Development of Magnesium Boride Etherates as Hydrogen Storage Materials

Dr. G. Severa (PI) and Prof. C. M. Jensen (Co-PI)

University of Hawaii at Manoa

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University of Hawai'i Mānoa

HNEI Hawai'i Natural Energy Institute University of Hawai'i at Mānoa

Project ID # ST138

Overview

Timeline and Budget

- Project Start Date: 10/01/2016
- Project End Date: 09/31/2019
- Percent Completion: 16 %

Barriers

Barrier	Target
Low System Gravimetric capacity	> 7 wt% H_2 system
Low System volumetric capacity	> 40 g/L system
Low System fill times	1.5 kg hydrogen/min

Timeline and Budget

- Total Project Budget FY17-FY19: $1,204,366
- Total Project Budget FY 17: $270,878
- Total Recipient Share FY 17: $ 27,086
- Total Federal Share FY17: $243,792
- Expended DOE Funds FY: $ $49,761.59 as of 3/31/17

Partners

- HyMARC Consortium
  - **SNL**: High Pressure Hydrogenation
  - **SNL**: Surface Characterizations
  - **LLBL & LLNL**: Theoretical Modelling

RELEVANCE

Objective: Synthesize and Characterize Magnesium Boride Etherates Hydrogen Storage Materials Capable of Meeting DOE 2020 Targets.

- Demonstrate ≥ 7.0 wt % hydrogen uptake by a MgB_2 etherate at ≤ 300 ˚C, 700 bars 48 hrs and reversible release of ≥ 2 wt% H_2 by at least one MgB_2 etherate.

Storage Parameter	**Units**	**2020 Target**	**Ultimate Target**
Low System Gravimetric capacity	kg H_2/kg system	0.055	0.075
System volumetric capacity	kg H_2/L system	0.040	0.070
System fill times (5 kg)	kg H_2/min	1.5	2.0
Min Delivery Pressure	bar	5	3
Operational cycle (1/4 tank to full)	cycles	1500	1500

Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan: https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

RELEVANCE: Recent Advances in $Mg(BH_4)_2$ Research

- **Recent improvements in magnesium borohydride research.**

	Hydrogenation			Dehydrogenation		Cycling wt%	
Dehydrogenation Product	Temp ˚C	P atm	time h	Temp ˚C	time h	Theory	Exp
MgB_2 (HP)	>400	>900	108	530	20	14.8	**11.4**
MgB_2 (reactive ball milling/HT-HP)	/400	10/400	10/24	390	-	14.8	**4**
$Mg_{0.75}Mn_{0.25}B_2$	380	150	38	225-400	-	>11	**1**
$Mg(B_3H_8)_2(THF)_x/2MgH_2$	200	50	2	180	12	<2.5	
$Mg(B_3H_8)_2/2MgH_2$	250	120	48	250	120	2.7	**2.1**
$Mg(B_{10}H_{10})_2(THF)_x/4MgH_2/X$	200	50	2	200	12	4.9	**3.8**

$Mg(BH_4)_2$ ammoniates

- Improved kinetics on dehydrogenation even though, NH_3, very stable BN products formed.

$Mg(BH_4)_2$ and Mg borane etherates

- Improved H_2 cycling kinetics on ether coordination, lower H_2 capacity.
- Strong coordination of ethers to magnesium at high temp.

Current state-of-the-art:

- Better H_2 cycling kinetics (lower pressures and temperatures).
- Lower gravimetric H_2 storage capacity.

Efforts show plausibility of greatly enhancing kinetics of Mg borohydride materials.

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Grigorii Soloveichik, Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Job Rijssenbeek, Matt Andrus, and J.-C. Zhao, Inorg. Chem. **2008**, 47, 4290-4298
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Relevance: Potential for Practical Hydrogen Storage Properties

$$MgB_2(ether)_x \longrightarrow Mg(BH_4)_2(ether)_x$$

Mols ether/ Mol MgB_2 (x)	**0.70**	**0.40**	**0.20**	**0.10**	**0.05**
Wt % Hydrogen					
$MgB_2(OMe_2)_x$	9.4	11.1	12.8	13.8	14.3
$MgB_2(THF)_x$	7.7	9.7	11.8	13.2	14.0
$MgB_2(OCH_2Me_2)_x$	7.6	9.6	11.7	13.1	14.0
$MgB_2(Dioxane)_x$	7.0	9.0	11.3	12.8	13.8
$MgB_2(polyether)_x$				>12	>12

Minimize ether:MgB_2 ratio

- Lower hydrogenation temperature.
- Lower hydrogenation pressure.
- Increase hydrogen sorption rates.
- Increase amount of cyclable H_2 at moderate temp and pressure.

Potential to improve practical hydrogen storage properties of $MgB_2/Mg(BH_4)_2$ system.

APPROACH: Synthesize, Characterize and Hydrogenate MgB_2 Etherate Materials

A. Synthesis of MgB_2 etherates by reactive ball milling and heat treatments from:

1. Mg borane etherates
2. MgB_2, in presence of ethers.

B. Hydrogenation reactions:

UH: ≤ 150 bars, ≤ 300 °C and HyMARC-SNL: ≤1000 bars, ≤ 400 °C, ≤ 72 hrs.

C. Characterizations: FTIR, TGA-DSC, XRD, ^{11}B and ^{1}H NMR, TPD-Mass Spec, X-Ray Scattering, TEM, SEM.

D. Theoretical Studies: HyMARC: LLBL and LLNL

Milestone #	Project Milestones	Quarter	Accomplished
1.1	Development of synthesis for MgB_2 etherates	1	95%
3.1	Characterize MgB_2 etherate by FTIR, ^{11}B and ^{1}H NMR, XRD.	2	65%
4.1	Demonstrate hydrogenation MgB_2 etherate to $Mg(BH_4)_2$ etherate.	3	50%
5.1	Demonstrate uptake of ≥7 wt H_2 by a MgB_2 etherate at 300˚C.	4	20%
6.1	Dehydrogenation of one hydrogenated MgB_2 etherate	4	10%

Go/No-Go Decision: Demonstrate ≥7.0 wt % hydrogen uptake by a MgB_2 etherate at ≤300 ˚C, 700 bars 48 hrs and reversible release of ≥ 2 wt% H_2 by at least one MgB_2 etherate.

