB₂ MRI Magnet: Assembly Design and Module Coils*. IEEE Transactions on Applied Superconductivity, 2014. **24**(3): p. 4400805.
5. Prikhna, T.A., et al., *Nanostructural inhomogeneities acting as pinning centers in bulk MgB₂ with low and enhanced grain connectivity*. Superconductor Science and Technology, 2014. **27**(4): p. 044013.
6. Patel, A., et al., *The Use of an MgB₂ Hollow Cylinder and Pulse Magnetized (RE)BCO Bulk for Magnetic Levitation Applications*. IEEE Transactions on Applied Superconductivity, 2013. **23**: p. 6800604.
7. Fang, H., et al., *Development of Fe-sheathed MgB₂ wires and tapes for electric power applications*. Ieee Transactions on Applied Superconductivity, 2005. **15**(2): p. 3200-3203.
8. Trevisani, L., M. Fabbri, and F. Negrini, *Long distance renewable-energy-sources power transmission using hydrogen-cooled MgB₂ superconducting line*. Cryogenics, 2007. **47**(2): p. 113-120.
9. Maeda, M., J.H. Kim, and S.X. Dou, *Structural Characteristic and Superconducting Performance of MgB₂ Fabricated by Mg Diffusion Process*. Intechopen. 2012.
10. Sanz, S., et al., *Superconducting light generator for large offshore wind turbines*. Journal of Physics: Conference Series, 2014. **507**: p. 032040.
11. Shintomi, T., et al., *Design Study of MgB₂ SMES Coil for Effective Use of Renewable Energy*. Ieee Transactions on Applied Superconductivity, 2013. **23**(3): p. 5700304.
12. Ballarino, A., *Development of superconducting links for the Large Hadron Collider machine*. Superconductor Science & Technology, 2014. **27**: p. 044024.
13. Hishinuma, Y., et al., *Development of Low Activation Superconducting Material for the Feedback Coil operated around Core D-T Plasma*. International Atomic Energy Agency, 2010. **43**: p. 419-420.
14. Nagamatsu, J., et al., *Superconductivity at 39 K in magnesium diboride*. Nature, 2001. **410**(6824): p. 63-64.
15. Chen, X., et al., *Microstructural transformation during combustion synthesis of MgB₂ superconductor*. Physica C-Superconductivity and Its Applications, 2007. **454**(1-2): p. 38-42.
16. Schmidt, J., et al., *Pulse plasma synthesis and chemical bonding in magnesium diboride*. Solid State Sciences, 2003. **5**(4): p. 535-539.
17. Przybylski, K., et al., *Synthesis and properties of MgB₂ obtained by SHS method*. Physica C: Superconductivity, 2003. **387**(1-2): p. 148-152.
18. Karpinski, J., et al., *Single crystals of MgB₂: Synthesis, substitutions and properties*. Physica C-Superconductivity and Its Applications, 2007. **456**(1-2): p. 3-13.

19. Lu, J., et al., *Low-Temperature Synthesis of Superconducting Nanocrystalline MgB₂*. Journal of Nanomaterials, 2010. **2010**: p. 1-5.
20. Koseoglu, Y., et al., *ESR studies on high-T_c superconductor MgB₂*. Physica C- Superconductivity and Its Applications, 2003. **390**(3): p. 197-203.
21. Likodimos, V. and M. Pissas, *Electron spin resonance and microwave absorption study of MgB₂*. Physical Review B, 2002. **65**(17): p. 172507.
22. F. Simon, et al., *Anisotropy of superconducting MgB₂ as seen in electron spin resonance and magnetization data*.
23. Simon, F. and F. Muranyi, *ESR spectrometer with a loop-gap resonator for cw and time resolved studies in a superconducting magnet*. Journal of Magnetic Resonance, 2005. **173**(2): p. 288-295.
24. Simon, F., et al., *Spin-lattice relaxation time of conduction electrons in MgB₂*. Physical Review B, 2007. **76**(2): p. 024519.
25. Bhide, M.K., et al., *Magnetic field dependent microwave absorption studies on a MgB₂ superconductor*. Superconductor Science & Technology, 2001. **14**(8): p. 572-575.
26. Shunsuke, M., et al., *Understanding routes for high connectivity in ex situ MgB₂ by self-sintering*. Superconductor Science and Technology, 2014. **27**(4): p. 044012.
27. Jiang, C.H., H. Hatakeyama, and H. Kumakura, *Effect of nanometer MgO addition on the in situ PIT processed MgB₂/Fe tapes*. Physica C: Superconductivity, 2005. **423**(1-2): p. 45-50.
28. Kováč, P., et al., *Properties of MgB₂ wires made of oxidized powders*. Physica C: Superconductivity, 2012. **477**: p. 20-23.
29. Tan, K.L., et al., *Enhanced critical current density in MgB₂ prepared by reaction of MgB₄ and Mg*. physica status solidi (a), 2013. **210**(3): p. 616-622.
30. Kovac, P., et al., *Properties of MgB₂ wires made of oxidized powders*. Physica C- Superconductivity and Its Applications, 2012. **477**: p. 20-23.
31. Chen, S.K., et al., *Strong influence of boron precursor powder on the critical current density of MgB₂*. Superconductor Science and Technology, 2005. **18**(11): p. 1473.
32. Zhang, Y., et al., *Influence of Nanocrystalline Boron Precursor Powder on Superconductivity in MgB₂ Bulk*. Journal of Nanoscience and Nanotechnology, 2009. **9**(12): p. 7402-7406.
33. Rablau, C.I., et al., *Point defects in Cd_{1-x}Zn_xTe: A correlated photoluminescence and EPR study*. Journal of Electronic Materials, 1998. **27**(6): p. 813-819.
34. Zhigadlo, N.D., et al., *Influence of Mg deficiency on crystal structure and superconducting properties in MgB₂ single crystals*. Physical Review B, 2010. **81**(5): p. 054520.
35. Baraki, R., et al., *Electron paramagnetic resonance study of ZnO varistor material*. Journal of Physics-Condensed Matter, 2014. **26**(11).
36. Dyson, F.J., *Electron Spin Resonance Absorption in Metals. II. Theory of Electron Diffusion and the Skin Effect*. Physical Review, 1955. **98**(2): p. 349-359.
37. Serquis, A., et al., *Synthesis, Characterization and Ageing of MgB₂*. MRS Online Proceedings Library, 2001. **689**: p. null-null.
38. Beuneu, F. and P. Vajda, *Spectroscopic Evidence for Large (>>1 μm) Lithium-Colloid Creation in Electron-Irradiated Li₂O Single Crystals*. Physical Review Letters, 1996. **76**(24): p. 4544-4547.
39. Xue, Y.Y., et al., *Nonstoichiometry, defects and transport properties in MgB₂*. Physica C- Superconductivity and Its Applications, 2002. **377**(1-2): p. 7-14.

40. Pacchioni, G. and A.M. Ferrari, *Surface reactivity of MgO oxygen vacancies*. Catalysis Today, 1999. **50**(3-4): p. 533-540.
41. Ricci, D., et al., *Paramagnetic defect Centers at the MgO surface. An alternative model to oxygen vacancies*. Journal of the American Chemical Society, 2003. **125**(3): p. 738-747.
42. Scorza, E., U. Birkenheuer, and C. Pisani, *The oxygen vacancy at the surface and in bulk MgO: An embedded-cluster study*. Journal of Chemical Physics, 1997. **107**(22): p. 9645-9658.
43. Wang, C.C., et al., *Intergrain connectivity of MgB₂ ceramics studied by impedance analysis*. Journal of Applied Physics, 2010. **108**(2): p. 023901.

Chapter 7

PXRD, Raman and EPR spectroscopy studies on C-doped MgB₂

7.1 Introduction

The relatively low density ($\rho = 2.55 \text{ g/cm}^3$) [1], high critical temperature ($T_c \approx 39 \text{ K}$) [2], its simple crystal structure and chemical composition are outstanding properties of magnesium diboride (MgB₂) that lead to promising applications in modern engineering.

The performance of MgB₂ as a superconductor is strongly influenced by the choice of starting materials; especially the degree of crystallinity and the particle size of the boron precursor are of utmost importance [3]. The main difficulty in preparing MgB₂ from crystalline boron is that at conventional temperatures it has a low chemical reactivity, which makes the reaction with Mg hard. This is mainly due to the thermodynamic stability of the β -rhombohedral crystal modification and the high Mohs hardness of crystalline boron (9.5). Thus, production of MgB₂ using crystalline boron requires long sintering times and quite high temperatures [4]. Enhanced reactivity of the boron precursor can be achieved by reducing the particle size to nano-dimensions and using the amorphous boron modification [4]. Recently, we could confirm that the quite high content of intrinsic defects in amorphous nanoboron, as supplied by the company Pavezyum, yields MgB₂ material with unique and superior characteristics [5]. Although various MgB₂ compounds have been extensively investigated over the past decades, there is still considerable controversy about its various properties. In particular, the defect structures of undoped and doped MgB₂ have remained unclear, especially when the crystallite or particle size is confined to nanometer dimensions. We previously reported that a significant reduction of the average particle size of MgB₂ can be achieved by using amorphous nanoboron precursors [5].