Synthesis Approach 1: Synthesis from Mg Borane Etherate

1. Syntheses of MgB_2 Etherates from Dehydrogenation of Mg Borane Etherates

- Synthesis from Mg borane etherates and MgH_2
  - $Mg(B_xH_y)_z(X)_g + MgH_2$ (X = Ether)
- Synthesis from Mg borane etherates and other metal hydrides
  - $Mg(B_xH_y)_g(X)_z + MH_2$ (M= LiH, NaH)

Dehydrogenation in presence or absence of free ether
• Heat Treatment Under Pressure
• Ball Milling Pretreatment followed by Heat Treatment Under pressure
• Ball Milling Pretreatment in ether followed by Heat Treatment Under pressure

Confirm ether coordination by : FTIR, TGA-DSC, XRD, ^{11}B and ^{1}H NMR, TPD-Mass Spec.

Multiple approaches to MgB_2 etherates Syntheses

Synthesis Approach 2: Synthesis from MgB_2

2. Syntheses of MgB_2 Etherates from MgB_2 or its Precursors and Ethers.

a. Synthesis from MgB_2

- MgB_2+ Ether
- $MgB_{2-x}Y_x/Mg_{1-x}B_2Y_x$ + Ether; Y=LiH, NaH, Al or transition metal.

b. Synthesis from other MgB_2 precursors

- $MgH_2/Mg + 2B$, in presence of ethers

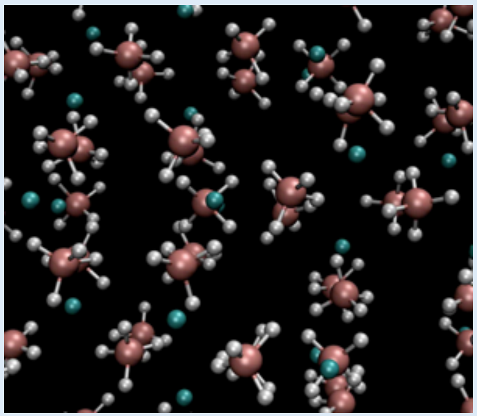
Synthesis Approach (in presence of ether)
• Heat Treatment Under Pressure
• Ball Milling Pretreatment followed by Heat Treatment Under Pressure
• Ball Milling Pretreatment in Ether followed by Heat Treatment Under Pressure
• Ball Milling Pretreatment followed by Ultra sonication

Characterization: Confirm ether incorporation by: FTIR, TGA-DSC, XRD, NMR, Mass Spec.

Multiple approaches to MgB_2 etherates Synthesis

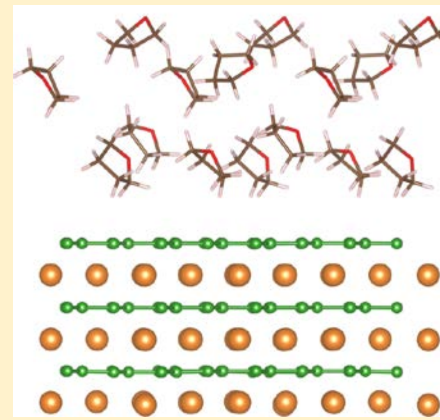
Approach: Molecular Dynamic Simulations

Ab initio molecular dynamics for chemistry and coordination analysis



Direct simulation of solute-solvent interactions, investigation of formation and/or dissociation of chemical bonds, charge transfer

Classical + Quantum mechanics for environment-dependent thermodynamics



Recipes for integrating different levels of theory for the solid/solvent interfaces, Analysis of materials stability depending on particle size and solvent environment

Reactive Quantum Molecular Dynamics Simulations of MgB_xH_y in Etherate Liquid

IR Simulations to identify coordinating species.

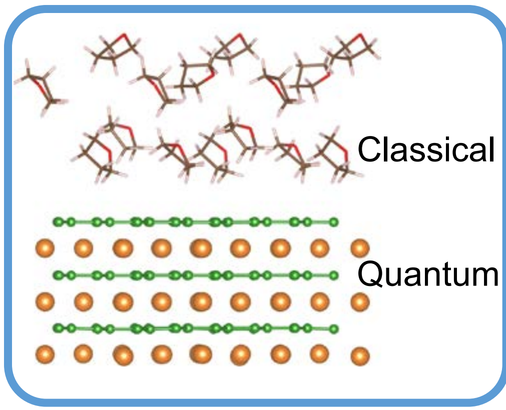
HyMARC Hydrogen Materials Advanced Research Consortium

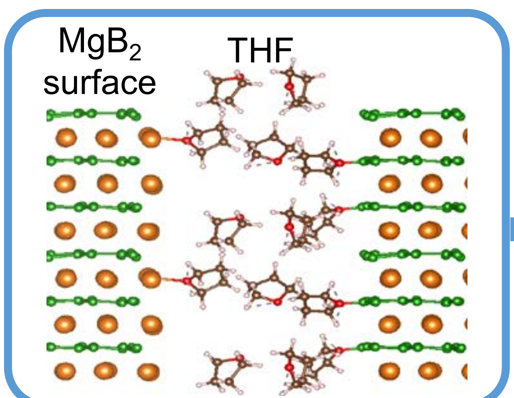
Enabling **twice the energy density** for onboard H_2 storage

Accomplishments and Progress

Stability and reactivity of MgB_2 surfaces in THF

MgB_2-THF interface simulated in classical + quantum mechanics and ab initio molecular dynamics