The origin and the role of defect centers were also identified: at bulk-scale and at nano-scale, undoped MgB_2 material contains plenty of O- and Mg-vacancies, respectively [5].

Although the various compound morphologies play a decisive role to control its properties, the synthesis method and doping define additional, crucial parameters that markedly impact the nature and concentration of intrinsic or extrinsic defects and the materials' electronic properties. To this end, it has been reported that carbon (C) doping significantly improves the electromagnetic properties [6] and the critical current density [7, 8] of MgB_2 . In addition, it has been reported that adding of single wall C nanotubes and nano-SiC in MgB_2 enhance the flux pinning, thus the superconducting performance [9, 10]. Nonetheless, the effect of C doping in MgB_2 has also been discussed controversially with respect to its substitution site and solubility limit [7, 8, 11, 12]. Moreover, previous studies on C doping into MgB_2 were mainly focused on its effect on superconductivity. From the defect structure point of view, the effect of C doping on the electronic properties is equally important and has to be investigated.

In this work, the defect structure of C-doped MgB_2 , and its impact on the material properties will be investigated by electron paramagnetic resonance (EPR) and Raman spectroscopy. EPR is well suited for this task because it provides a direct method to monitor different paramagnetic states of defects and, thus, complements other experimental techniques, such as X-ray powder diffraction (PXRD) and Raman spectroscopy. In this sense, EPR does not only allow for an identification of paramagnetically active intrinsic and extrinsic defects, but also yields insight into the correlation of such defects to the structural and superconductive properties of MgB_2 . Therefore, the correlation of Raman and EPR results would give plausible information about the defect related electron–phonon or phonon-defect interactions, which most likely contribute to the Raman and EPR spectra of undoped and C-doped MgB_2 .

7.2 Experimental Procedure

7.2.1 Synthesis of carbon-doped MgB₂ powders

Solid-state synthesis was chosen for all sample preparations. Two sets of mixtures with different boron precursors have been used as starting materials. To distinguish between different boron precursors, amorphous nanoboron and as-received amorphous C-doped nanoboron, were labeled as P1 and P2, respectively.

Set1: One set of undoped and C-doped P1 mixtures was prepared using starting powders of the following purity grades: Mg (99.8 %, Pavezyum), amorphous nanoboron (B > 98.5 %, Pavezyum), DL-malic acid (MA) (C₄H₆O₅ (99 %, Merck)). Systematic C doping was performed on all powders by using DL-malic acid as a C source with a method reported previously [13]. P1 is mixed with 0, 0.1, 1, 5, 10, 30 wt % of MA in a toluene medium for 1 h. Subsequently, toluene was evaporated at 150 °C for 3 h to remove all volatile organics.

Set2: Another set of undoped and C-doped P2 blends was prepared using starting powders of following purity grades: Mg (99.8 %, Pavezyum), as-received C-doped amorphous nanoboron with 1.85 wt % (~2 mol %) C concentration (Pavezyum).

In all series, Mg- and C-doped precursors (P1 and P2) were placed into diamagnetic zirconia air-tight milling vials in a stoichiometric ratio in a glove box and mixed at 500 rpm using a Fritsch P7 planetary ball mill for 30 minutes. Afterwards, pellets of 13 mm diameter were pressed with a hydraulic press employing a pressure of 10 t/cm². The samples were put into small iron crucibles and placed in an iron reactor, which was purged by Ar gas during the heating process to avoid oxidation. The details of the synthesis procedure are as follows: 2 h fast heating to close to the melting point of magnesium (25-600 °C) and slow heating to minimize Mg evaporation for 5 h up to 800 °C (600-800 °C) and allowing to cool down in the furnace.

MgB₂ samples produced from Set1 were labeled according MA concentration (wt %): 0CS1 (0 wt %), 0.1CS1 (0.1 wt %), 1CS1 (1 wt %), 5CS1 (5 wt %), 10CS1 (10 wt %), and 30CS1 (30 wt %). Two MgB₂ samples synthesized by using Set2 were coded based on C concentration (wt

%) as 0CS2 (0 wt%) and 1.85CS2 (1.85 wt %) for undoped and 1.85 wt % (~2-mol %) C-doped samples, respectively.

Table 7. 1 Sample codes and corresponding wt % values for the doping concentration.

Sample name	wt % of added dopants
0CS1	0
0.1CS1	0.1
1CS1	1
5CS1	5
10CS1	10
30CS1	30
0CS2	0
1.85CS2	1.85

7.2.2 Methods of sample characterization

All samples were analyzed by X-ray powder diffraction (PXRD). PXRDs were recorded with a BRUKER D8 Phaser diffractometer (Cu radiation with VANTEC detector). Rietveld refinement was carried out on all samples for phase characterization and determination of the lattice parameters a and c by using the TOPAS software using fundamental parameter approach. Raman analysis were done using nearly 5 mg of sample in sealed Pyrex tube ($\varnothing = 4$ mm) in the range of 2500-1000 cm^{-1} with a BURKER RFS 100/S spectrometer (Nd:YAG-Laser, 1064 nm, 200 mW). X-band (9.86 GHz) continuous-wave-EPR measurements were performed with a Bruker EMX spectrometer. We have used a rectangular TE102 (X-band) resonator from Bruker. The offset in the magnetic field and the exact g -factors in X-band measurements were determined with a polycrystalline DPPH (2-diphenyl-1-picrylhydrazyl) reference sample with well-known g -factor ($g = 2.0036$). For cooling (to liquid helium temperatures) an Oxford CF-935 cryostat was used. The temperature was regulated by a temperature controller (Oxford ITC-503). The EPR spectral analysis has been performed using the WINEPR program from Bruker.

7.3 Result and Discussion

7.3.1 Structural analysis

PXRD results of MgB₂ synthesized from set1 samples with 0, 0.1, 1, 5, 10, 30 wt% of MA are plotted in Fig.7.1 (a). MgB₂ (ICSD Collection Code: 93925) is the main product but small amounts of MgO (ICSD Collection Code: 26958) are also detected in all samples. An excess amount of Mg is observed at higher C concentrations in C-doped MgB₂ samples due to restricted availability of boron. To learn more on the effect of C doping into the MgB₂ structure, a Rietveld analysis was performed on all synthesized samples and the c/a -ratio with the lattice parameters a and c (in the inset) are plotted in Fig.7.1 (b). With rising C content, the c/a -ratio increases steadily along with a decrease in a , while c remains nearly unchanged except for the highest C concentration. The contraction of the lattice parameter a and the accompanying increase of the c/a ratio is attributed to progressing substitution of C (atomic radius 0.77 Å) into boron sites with (atomic radius 0.97 Å) [7, 14-16].

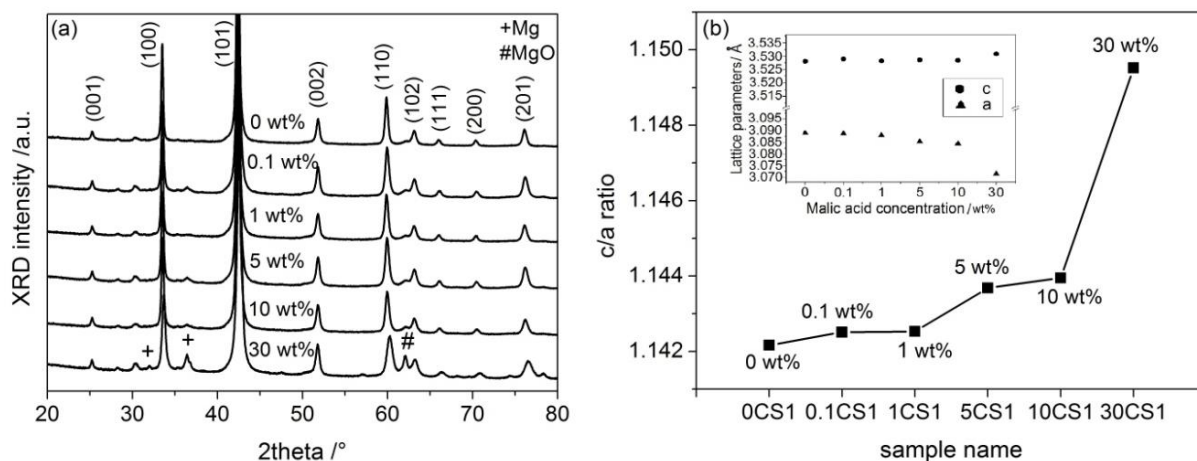


Fig.7.1 (a) PXRD patterns, (b) c/a ratio and lattice parameters a and c (inset), which were obtained from a Rietveld refinement analysis of set1 samples (set1) with 0, 0.1, 1, 5, 10, 30 wt % of MA.

It should be noted that for C doping into MgB_2 , the C can either substitute into boron sites or into interstitial sites within boron rings and grain boundaries [7, 17]. The very small increase in lattice parameter c shown in Fig.7.1 (b) may be related to interstitial C substitution into MgB_2 [7, 18]. Therefore, there is a difference between the real C doping into B sites and the nominal C concentration, which is the total amount of added C, and the terms "real" and "nominal" are used in the literature to differentiate between them [11-13, 19]. In the literature, various methods can be found to calculate the real C concentration. The real C concentration in $\text{Mg}(\text{C}_x\text{B}_{1-x})_2$ can be calculated from the semi-empirical formula $x = 7.5\Delta(c/a)$, in which $\Delta(c/a)$ is the difference between the c/a ratio of C-doped samples and the c/a ratio of undoped sample ($\Delta(c/a) = (c/a)_{\text{undoped}} - (c/a)_{\text{doped}}$) [20]. MA, nominal and real C doping concentration in MgB_2 are compiled in Table 7.2.\

Table 7.2 MA, nominal C and real C doping concentrations in MgB₂

Sample name	Dopant concentration wt %	Nominal C concentration $x \times 10^{-2}$ (mole %)	Real C concentration $x \times 10^{-2}$ (mole %)
0CS1	0	0	0
0.1CS1	0.1	0.036	0.25
1CS1	1.0	0.360	0.276
5CS1	5.0	1.790	1.140
10CS1	10.0	3.580	1.340
30CS1	30.0	10.700	5.520
0CS2	0	0	0
1.85CS2	1.85	2.0	1.530

From Table 7.2, it can be seen for sample 0.1CS1, that the real C doping amount is exceeding the nominal C-doped concentration. This may be related to the formation of MgO, which is reducing the Mg amount relative to C-doped concentration [12, 19].

7.3.2 Raman spectroscopy

The Raman modes of MgB₂, and in particular those of the C-doped ones, have not been fully understood for a very long time [21-24]. Specifically, the background signal and the broad linewidth of the soft mode (E_{2g} phonon mode) were made the Raman interpretation quite difficult. Clearly, MgB₂ represents a two-gap superconductor with the Fermi surface consisting of two-dimensional σ -bands and three-dimensional π -bands. Group theory predicts for the $P6/mmm$ space group in MgB₂ the following four vibration modes: a silent B_{1g} mode, the E_{2g} Raman mode, and the infrared-active u modes E_{1u} and A_{2u} . Among them only the E_{2g} mode (soft mode) is Raman active. This mode mainly results from the strong coupling between electrons and phonons and is located around 590–660 cm⁻¹ with the wide linewidth (~ 200 cm⁻¹) [22-26]. The strong interaction of the E_{2g} phonon with the σ electronic bands is believed to be the main contribution to superconductivity in MgB₂[24]. Motaman *et al.* reported also that the E_{2g} phonon mode is related to the in-plane vibration mode of the boron atom [23]. Therefore, the E_{2g} phonon mode can be easily influenced by lattice distortion (defects) or atomic substitution (doping).

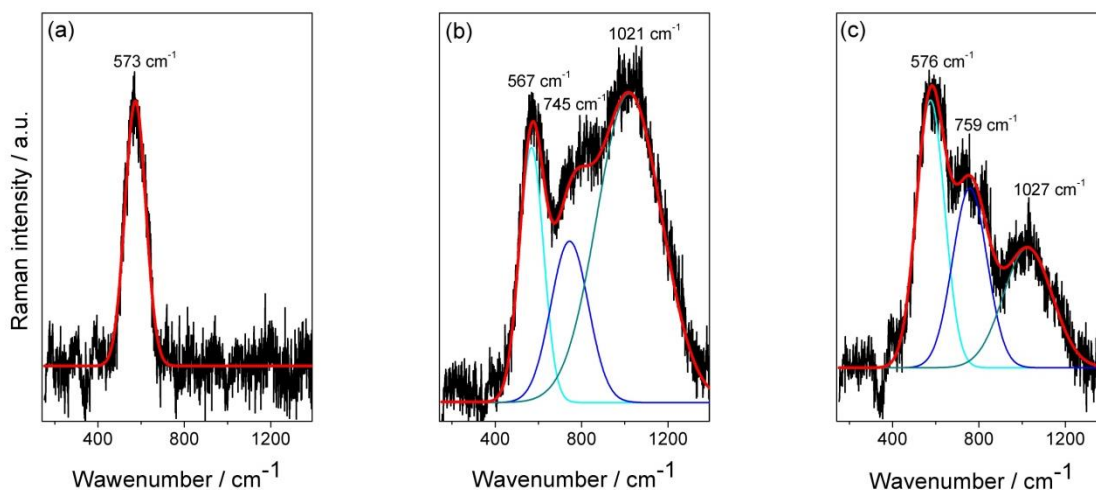


Fig.7.2 Raman spectra of samples (set1) with (a) 0 wt% (b) 0.1 wt% and (c) 10 wt% of MA.

In this study we have measured Raman spectra of nanoparticle-sized samples of pure MgB_2 , as well as of doped ones with 0, 0.1 and 10 wt% of MA (named as: 0CS1, 0.1CS1 and 10CS1, respectively), to examine the C doping effects on the phonon modes. In Fig.7.2 (a), the most prominent boron-atom-related E_{2g} phonon mode was observed at 573 cm^{-1} , however, it appeared at slightly lower wavenumbers than in bulk MgB_2 ($< 590\text{--}660\text{ cm}^{-1}$ band). This shift results from the unique property of nanoboron [5] due to size effect, which is used as starting precursor for MgB_2 syntheses. The decrease (red shift) in phonon-mode energy in nanoboron MgB_2 sample can be mainly attributed to the decreased density of states due to filling of the vacancies by C doping. As depicted in Fig.7.2 (b), the E_{2g} phonon peak shifts to the lower energy side with 0.1 wt % of MA with respect to undoped MgB_2 and shifts further very slightly to the lower energy side with 10 wt % of MA (refer Fig.7.2 (c)). The two additional peaks around 745 and 1027 cm^{-1} are only visible in MA-doped (as a C source) samples indicating their strong relationship with the doping effect, i.e., C addition. Both modes show red shifts with increasing amount of MA. The decrease in the intensity of the E_{2g} phonon mode has been reported by several groups and is also attributed to local symmetry breaking due to substitution effects, hence C-related defects

[21, 24, 27]. In particular, the Raman mode at 745 cm⁻¹ has been reported earlier and explicitly assigned to the phonon density of states due to disorder [27].

7.3.3 EPR spectroscopy

Based on results which is shown in Fig.7. 3 (a), all measured EPR signals exhibit no hyperfine structure (splitting energy levels and as a result and increase in the number observed signals), hence, a localization of the unpaired electron spin on magnesium or boron can be ruled out. Instead, the observed EPR signals in Fig.7. 3 (a) can be assigned to either paramagnetic C-based ‘dangling bond’ (DB) species [28] or to intrinsic defects, such as Mg vacancies [5]. For an assignment of the observed DB centers to either C- or Mg-vacancy species, the *g*-values as determined from EPR data can be used. C radical centers typically occur in an interval of *g*-values ranging from $g_C \sim 2.0020\text{--}2.0030$ [29-33]. In contrast, Mg-vacancy centers in nanosized MgB₂ typically exhibit *g*-values around 2.0017 [5]. Obviously, as presented in Fig.7. 3 (b), the observed EPR signals of MA-doped MgB₂ can be assigned to C ‘dangling bonds’ whereas the undoped signal to Mg-vacancies.

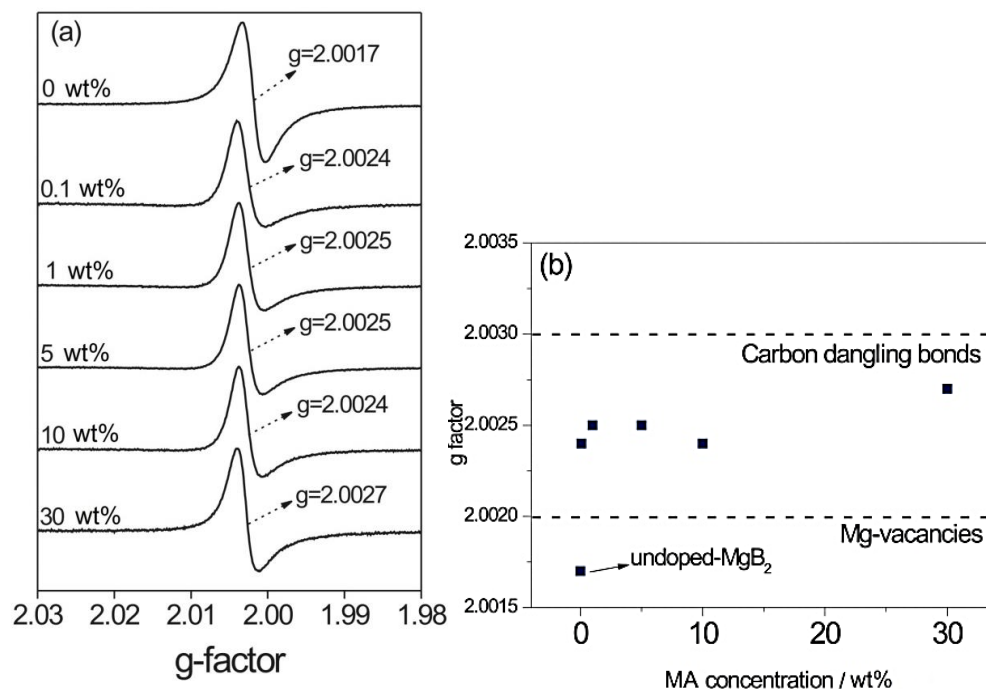


Fig.7. 3 (a) Room-temperature EPR spectra (first derivatives with respect to B_0) of undoped MgB_2 and doped MgB_2 with various MA doping levels. (b) Electron g -factors of MgB_2 both for doped and undoped case determined from the inflection points of the spectra. The corresponding regions for C related and vacancy related centers are indicated [5, 29-33].