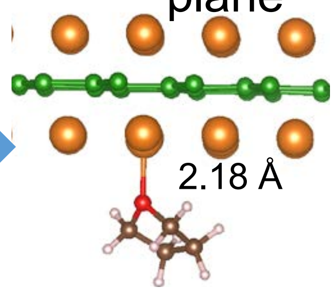
Change in MgB_2 surface energies by contacting with THF

$\Delta\gamma = \gamma_{THF} - \gamma_{vacuum}$

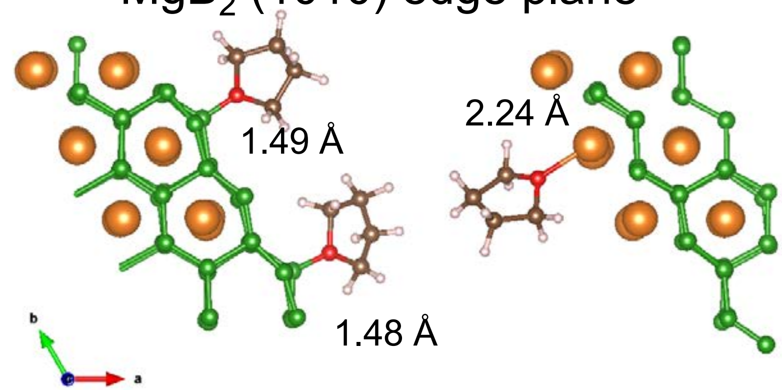
(0001) basal	Δγ (eV/Å²)	(10-10) edge	Δγ (eV/Å²)
Mg-terminated	−0.23	Mg-edges	−0.19
B-terminated	−0.20	B-edges	−0.15

Interaction with THF stabilizes MgB_2 surfaces, especially for Mg-exposed surfaces

MgB_2 (0001) basal plane



MgB_2 $(10\bar{1}0)$ edge plane



HyMARC Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

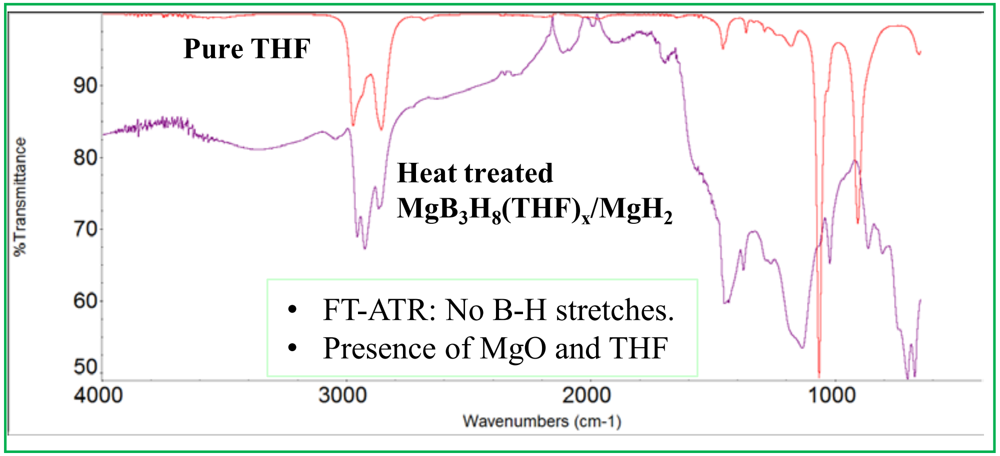
Explicit observation of bond formation between MgB_2 and THF

Accomplishments and Progress

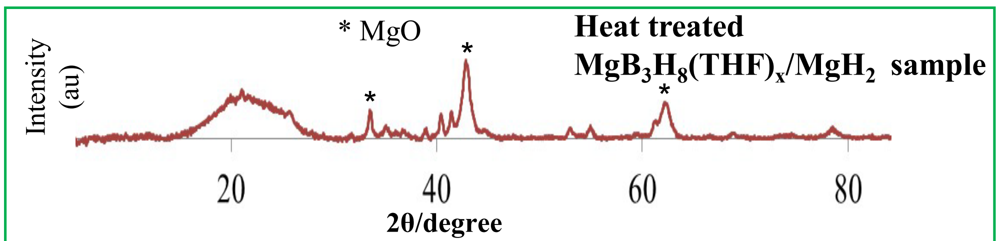
1. MgB_2 Etherate from Mg Borane Etherate: Synthesis from Mg Triborane THF

$$2MgB_3H_8(THF)_2 + MgH_2 \xrightarrow[390\ ^oC,\ 24\ h;\ 100\ ^oC,\ 24\ h]{THF} 3MgB_2(THF)_x + 9H_2$$

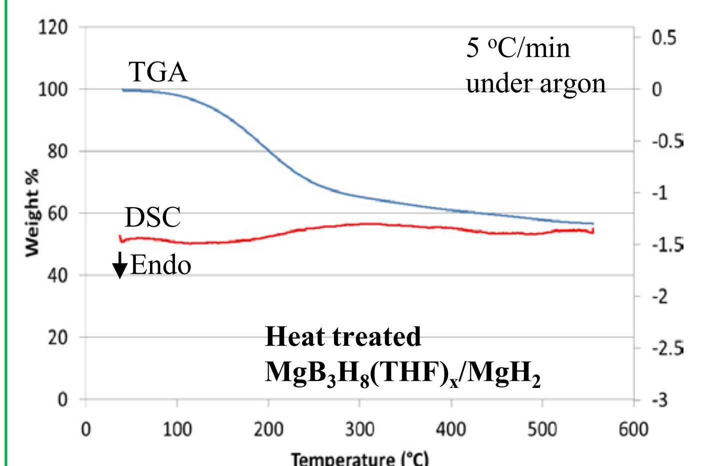
Characterization of synthesized product



^{11}B Solution NMR in D_2O indicates no soluble boron species.
Confirming absence of Mg borane etherates.



XRD: Preliminary XRD indicate mostly MgO and broad peak? at ~20^o



Weight loss at 80-400 ^{o}C indicate release of strongly coordinated species (e.g. THF or H_2)

- **FTIR and TGA suggest formation of coordinated species.**
- **Direct confirmation of strongly coordinated THF to be performed by TPD Mass Spec.**

Accomplishments and Progress

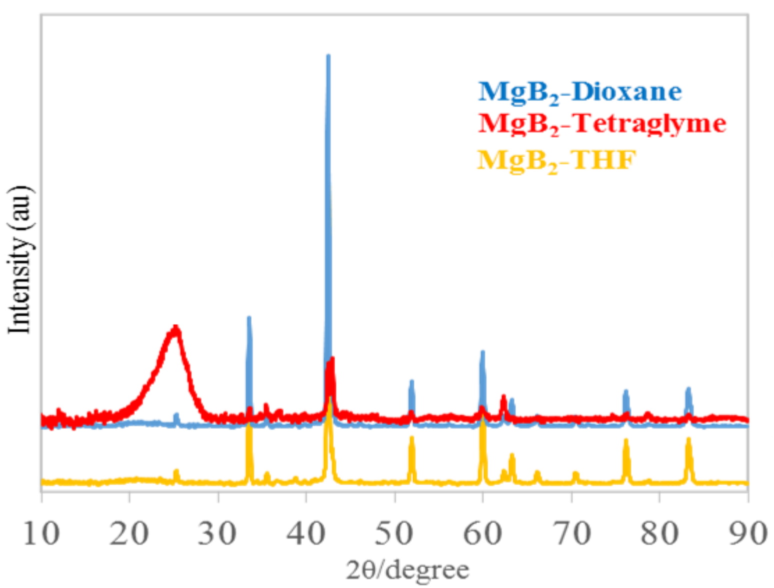
2. MgB_2 Etherates Syntheses from MgB_2

A. Synthesis By Heat Treatment

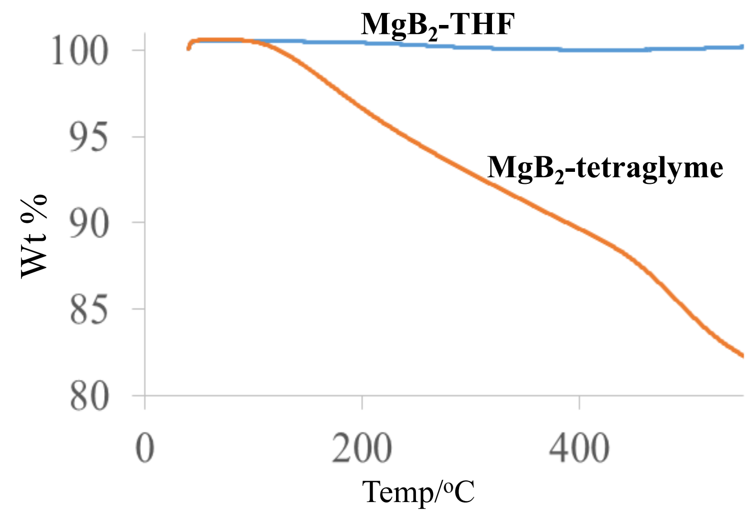
$$MgB_2 + xX \xrightarrow[\leq 24\ h]{\leq 300\ ^oC} MgB_2(X)_x$$

X= THF, Tetraglyme (TG), Dioxane

Characterization of synthesized products



All Samples: MgB_2 and some MgO.
MgB_2-tetraglyme: Decreased MgB_2 peak intensity and amorphous phase?



TGA Analyses at 5 ^oC/min in Ar

Significant weight loss observed in MgB_2-TG

XRD and TGA indicates reactivity of ethers with Mg boride.

Accomplishments and Progress

2. MgB_2 Etherates Syntheses from MgB_2

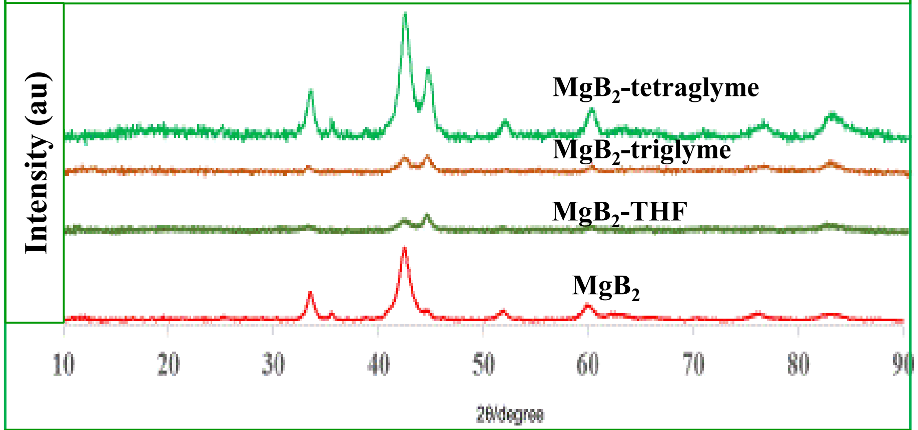
B. Synthesis By Ball Milling Approach

$$MgB_2 + xX \xrightarrow[\text{400 rpm}]{\text{<9 hrs total, <6 hrs in ether}} MgB_2(X)_x$$