Fig.7. 4 (a,b) shows X-band EPR spectra recorded in the temperature range between 40 and 10 K. This range is important since it includes the critical temperature of MgB_2 . Therefore, it is quite important to compare EPR results of undoped and C-doped MgB_2 at low temperatures. In the former material the EPR signal is induced by Mg-vacancies whereas in the latter C-dangling bonds give rise to the intense EPR signal. Due to the different driving forces, one can expect unequal temperature-dependent EPR responses from undoped and C-doped MgB_2 .

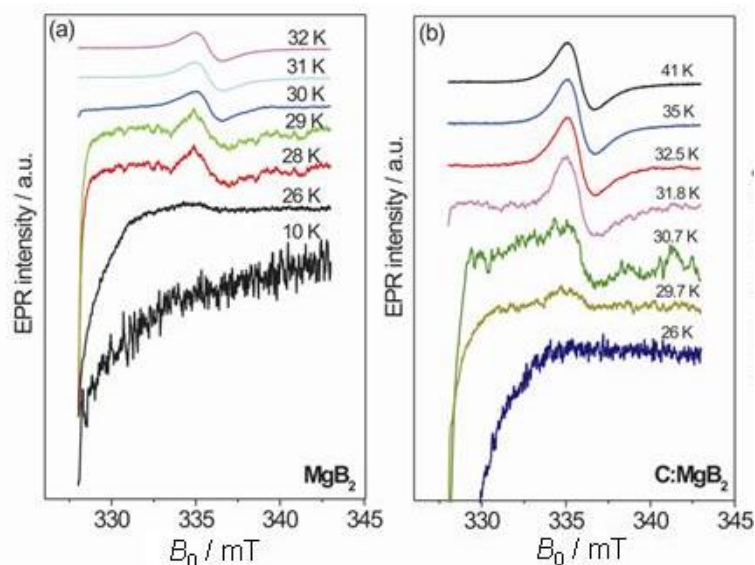


Fig.7. 4 Low-temperature EPR measurements (a) for undoped and (b) for nominally 1.85 wt % (2 mol %) C-doped MgB_2 synthesized from set2.

It can be seen in Fig.7. 4 (a) and (b), below T_c , paramagnetic defects in MgB_2 completely smeared out and the materials become superconductive. However, it can be clearly seen that, by approaching the T_c value, the signal-to-noise ratio of EPR spectra becomes worse compare to higher temperatures. In particular, the lineshape of undoped MgB_2 , especially for EPR spectra measured at 29, 28 and 26 K differs substantially from a pure Lorentzian, mainly as a result of the inhomogeneous distribution of the magnetic field inside the material, caused by the appearance of the vortices (due to paramagnetically active defects (V_{Mg} or C radicals)). Such an EPR signal at the superconducting state was described recently by the realization of vortex structure in MgB_2 samples. This effect has been also reported for different impurity centers in MgB_2 [35]. This effect has been also reported for different impurity centers in MgB_2 [35]. It can be also seen that the superconducting state starts in the temperature region 25–30 K. That means that defect-induced paramagnetism, quite interestingly, still holds even below the bulk T_c value (34 K). The decrease in T_c has been also reported for increasing level of C and rare-earth oxide

doped MgB₂ [36]. This can be explained by three ways: (i) MgB₂ synthesized by nanoboron precursor reduce the T_c due to its unique properties, (ii) interaction defects between phonons or between each other alter the superconducting temperature and/or (iii) defects or C doping enhances the lattice distortion. Moreover, these EPR results are highly in agreement with the above Raman spectroscopy results. Lowering of T_c found in this work from EPR data has been also reported from Raman studies and was identified with the disorder due to chemical substitution, crystal lattice contraction and electron doping induced electronic structure variation. This shows close correlation between the defect centers and vibration phonon modes, and hence, the superconductivity of MgB₂.

7.4 Conclusion

In this work MgB₂ was synthesized as nanomaterial by a solid-state synthesis route. Importantly, amorphous nanoboron transfers its unique character to the nanosized undoped and C-doped MgB₂. The real C doping levels in MgB₂ samples were determined using the PXRD and the Rietveld refinement data. So far, the defect structure has not been taken into account for MgB₂ superconductor and tremendous work has been published for understanding macroscopically the superconductivity in this material. Here, we tried to achieve a more detailed understanding of the microscopic structure of defects in MgB₂. In particular, Raman spectroscopy results showed nicely the effect of defect centers on electron-phonon interaction deviated E_{2g} mode, which suppressed by increasing defect concentrations. By EPR we clearly distinguished the Mg vacancies and C radicals (dangling bonds) via their g -values. It is also worth mentioning that in this work it was shown that EPR spectroscopy is an effective tool to understand the critical temperature in superconducting materials. EPR showed suppression of T_c , which is consistent with present Raman results. Hence, in literature it has been frequently reported that any kind of defects can cause lattice distortion and this distortion is responsible for the decrease in T_c [22, 24].

7.5 References

1. Buzea, C. and T. Yamashita, *Review of the superconducting properties of MgB_2* . Superconductor Science & Technology, 2001. **14**(11): p. R115-R146.
2. Nagamatsu, J., et al., *Superconductivity at 39 K in magnesium diboride*. Nature, 2001. **410**(6824): p. 63-64.
3. Chen, S.K., et al., *Strong influence of boron precursor powder on the critical current density of MgB_2* . Superconductor Science & Technology, 2005. **18**: p. 1473-1477.
4. Patel, D., et al., *Rational design of MgB_2 conductors toward practical applications*. Cryogenics, 2014. **63**: p. 160-165.
5. Bateni, A., et al., *Defect structure of ultrafine MgB_2 nanoparticles*. Applied Physics Letters, 2014. **105**(20): p. 202605.
6. Chen, S.K., et al., *Reaction method control of impurity scattering in C-doped MgB_2 : proving the role of defects besides C substitution level*. Superconductor Science & Technology, 2013. **26**(12): p. 125018.
7. Bengtson, A.K., et al., *Impact of substitutional and interstitial carbon defects on lattice parameters in MgB_2* . Journal of Applied Physics, 2010. **107**: p. 023902.
8. Wang, C.D., et al., *Significant improvement in critical current densities of C-doped MgB_2 tapes made by high-energy ball milling*. Superconductor Science & Technology, 2012. **25**(7): p. 075010.
9. Vajpayee, A., et al., *The effect of synthesis temperature on the superconducting properties of n-SiC added bulk MgB_2 superconductor*. Superconductor Science & Technology, 2011. **24**(4): p. 045013.
10. Vajpayee, A., et al., *Effect of single-walled carbon nano-tube (CNT) addition on superconducting properties of bulk MgB_2 superconductor*. Physica C-Superconductivity and Its Applications, 2010. **470**: p. S653-S654.
11. Bharathi, A., et al., *Carbon solubility and superconductivity in MgB_2* . Physica C-Superconductivity and Its Applications, 2002. **370**(4): p. 211-218.
12. Gruner, W., et al., *Reactive nanostructured carbon as an effective doping agent for MgB_2* . Superconductor Science and Technology, 2007. **20**(7): p. 601-606.
13. Kim, J.H., et al., *Carbohydrate doping to enhance electromagnetic properties of MgB_2 superconductors*. Applied Physics Letters, 2006. **89**(14): p. 142505.
14. Flukiger, R., et al., *Superconducting properties of MgB_2 tapes and wires*. Physica C-Superconductivity and Its Applications, 2003. **385**: p. 286-305.
15. Mickelson, W., et al., *Effects of carbon doping on superconductivity in magnesium diboride*. Physical Review B, 2002. **65**(5).
16. Zhao, Y., et al., *Cooperative doping effects of Ti and C on critical current density and irreversibility field of MgB_2* . Journal of Applied Physics, 2006. **100**(12): p. 123902.
17. Mudgel, M., et al., *Enhanced critical parameters of nanocarbon doped MgB_2 superconductor*. Journal of Applied Physics, 2009. **106**: p. 033904.