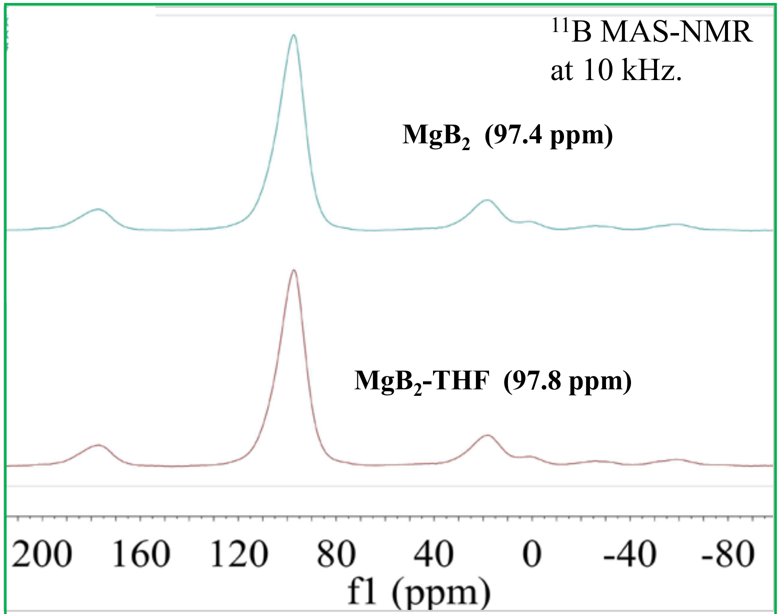
X= THF, tetraglyme, 1,4 dioxane, triglyme, 1,3 dioxalane

Characterization of synthesized products.

- MgB_2 peaks decrease for THF and Triglyme samples.
  - Ether role in decreasing MgB_2 crystallinity.
- Products different from heat treated synthesis.



XRD of pure MgB_2 ball milled (BM) 5hrs; MgB_2-ether samples BM total of 9 hrs, including 4 hrs with ethers.



Solid State ^{11}B NMR indicates presence of MgB_2

Small change in MgB_2 chemical shift

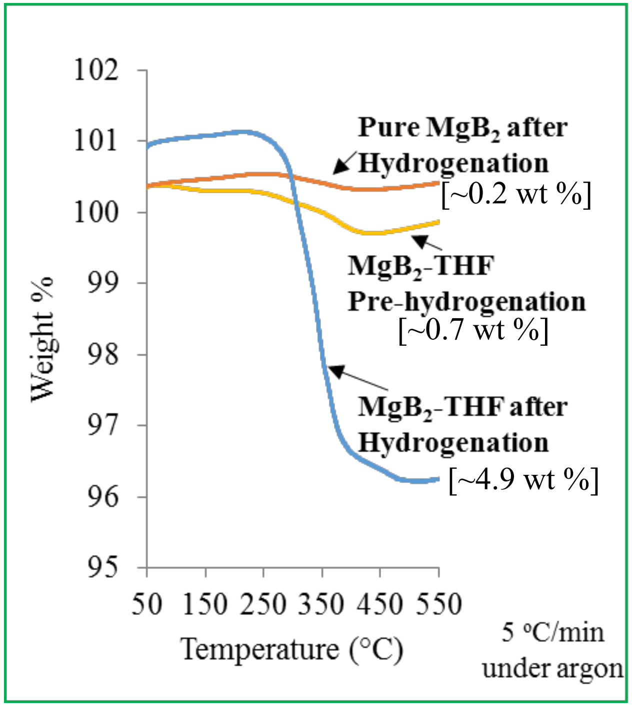
NMR, XRD and FTATR inconclusive in directly confirming presence of sub-stoichiometric amounts of ether.

Accomplishments and Progress

Hydriding of MgB_2 Etherates Synthesized by Ball Milling Approach

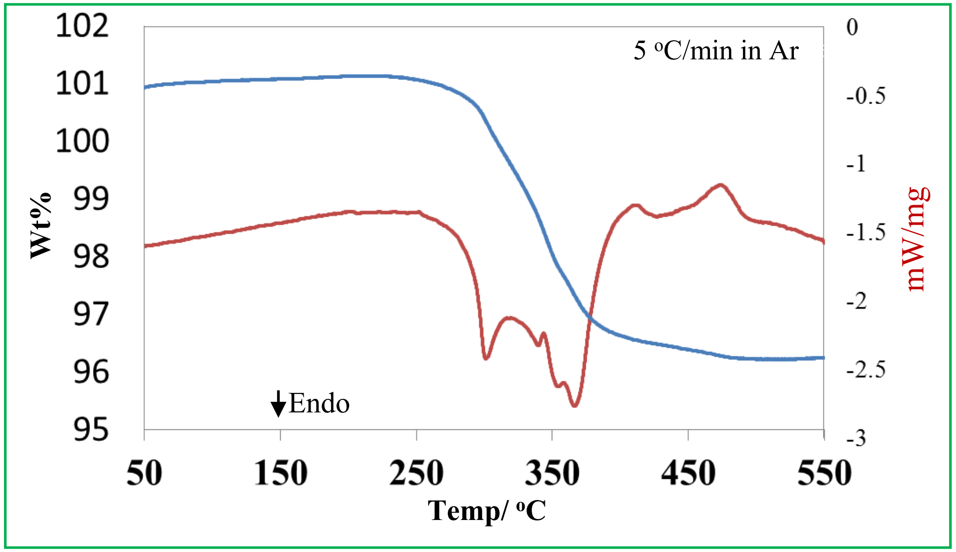
Currently Ball Milled MgB_2-THF shows greatest promise at 300 °C hydrogenations.

$$MgB_2(THF)_x + H_2 \xrightarrow[300\,^{o}C,\ 72\ hrs]{1000\ bar} \text{Magnesium borohydride species}$$



Hydrided MgB_2-THF

No indication of hydrogenation observed with ball milled MgB_2-tetraglyme and MgB_2-triglyme samples at 300 °C from XRD and IR.



Preliminary TGA analysis of hydrogenated ball milled MgB_2-THF indicates significant weight loss (~4.9 wt %) at 300 °C.

Typical β-$Mg(BH_4)_2$ DSC profile

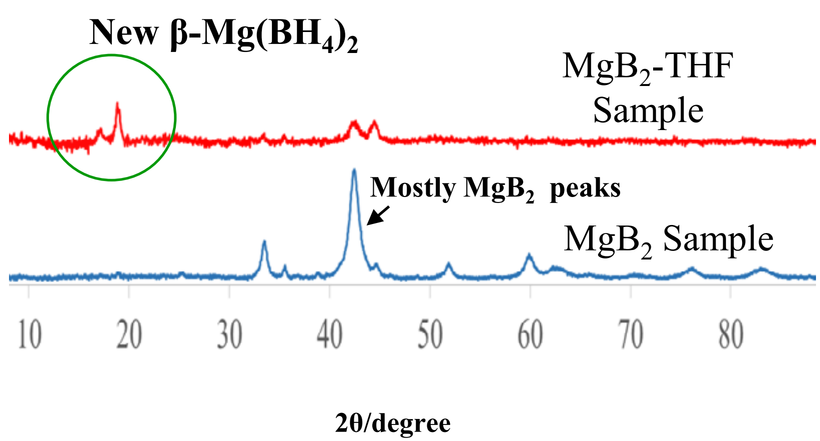
Preliminary hydrogenations confirm for the FIRST TIME formation significant amounts of β-$Mg(BH_4)_2$ at 300 °C!

Accomplishments and Progress

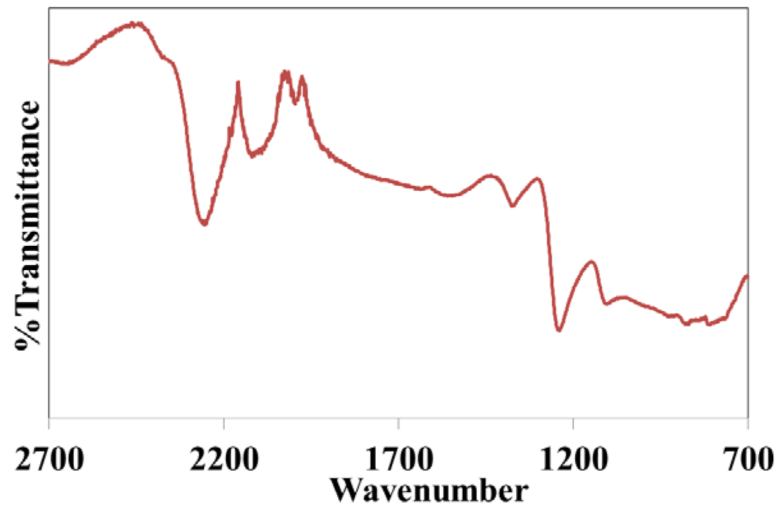
Hydriding of MgB_2 Etherates Synthesized by Ball Milling Approach

Currently Ball Milled MgB_2-THF shows greatest promise at 300 °C hydrogenations.

$$MgB_2(THF)_x + H_2 \xrightarrow[300\ ^oC,\ 72\ hrs]{1000\ bar} \text{Magnesium borohydride species}$$



XRD of hydrogenated ball milled samples: MgB_2 and MgB_2-THF confirming β-$Mg(BH_4)_2$ formation at 300 °C.



FTIR of hydrogenated MgB_2-THF shows typical intense $Mg(BH_4)_2$ stretches at 2260 and 1240 cm^{-1}

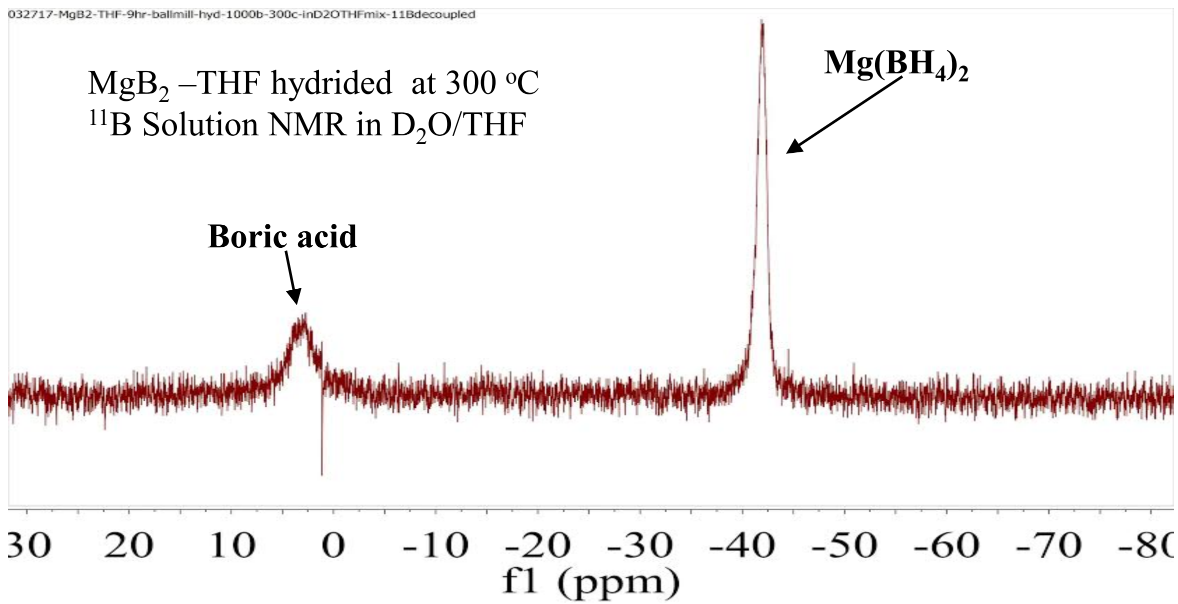
FTIR and XRD of hydrogenated material confirm β-$Mg(BH_4)_2$ synthesis at 300 °C!