18. Maeda, M., J.H. Kim, and S.X. Dou, *Structural Characteristic and Superconducting Performance of MgB₂ Fabricated by Mg Diffusion Process*. Intechopen.
19. Herrmann, M., et al., *The effect of reactive nanostructured carbon on the superconducting properties of mechanically alloyed MgB₂*. Superconductor Science and Technology, 2007. **20**(12): p. 1108-1114.
20. Avdeev, M., et al., *Crystal chemistry of carbon-substituted MgB₂*. Physica C: Superconductivity, 2003. **387**(3-4): p. 301-306.
21. Alarco, J.A., et al., *Phonon modes of MgB₂: super-lattice structures and spectral response*. Physical Chemistry Chemical Physics, 2014. **16**: p. 24443-24456.
22. Bharathi, A., et al., *Superconductivity in MgB₂: Phonon modes and influence of carbon doping*. Sadhana-Academy Proceedings in Engineering Sciences, 2003. **28**: p. 263-272.
23. Motaman, A., et al., *A comprehensive study of the pinning mechanisms of MgB₂ wires treated with malic acid and their relationships with lattice defects*. Superconductor Science & Technology, 2013. **26**: p. 085013.
24. Parisiades, P., et al., *Raman Investigations of C-, Li- and Mn-Doped MgB₂*. Journal of Superconductivity and Novel Magnetism, 2009. **22**(2): p. 169-172.
25. Bohnen, K.P., R. Heid, and B. Renker, *Phonon dispersion and electron-phonon coupling in MgB₂ and AlB₂*. Physical Review Letters, 2001. **86**(25): p. 5771-5774.
26. Goncharov, A.F., et al., *Raman spectrum and lattice parameters of MgB₂ as a function of pressure*. Physical Review B, 2001. **64**: p. 100509.
27. Li, W.X., et al., *Raman study of element doping effects on the superconductivity of MgB₂*. Physical Review B, 2008. **77**: p. 094517.
28. Chauvet, O., L. Zuppiroli, and I. Solomon, *ELECTRONIC-PROPERTIES OF DISORDERED SIC MATERIALS*. Materials Science and Engineering B-Solid State Materials for Advanced Technology, 1992. **11**: p. 303-306.
29. Walters, G.K. and T.L. Estle, *PARAMAGNETIC RESONANCE OF DEFECTS INTRODUCED NEAR SURFACE OF SOLIDS BY MECHANICAL DAMAGE*. Journal of Applied Physics, 1961. **32**(10): p. 1854-&.
30. Mucalo, M.R., D.G. McGavin, and N.B. Milestone, *Electron spin resonance studies of amorphous and crystallized residues derived from pyrolysis of pre-ceramic polymers*. Journal of Materials Science, 1997. **32**: p. 3271-3276.
31. Jeschke, G., M. Kroschel, and M. Jansen, *A magnetic resonance study on the structure of amorphous networks in the Si-B-N(-C) system*. Journal of Non-Crystalline Solids, 1999. **260**: p. 216-227.
32. Prasad, B.L.V., et al., *Heat-treatment effect on the nanosized graphite pi-electron system during diamond to graphite conversion*. Physical Review B, 2000. **62**: p. 11209-11218.
33. Berger, F., et al., *Solid-state NMR investigations on Si-B-C-N ceramics derived from boron-modified poly(allylmethylsilazane)*. Zeitschrift Fur Anorganische Und Allgemeine Chemie, 2005. **631**: p. 355-363.
34. Odkhuu, D., et al., *Conversion of multilayer graphene into continuous ultrathin sp(3)-bonded carbon films on metal surfaces*. Scientific Reports, 2013. **3**: p. 3276.
35. Garifullin, I.A., *EPR study of superconductors*. J Low Temp Phys 2015. **178**: p. 243-271.

-
36. Ojha, N., et al., *The effect of carbon and rare earth oxide co-doping on the structural and superconducting properties of MgB₂*. Superconductor Science & Technology, 2010. **23**.

Chapter I

Characterization methods and analysis theory

ii. Powder X-ray Diffraction

X-ray diffraction (XRD) is a structural analytical technique based on the interaction of X-rays and the sample's crystalline lattice. As X-rays are electromagnetic waves with wavelength of 0.5-2.5 Å near to the interatomic spacing of crystals (2-3 Å), they can diffract from crystals [1].

X-rays are generating while electrically charged particles (electrons) of sufficient kinetic energy from cathode are rapidly decelerated by metal target (e.g. Tungsten) or anode in X-ray tube. The interaction of the generated X-rays with the electrons in the crystal lattice produces constructive interference and a diffracted X-ray when conditions satisfy Bragg's Law (Eq. 1.2). The geometrical explanation of Bragg's Law is shown in Fig I.1.

$$n\lambda = 2d_{hkl} \sin\theta_{hkl} \quad (1.2)$$

In Eq.1.2, λ is the wavelength of the incident X-rays, θ is the angle of incidence and d spacing between the crystal lattice planes of atoms [2].

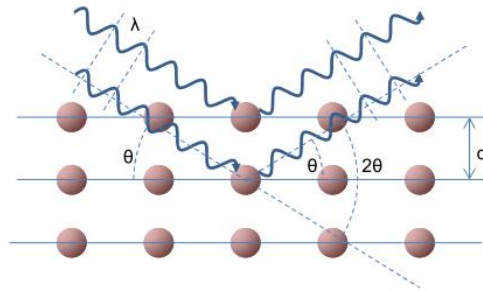


Fig.I.1 Geometrical illustration of the Bragg's law [3].

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. There are also many optical devices between X-ray tube and detector with different configurations. In this thesis, all XRD diagrams were measured using Bruker D8 ADVANCE (Cu radiation with VÅNTEC-1 detector) and Bruker D2 PHASER (Cu radiation with LYNXEYETM detector). Bruker D8 ADVANCE machine is using Bragg-Brentano geometry with DAVINCI design and Gobel mirror to produce highly parallel X-ray beam. D8 and D2 instruments are shown in Fig. I.2.



Fig.I. 2 Bruker a) D2 PHASER and b) D8 ADVANCE XRD machines.

iii. X-ray Fluorescence Spectroscopy (XRF)

The XRF depends on fundamental principle method of interaction between the X-ray beams and electrons within the sample. XRF is a non-destructive method that can be used for the qualitative and quantitative determination of the elemental composition of a material.

The operational principle of XRF is based on the secondary X-rays the Fluorescence-radiation of specimen atoms, when the sample irradiated with X-rays. X-ray has extremely short wavelength, measuring from $100\text{\AA}$ to $0.1\text{\AA}$ and consequently, has very high ionization energy. Therefore, X-ray easily passes through material and ionization, ejection of one or more electrons from the specimen atoms, may take place. Irradiated X-ray, expels the specimen atom's inner-

shell electrons to the outer shell. The removal of an electron in this way makes the electronic structure of the atom unstable and an outer electron replaces the missing inner electron. There are multiple types of allowed transitions that occur which are governed by the laws of quantum mechanics, each transition having its own specific energy or line [4, 5]. During this transition, energy is released in the form of a photon, with the energy equal to the energy difference of the two orbitals involved. The emitted radiation is of lower energy than the primary incident X-rays and is called fluorescent radiation, which has energy characteristic of the atoms present. Since the wavelength and energy of the fluorescence radiation is specific for each element, XRF analysis with the light of Moseley's law, enables qualitatively elemental and chemical characterization of the specimen. Additionally, quantitative analysis can be carried out by calculating the intensity of the fluorescence radiation one may obtain a complete breakdown of the composition of known or unknown material.

XRF instruments in use today can be broadly categorized in two spectrometers as, energy-dispersive (ED) and wavelength-dispersive (WD) spectrometers. There is tremendous variety of differing configurations, X-ray sources and optics, and detector technologies within these two different categories. Generally, WD disperses the fluorescent in the sample using dispersion crystal and uses goniometer to measure the intensity, resulting in a large size device. On the other hand, the detector in EDX leads superior energy resolution and requires no dispersion system, which enables downsized device [4].

In order to excite the atoms, a source of radiation with sufficient energy should be used to dislodge a tightly held inner electrons. Conventionally, X-ray generators are used due to their high power. Additionally, gamma ray sources can be used due to their high output, which allows an easier use in small portable instruments. The X-ray tube generates the X-radiation when the tube accelerates the electrons at high voltage and bombards them through metal anode. The electrically heated cathode emits electrons. Accelerated by the applied high voltage to very high speeds, the electrons bombard the anode material. This generates the primary X-radiation. With the optics like a polycapillary or with the systems like synchrotron very narrow and intense X-ray beams can be produced. As a result, atomic information on the subatomic scale can be obtained. X-ray generators in the range 1–50 kV are used, which allow excitation of a broad

range of atom. While a high intensity of low energy is required, i.e. 1-10 keV, for detection of light elements, heavy elements require excitation at higher energies up to 50 keV [5, 6] In wavelength dispersive analysis (WDS), the fluorescent X-rays emitted by the material sample are directed into a diffraction grating monochromator. As the d value of the diffracting crystal is known, the detector and diffracting crystal can be moved (using the goniometer) through an angle θ , so that only X-rays with a specific wavelength arrive at the detectors. Therefore, the X-ray detector can be adjusted to measure only the X-rays produced by fluorescence of atoms of one element; the intensity of this radiation is proportional to the abundance of that element within the sample.

On the other hand, in energy dispersive analysis (EDS), dispersion is accomplished by the usage of a semiconductor-type detector. This detector produces a "continuous" distribution of pulses, the voltages of which are proportional to the incoming photon energies. This signal is processed by a multichannel analyzer, which produces an accumulating digital spectrum that can be processed to obtain analytical data [6].

In this thesis, Bruker S8 Tiger XRF spectrometer having a 4 KW, Rh anode X-ray tube is used for XRF measurement which is shown in Fig.I.1.



Fig.I.2 Bruker S8 Tiger XRF spectrometer.

iv. Thermal analysis (Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermal Gravimetric (TG)

Differential Thermal Analysis (DTA) is a technique, which the differences in temperature between a sample and a reference is measured as a function of temperature while are exposed to the same heating rate. The temperature difference between sample and reference is measured by differential thermocouple in which one junction is in contact with the underside of the sample crucible and other is in contact with the reference [7].