Accomplishments and Progress

Hydriding of MgB_2 Etherates Synthesized by Ball Milling Approach

Currently Ball Milled MgB_2-THF shows greatest promise at 300 ^{o}C hydrogenations.

$$MgB_2(THF)_x + H_2 \xrightarrow[\text{300 }^{o}\text{C, 72 hrs}]{\text{1000 bar}} \text{Magnesium borohydride species}$$



^{11}B NMR indicates mostly β-$Mg(BH_4)_2$

Remaining Challenges and Barriers

- Optimization of hydrogenation to 700 bar at 300 ^{o}C with $\geq$7 wt% H_2 uptake.
- Complete characterization of boride etherates.
- Understanding mechanism of hydrogenation enhancement by ethers, especially THF.

Proposed Future Work

FY 2017

- Syntheses:
  - Continue optimizing synthesis of magnesium boride etherates.
  - Emphasis on MgB_2-THF system.
- Characterizations:
  - Characterizations of synthesized and hydrogenated MgB_2 etherates by various techniques e.g. XRD, FTIR, NMR, TGA-DSC, TEM and TPD-Mass spec.
- Hydrogenation of Mg boride etherates to Mg borohydride etherates:
  - Variable pressure and variable time studies
    - Demonstrate hydrogen uptake of 7 wt% at 300 ^oC.
    - Demonstrate H_2 uptake at 700 bar and 48 hrs, maintaining 7 wt% H_2 at 300 ^oC.
- Computational:
  - Size-dependent stability and morphology of MgB_2 clusters + particles
  - Coordination analysis of solutions and solvent-dependence of stability

FY 2018

- Hydrogen cycling studies of magnesium boride etherates.
  - Confirm presence of etherates through cycling.
- Understanding mechanism of kinetic enhancement by etherates.
- Determine the factors that limit H_2 cycling kinetics.
  - TEM and X-ray scattering for size and morphology effects; integrate with theory.
- Optimize cycling capacity of MgB_2 etherates.
  - Demonstrate reversible H_2 uptake ≥8.0 wt % at ≤300 ˚C and cycling stability of MgB_2 etherates.

Any proposed future work is subject to change based on funding levels

Summary: Progress and Accomplishments

- **Syntheses**: Magnesium boride etherates have been synthesized by ball milling and heat treatment techniques.
  - **Characterizations**: Synthesis of magnesium boride etherates is being confirmed by a variety of techniques including FT-ATR, XRD, NMR and TGA-DSC.
- **Hydrogenations**: Magnesium boride etherates were hydrided at $\leq$1000 bar, 300-400 ^{o}C and $\leq$72 hours.
  - The ball milled Mg boride and THF samples have best performance with significant hydriding to Mg borohydride at **300 ^{o}C!**
    - About 4.9 % weight loss observed from the Mg boride THF hydrided at 300 ^{o}C.
  - **Characterization**: $Mg(BH_4)_2$ syntheses confirmed by XRD, FTIR and DSC.
- **Theoretical Modeling**: Molecular Dynamic Simulations indicate strong coordination between THF and MgB_2.

Collaborations

Partners	Project Roles
Sandia National Laboratories (HyMARC)	Collaborating with Dr. Stavila, Dr. White and Dr. Allendorf: ➢ High pressure hydrogenation experiments. ➢ Characterization of samples by XRD and TGA-DSC.
Lawrence Livermore National Laboratory (HyMARC)	Collaborating with Dr. Wood and Dr. Kang: ➢ Molecular dynamic simulations of magnesium boride etherates.
Lawrence Berkeley National Laboratory (HyMARC)	Collaborating with Dr. Prendergast's Group: ➢ Reactive quantum molecular dynamics simulations of MgB_xH_y in etherate liquids.
National Renewable Energy Laboratory (HySCORE)	Collaborating with Dr. Gennett: ➢ Temperature programmed desorption. ➢ Mass spec analyses of desorbed gas.

Acknowledgement

University of Hawaii Team
Prof. C.M. Jensen
Mr. Stephen Kim
Mr. Cody Sugai

HyMARC Consortium: Making facilities and expertise available to the Project.

NREL: Dr. Tom Gennett for assistance with TPD and Mass Spec.

PNNL: Dr. Mark Bowden for XRD of some of the samples.

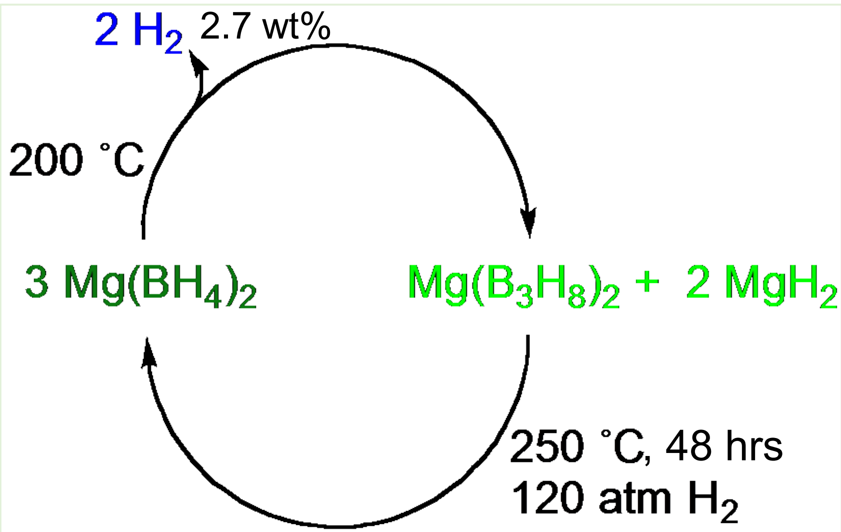
EERE's Fuel Cell Technologies Office: Funding.