When the sample undergoes a transformation, e.g. melting which absorb (endothermic) heat, the instrument will notice that the sample is cooler than the reference and will indicate the transformation as an “endotherm” on a plot of differential temperature versus time [8]. The reference material is any substance, with about the same thermal mass as the sample, which undergoes no transformations in the temperature range of interest. The sample temperature is measured via the voltage across the appropriate screw terminals and similarly for the reference temperature; generally only one or the other is recorded [8].

Although the outputs of a differential scanning calorimeter (DSC) are visually similar to a DTA, the operating principle of this device is entirely different. There are separate containers for both sample and reference, and associated with each are individual heating elements as well as temperature measuring devices. Both cells are surrounded by a refrigerated medium which permits rapid cooling. The sample and reference chambers are equally heated according to a temperature regime in which a transformation takes place within the sample. As the sample temperature infinitesimally diverges from the reference temperature, the device detects it and reduces the heat input to one cell while adding heat to the other, so as to maintain a zero temperature difference between the sample and reference, establishing a null balance. The quantity of electrical energy per unit time which must be supplied to the heating elements, in order to maintain this null balance, is assumed to be proportional to the heat released per unit time (Watts) by the sample [8].

There are two main types of DSC design; heat flux and power compensated (see Fig.I.4). A heat flux DSC has a temperature controlled heat sink, and a thermal resistor is placed between the reference, sample and heat sink. The temperature difference is detected at fixed points of the

thermal resistor. Power compensated DSC has no heat sink, and only warms and cools the area around the sample and reference with a micro heater so it is suitable for quick heating and cooling [9].

Thermogravimetric analysis (TG) is the study of weight changes of a specimen as a function of temperature. The technique is useful for transformations involving the absorption or evolution of gases from a specimen consisting of a condensed phase. The balances associated with TG's are highly sensitive, with resolutions down to 1 μg [8].

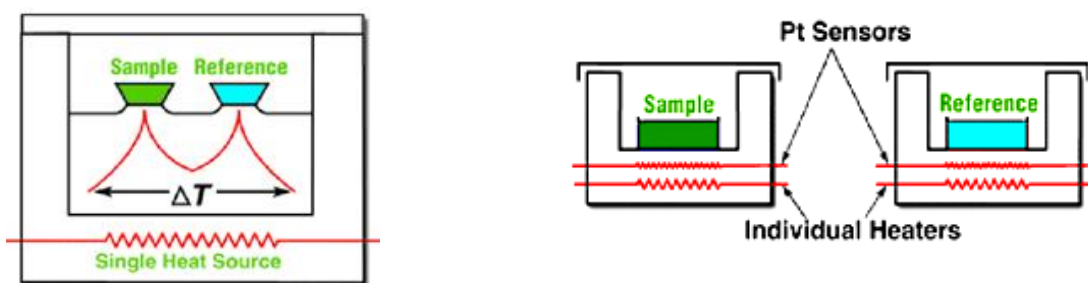


Fig.I.4 Power compensated and heat flux DSC [10].

A popular and useful device is a combined DTA/TG (Simultaneous Thermal Analysis: STA) system in which both thermal and mass change effects are measured simultaneously on the same sample. The individual balance beams for the sample and the reference are placed in the furnace horizontally, mass is measured with drive coils sensitivity-calibrated for the sample and the reference independently, and the difference in mass is output as TG signal. By conducting mass measurements differentially, effects of beam expansion, convection and effects of buoyancy are cancelled and high sensitivity thermal mass measurement is achieved.

By using independent drive coils for the sample and reference measurements, TG baseline drift (baseline movement due to temperature change) can be adjusted easily and electrically. A thermocouple is also placed directly below the individual holders for the sample and reference, measuring sample temperature while outputting DTA signal simultaneously [9].

In this thesis, DTA/TG is measured using SII EXSTAR 6300 coupled with Pfeiffer Thermostar 220 mass spectrometer (MS). DSC studies have done using NETSZCH DSC 204 with controller TASC 414/3A which are shown in Fig.I.5.



Fig.I.5 a) DSC NETSZCH b) DTA/TG/MS SII EXSTAR 6300 coupled with Pfeiffer ThermoStar devices.

v. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR)

FTIR is a sensitive and non-destructive technique for identifying unknown substances. It provides specific information about the vibration and rotation of the chemical bonding and molecular structures of organic materials and certain inorganic materials. IR spectroscopy identifies the presence of certain functional groups in a molecule. Additionally, since it is an absorption spectroscopy, obtained information about the absorption bands can be used to confirm the identity of a pure compound or to detect the presence of impurities in semiconductor materials [11].

IR absorption spectroscopy is the study of interaction between matter and electromagnetic radiation in the IR region as a function of photon frequency. The total internal energy of a molecule in a first approximation is the sum of rotational, vibrational and electronic energy levels. In IR region, the electromagnetic waves mainly couple with the molecular vibrations, since a molecule can be excited to a higher vibrational state by absorbing the IR radiation. Like electronic transitions, these vibrational transitions correspond to distinct energies. Means, chemical bonds vibrate at characteristic frequencies. Molecules absorb infrared radiation, if only the photon energy coincide with the vibrational energy levels of the molecule. Therefore,

infrared spectrum represents a fingerprint analyze of a sample with absorption peaks, since each material is a unique combination of atoms, no two compounds produce the exact the same infrared spectrum. In addition to the qualitative analyze, the intensity of the peaks in the spectrum is directly proportional with the amount of the material present. Identification of the spectroscopy cannot be carried out directly. A means of “decoding” of the individual frequencies is required. This can be accomplished via a well-known mathematical technique called Fourier transformation is performed by the software algorithms.

In FTIR spectroscopy, an interference wave, which is produced in an interferometer, interacts with the sample in contrast to a dispersive instrument, where the interacting energy assumes to have a well-defined wavelength range [12] Interferometer divides radiant beams by generating an optical path difference between the beams, which is controlled by a computer. Produced interference signals measured as a function of optical path difference by a detector. Commonly used interferometer is a Michelson interferometer.

The beam splitter in the Michelson interferometer divides a collimated light beam from the IR source. One-half of the beam is reflected from a fixed mirror while the other half reflects from a moving mirror. These two beams recombine after reflections and reconstruct an interference wave. This interference wave is irradiated on the sample and its modification after the interaction with the sample gives the information about the specimen[12].

One cycle of mirror movement should be accomplished to construct a complete FTIR spectrum by using fast Fourier transform algorithm [13] and an average interferogram is calculated after each addition scans. An interferogram is an electric signal that is a function of the time delay (retardation) of the two light beams, which were split up in the interfereferometer. Finally, Fourier transformation enables to convert the signal from the so-called time domain to the frequency domain, where it is a function of frequency [13].

In this thesis, Thermo Scientific iS10 FT-IR single reflection equipped with diamond ATR is used which is shown in Fig.I.6.



Fig.I.6 Thermo Scientific iS10 ATR-FTIR instrument.

vi. Raman spectroscopy

Its operational principle relies on the inelastic scattering of monochromatic light. It relies on the light-matter interaction. Since elastic scattering takes place, the frequency of the monochromatic light changes after its interaction with the sample. The photons of the monochromatic light absorbed by the material and the reemitted with a shifted frequency. The comparison of these shifting with the original monochromatic frequency is called Raman Shifts. These shifting provide information about the vibrational and rotational frequency transitions in molecules [14].

Atoms of a molecule can perform periodic motions due to the elastic bonds, which are connected to each other with. All motions of the atoms in a molecule are a superposition normal vibrations, in which all atoms are vibrating with the same phase and normal frequency. These vibration's amplitudes are described by a normal coordinate. Vibration spectra depends on the masses of the atoms, their geometrical arrangement and strength of their chemical bonds [14]. IR and Raman spectroscopies are two most important tools to obtain vibrational spectra. Vibrations may be active or forbidden in the IR or Raman spectrum, depending on the symmetry of the molecule.

The absorption frequency depends on the molecular vibrational frequency, on the other hand the absorption intensity depends on how effectively the IR radiation can be transferred to the

molecule, and this depends on the change in the dipole moment that occurs as a result of molecular vibration. Dipole moment is the measure of the electrical polarity of a system of charges. The electric field component of the electromagnetic radiation exerts force on the molecular charges and by definition the forces on opposite charges will be exerted in the opposite directions. As a result, oscillating electric field of the photon will exert induce the dipole moment of the molecule to oscillate at the frequency of the photon. At certain frequencies both dipole moment and the nuclei oscillate simultaneously. These are molecular vibrational frequencies where the vibration results in a change in the dipole moment. Forced dipole moment oscillation activates a nuclear vibration. If a molecular vibration causes no change in the dipole moment, then forced dipole moment oscillation cannot activate that vibration [15].

A Raman spectrometer requires four elements including; light source, sample, wavelength selector and detector. Scattering spectroscopy (Raman) experiences much smaller cross section compared to absorption spectroscopy (IR). As a result, Raman scattering intensity is much weaker than that IR absorption intensity. Therefore, a powerful light source is essential. Raman spectrometers use lasers exclusively as the light source. Generally, a laser source with the wavelength in the range of visible (390-700 nm), near infrared (700nm-1400nm) or near ultraviolet (300-400nm) is used. The laser light is called the excitation light or incident beam. The optical path from laser to sample is called the incident beam path.

A dispersive Raman spectrometer uses a monochromator as wavelength selector. A dispersive Raman microscope is a dispersive Raman spectrometer coupled with (typically) optical microscope. An array detector such as charge coupled device (CCD) camera records a thousand(s) spectral points at once. Because a CCD detector is made of very small pixels, each slit serves as an exit slit (pixel size = exit slit width), the light from the monochromator is directly imaged onto the CCD.

In this thesis, Raman spectroscopy were done with using FT Raman BURKER RFS 100/S spectrometer (Nd: YAG-Laser, 1064 nm, 200 mW) as well as Raman microscope RENISHAW inVia equipped with 785nm, 633nm, 532nm excitation laser sources which are shown in Fig.I.7.



Fig.I.7 RENISHAW inVia Raman microscope and BURKER RFS 100/S FT Raman spectrometer.

vii. Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) uses finely focused beam of high-energy electrons in order to generate a variety of signals to study surface fine structures [16]. The signal derivation is based on the electron-sample interactions. SEM analysis provides structural and chemical information about the sample including surface topography, chemical composition, crystalline structure and orientation of materials on a local scale. Depending on the type of the specimen and the resolution needed wide range of voltages can be used during SEM analysis [17]. High magnification and high-resolution SEM images with detail on nanometer scale can be obtained to analyze individual crystals. The spatial resolution is better than that of the optical microscope, but not as good as for the transmission electron microscope (TEM). Lower accelerating voltage (typically 30 keV) than for a TEM, due to its smaller electron gun, and also smaller axially-symmetric magnetic lenses result in lower resolution for SEM [18]. SEM is also capable of performing analyses of selected point locations on the sample. Using SEM in conjunction with the technique of energy-dispersive X-ray microanalysis (EDX), qualitatively or semi-quantitatively the chemical composition of individual crystals or substance can be determined.

The basic principle behind the SEM operation is the bombardment of the specimen by a convergent beam of electrons, which is scanned across the surface. After the impingement of the

fast primary electrons with the specimen surface, secondary electrons come out and they detected by an electron collector [19]. Since the accelerated electrons carry significant amounts of kinetic energy, this energy is dissipated as a variety of signals other than secondary electrons. These signals include backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence–CL), and heat. The collector can be adjusted to deal with all the other signals as well, either in turn or simultaneously. Secondary electrons and backscattered electrons are commonly used for imaging samples. While detecting secondary electrons are good to create image the morphology and topography on samples, detecting backscattered electrons enables illustration contrasts in composition in multiphase samples. These detected signals and the intensity of one of the signals (at a time) is amplified to be used as the intensity of a pixel on the image on the computer screen. The electron beam then moves to next position on the sample and the detected intensity gives the intensity in the second pixel and so on [17].

SEM consists of an electron optical system which includes electron gun, optic lenses and a scanning coil to scan the electron probe and a specimen stage to place the sample, a detector, an image display unit and additional operational system units for various operations.

The SEM operates at very high vacuum environment to prevent electrons to disperse or scatter due to collisions with other molecules. Without sufficient vacuum in the SEM, the electron beam cannot be generated. To operate the SEM, vacuum should be below 10^{-4} Torr. The higher the vacuum (the lower the pressure), the better the microscope will function. To pump from atmospheric pressure down to 10^{-6} Torr, two classes of pumps are used: mechanical pump (rough pump) (atmosphere down to 10^{-3}) and a high vacuum pump (diffusion pump, turbo molecular pump, ion-getter pump, cryopump) (10^{-3} down to 10^{-6} or greater depending on type of pump). The mechanical pump lowers the pressure to 10^{-3} Torr and with the high vacuum pump the pressure decreases to values lower than 10^{-4} Torr [19].

The electron gun generates beam in the electron microscope. It composed of three components. A tungsten filament or hot cathode, combined thermal and field emission, pure field emission, borides or oxides, pulsed, pointed or flat or curved. Secondly, a grid cap to control the

flow of electrons, and a positive charged anode plate to accelerate the electrons through the specimen. The voltage used in SEM ranges from 0.1 to 40 kilovolts (keV). 10 keV is most common value for biological specimens or heat sensitive samples (e.g. plastics and rubber) and 20 keV is ideal inorganic specimens. The higher the voltage leads to better the resolution but the greater the heat generation on the specimen [18].

The electron beam is accelerated through a high voltage and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons and the electron source is formed in the plane of the specimen. Electrons in motion are affected by two fields: electrostatic fields and magnetic fields. In the electron gun, electron motion is controlled by an electrostatic field, while as the source moving on the specimen surface it controls by magnetic lenses. Electron beam deflection (1, 2, 3, ..., n times) along the path by fields can be controlled by the scanning generator. As a result the beam is moved over the surface of the specimen in a predetermined form following a digital input [18].

Signal detection begins when a beam of electron irradiates on a specimen. These electrons will be scattered by an electron or a nucleus and they will have a new trajectory. These scatterings are detected by the detector. The primary beam hitting the specimen results in the formation of a teardrop shaped reaction vessel, where all the scattering takes place. The volume of a reaction vessel depends upon the atomic density of the specimen, topography of the specimen and the acceleration potential of the primary electron beam [16]. While small reaction vessels give better resolution, the deeper vessels provide higher signals.

In this thesis, Zeiss Ultra Plus field emission SEM is used which is shown in Fig I.8.



Fig.I.8 Zeiss Ultra Plus FE SEM instrument which is used in this thesis.

viii. CNHS/O Analyzer

CNHS analyzer, operates according to Pregl-Dumas method (combusting a sample with a known mass in a high temperature ($\sim 900^{\circ}\text{C}$) and in the atmosphere of oxygen) to determine Carbon, Nitrogen, Hydrogen Sulfur. The combustion can be performed under static (fixed volume of oxygen) or dynamic condition (fixed time of oxygen flow). The sample in very small amount (2-3 mg) are wrapping into a Tin capsules and will enter to the combustion chamber along with an oxygen. They will flash combust with oxygen at temperatures of $900\text{--}1000^{\circ}\text{C}$ and the carbon, nitrogen, hydrogen and sulfur are converting into, CO_2 , N_2 , H_2O and SO_2 , respectively. They will pass then over a high purity copper (heated at around 600°C) with a He carrier gas in order to remove excess and unreacted oxygen. There are also additional absorbents to remove unwanted combustion products. Finally, the produced species are brought into a gas chromatography (GC) system in order to separate combustion gases. This will be followed by detection using thermal conductivity detection (TCD). Total run time is approximately is 10 min. For oxygen there is a separate chamber which is operate in pyrolysis mode [20-22]. In this thesis

FLASH 2000 CHNS/O Elemental Analyzer made by Thermo Scientific is used. The schematic of instrument and device which is used is shown in Fig.I.9 and Fig.I.10.

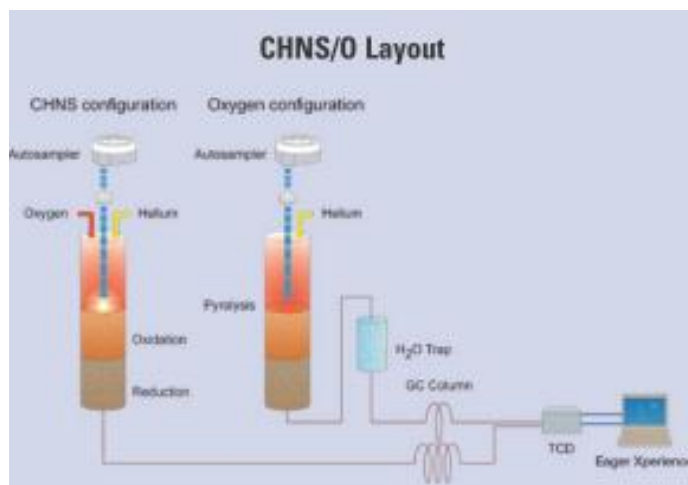


Fig.I.9 CHNS/O configuration with TCD detector [22].



Fig.I.10 FLASH 2000 CHNS/O Elemental Analyzer instrument.

ix. Electron Paramagnetic Resonance Spectroscopy (EPR)

Electron paramagnetic resonance (EPR) is a spectroscopic technique for studying the structure and dynamics and the spatial distribution of paramagnetic species, which have at least one unpaired electron and chemically reactive [23]. EPR spectroscopy is a useful technique for analyzing metal complexes or organic radicals. The basic concepts of EPR are similar to those of nuclear magnetic resonance (NMR), but the energy required for flipping the spins provided in the form of electromagnetic radiation in this case is absorbed not by nuclei as in NMR, but by molecules, ions or atoms with at least one unpaired electron spins. The g values and unpaired electrons of solid or liquid paramagnetic specimens provide fingerprint information [24].

Every electron has a spin quantum number $S=1/2$, with magnetic components $m_s=+1/2$ and $m_s=-1/2$. When a molecule or compound with an unpaired electron is placed in a strong magnetic field, the spin of the unpaired electron can align itself either the parallel to the magnetic field which corresponds to the lower energy state $m_s = 1/2$ or o antiparallel to the applied magnetic field $m_s = + 1/2$. The two alignments have different energies and this difference in energy lifts the degeneracy of the electron spin states. The energy difference is given by:

$$\Delta E = g_e \mu_B B_0$$

where g_e is a unitless measurement of the intrinsic magnetic moment of the electron, $g_e = 2.0023$ for the free electron [25], μ_B is the Bohr magneton. An unpaired electron in the specimen can move between the two energy levels by either absorbing or emitting a photon of energy $h\nu$ such that the resonance condition, $h\nu = \Delta E$, is obeyed. This leads to the fundamental equation of EPR spectroscopy $h\nu = g_e \mu_B B_0$.

In an EPR spectroscopy, while the sample is exposed to fixed microwave irradiation, the field of the spectrometer magnet is swept linearly to excite some of the electrons in the lower energy level to the upper energy level. EPR spectrum is the absorption of microwave frequency radiation plotted against the magnetic field intensity. Different microwave frequencies may be used and they are denoted as S-band (3.5 GHz), X-band (9.25 GHz), K-band (20 GHz), Q-band (35 GHz) and W-band (95 GHz).

The microwave bridge supplies microwaves at a fixed frequency and chosen power, however, the microwave frequency can be adjusted over a limited frequency range. Klystron or a gundiode is used as the microwave source. The most commonly used and commercially available frequency is ca. 9.25 GHz (X-band) corresponded resonance field for $g=2$ is 0.3300 T. Generated microwaves are transmitted to a sample cavity via a waveguide. If one wants to determine g -values from EPR spectra, one has to know both the field B_0 and the microwave frequency [24].

In this thesis EPR measurements were performed with a Bruker EMX spectrometer. We have used a rectangular TE102 (X-band) resonator from Bruker which are shown in Fig.I.11.



Fig.I.11 Bruker EMX spectrometer and rectangular TE102 (X-band) resonator.

x. Rietveld analysis

The total-pattern-fitting structure refinement or profile refinement known as Rietveld method, is a powerful and relatively new method for extracting detailed crystal structural information from X-ray and neutron powder diffraction data. In the Rietveld analysis, the nonlinear least-squares refinements are applied until the best fit is obtained between the whole observed powder diffraction pattern and the entire calculated pattern based on the simultaneously refined models for crystal structures, diffraction optics effects, instrumental factors and other sample characteristics [26, 27].

The method, which decomposes the powder pattern into individual Bragg components (as many hkl and intensity values as possible) without reference to a structural model, is called the

pattern decomposition method which is first proposed by Pawley in 1981 [28] and later is modified in order to overcome some problems of Pawley method by LeBail [29]. LeBail used very different simple approach to extract the peak intensity from powder profile. The Rietveld analysis is using these methods [30].

Rietveld method is mainly a computational technique and uses non-linear least square method, in which initial approximation of many free variables is required. These variables consist of peak shape, unit cell dimensions and coordinates of all atoms in the model of crystal structure. The success of this method is directly related to the quality of powder diffraction data and also the experience and the ability of the user in the refinement sequence.

Profile fitting methods can be categorized into two categories:

- 1) *Analytical profile fitting*: All these peak shape functions are using analytical approach to profile fitting (Gaussian, Lorentzians, Voigt, pseudo-Voigt and Pearson VII) and angular dependence of the peak shape is described by smoothly varying functions with 2θ . On the other hand, for profile fitting using these function, one generally perform fitting by peak shape functions with a clear and relatively simple mathematical form which can be differentiated analytically with respect to each of the refined parameters within the least squares refinement procedure [31].
- 2) *Direct convolution approach*: In this method, profiles are produced by convolution where various function are convoluted to form the observed profile shape. Fundamental Parameter approach(FPA) is using physically based model to describe both instrumental broadening and any diffraction broadening causing by specimen (approach is numerically and empirically). One of the advantages of FPA is that good fit can be obtained over whole 2θ range using the known parameters of diffractometer such as slit size and diffractometer radius [31, 32].

In this thesis, TOPAS software from Bruker is used for profile fitting. This software is integrating all currently employed profile-fitting techniques. It is using FPA for profile fitting and Double-Voigt approach for size and strain determination. In this software, Double-Voigt approach is implemented to calculate volume weighted mean crystallite sizes (LVol-IB and

LVol-FWHM) and a means strain value (ϵ_0) in terms of Lorentzian and Gaussian type line broadening [31, 33].

xi. References

1. Cullity, B.D., *Elements Of X Ray Diffraction*. 1956: Addison-Wesley Publishing Company, Inc.
2. Zavalij, V.K.P.a.P.Y., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. 2005, Springer: New York. p. 713.
3. Döbelin, N. *Diffraction and Phase Identification*. 2013.
4. Ron, J., *X-Ray Fluorescence Spectrometry*. 1988: John Wiley & Sons, Inc. .
5. Pella, P.A., *X-ray fluorescence spectrometry by Ron Jenkins Published by John Wiley & Sons, New York, 1988; ISBN 0-471-83675-3*. X-Ray Spectrometry, 1989. **18**(4): p. 187-187.
6. Douglas A. Skoog, F.J.H., Timothy A. Nieman, *Principles of Instrumental Analysis*. Fifth Edition ed. 1998: Thomson Learning, Inc. .
7. Robinson, J.W., *Undergraduate instrumental analysis* 5th ed. 1994, New York: M. Dekker.
8. F.Speyer, R., *Thermal Analysis of Materials*. Materials Engineering, 5. 1994: Marcel Dekker, Inc. 285.
9. PerkinElmer, *Diamond Thermogravimetric/Differential Thermal Analyzer Manual*. 2006.
10. Papánková, B. *LABORATORY OF CALORIMETRY*.
11. Smith, B.C., *Fundamentals of Fourier Transform Infrared Spectroscopy, Second Edition*. Second Edition ed. 2011: CRC Press.
12. Faix, O., *Fourier Transform Infrared Spectroscopy*, in *Methods in Lignin Chemistry*, S. Lin and C. Dence, Editors. 1992, Springer Berlin Heidelberg. p. 83-109.
13. Cooley, J.W. and J.W. Tukey, *An Algorithm for the Machine Calculation of Complex Fourier Series*. Mathematics of Computation, 1965. **19**(90): p. 297-301.
14. *Infrared and Raman Spectroscopy: Methods and Applications*. 2007: Wiley Online Library.
15. Norman Colthup, L.D., Stephen Wiberley, *Introduction to Infrared and Raman Spectroscopy*. 2nd Edition ed. 1975: Academic Press Inc.
16. Joy, D.C., *Scanning electron microscopy: Second best no more*. Nat Mater, 2009. **8**(10): p. 776-777.
17. Dunlap M., A.J.E., *Introduction to the Scanning Electron Microscope Theory, Practice, & Procedures Prepared*. U. C. Davis 1997.
18. Egerton, R., *Physical Principles of Electron Microscopy: An Introduction to TEM, SEM, and AEM*. 2005: Springer Science+Business Media, Inc. .
19. Nixon, W.C., *The General Principles of Scanning Electron Microscopy*. Philosophical Transactions of the Royal Society of London B: Biological Sciences, 1971. **261**(837): p. 45-50.
20. Thompson, M., *CHNS Elemental Analysers Analytical Methods Committee*, 2008. **29**.
21. *Elemental Combustion System CHNS-O*, C.A.T. Inc., Editor. 2010.
22. Liliana Krotz, G.G., *Organic Elemental Analysis for Carbon Characterization by the Thermo Scientific FLASH 2000 CHNS/O Elemental Analyzer*, in Italy, T.F. Scientific, Editor. 2012.
23. Jeschke, A.S.a.G., *Principles of Pulse Electron Paramagnetic Resonance*. 1st Edition ed. 2001: Oxford University Press.
24. Goodman, B.A. and P.L. Hall, *Electron paramagnetic resonance spectroscopy*, in *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods*, M.J. Wilson, Editor. 1994, Springer Netherlands. p. 173-225.

25. Odom, B., Hanneke, D., D'Urso, B., and Gabrielse, G., *New Measurement of the Electron Magnetic Moment Using a One-Electron Quantum Cyclotron*. Physical Review Letters, 2006. **97**: p. 030801.
26. Young, R.A., ed. *The Rietveld method* 1993, International Union of Crystallography New York
27. Vitalij K. Pecharsky, P.Y.Z., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. Second Edition ed. 2009: Springer.
28. Pawley, G., *Unit-cell refinement from powder diffraction scans*. Journal of Applied Crystallography, 1981. **14**(6): p. 357-361.
29. Le Bail, A., H. Duroy, and J. Fourquet, *Ab-initio structure determination of LiSbWO₆ by X-ray powder diffraction*. Materials Research Bulletin, 1988. **23**(3): p. 447-452.
30. Toraya, H., *WHOLE-POWDER-PATTERN DECOMPOSITION METHOD*. The Rigaku Journal, 1989. **6**(2).
31. Coelho, A., *TOPAS Academic Users Manual Version 5*. 2012.
32. R. W. Cheary, A.A.C., J. P. Cline, *Fundamental Parameters Line Profile Fitting in Laboratory Diffractometers*. Journal of Research of the National Institute of Standards and Technology, 2004. **109**: p. 1-25.
33. Girgsdies, F., *X-ray Powder Diffraction in Catalysis*. 2006, Fritz-Haber-Institut der Max-Planck-Gesellschaft: Berlin, Germany.