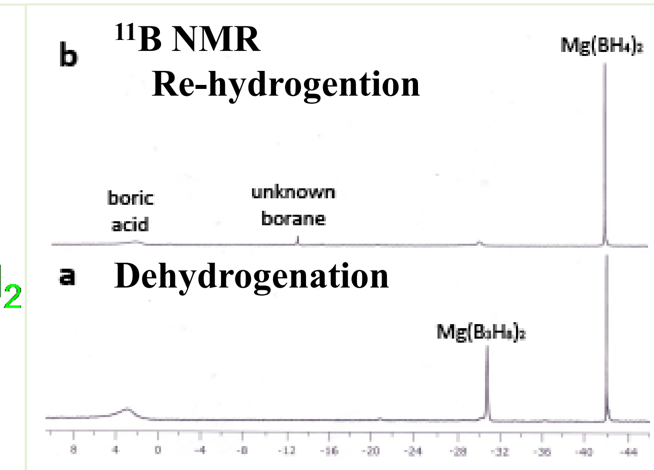
Technical Back-Up Slides

Kinetic Enhancement in $Mg(BH_4)_2$/Mg borane System

- **Ether coordination decreases hydrogenation pressure, time and temp.**

A. None etherated borohydrides

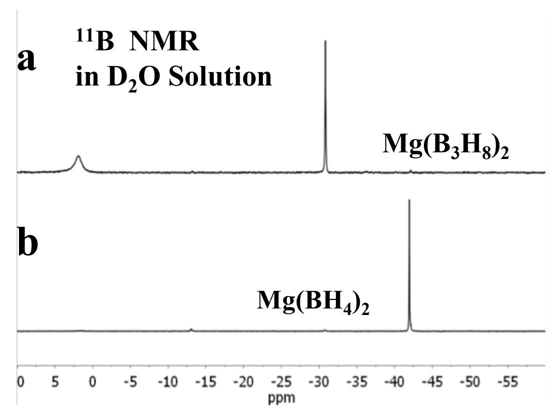




B. Etherated borohydrides

$$2MgH_2 + Mg(B_3H_8)_2(THF)_2 \xrightarrow[200\ ^\circ C,\ 2\ hrs]{50\ atm\ H_2} 3Mg(BH_4)_2(THF)_x$$

- **Strong coordination of THF to Mg boranes/borohydrides.**
  - **Enhanced hydrogen cycling kinetics**
  - **Lower ΔH of dehydrogenation**

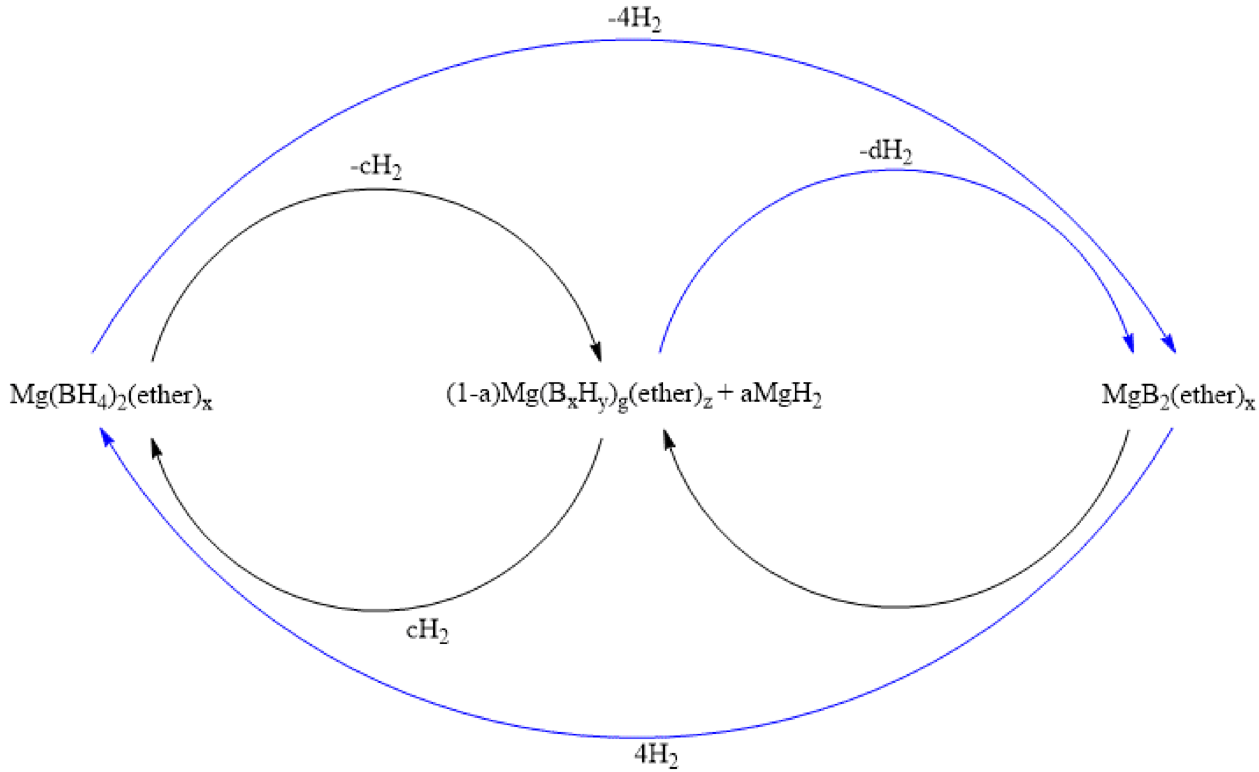


M. Chong, A. Karkamkar, T. Autrey. S. Jalisatgi, S. Orimo, C.M. Jensen; *Chem. Commun.* **2011**, *37*, 1330.

M. Chong, M. Matsuo, S. Orimo, C.M. Jensen Iinorg. Chem. **2015,** *54***,** 4120.

Motivation: High Impact of MgB_2 Etherates

- **No studies on hydrogen storage properties of MgB_2, (Mg + 2B), (MgH_2 + 2B) coordinated with ethers.**
  - ➢ Strong, stable ether coordination up to 250 °C for THF!



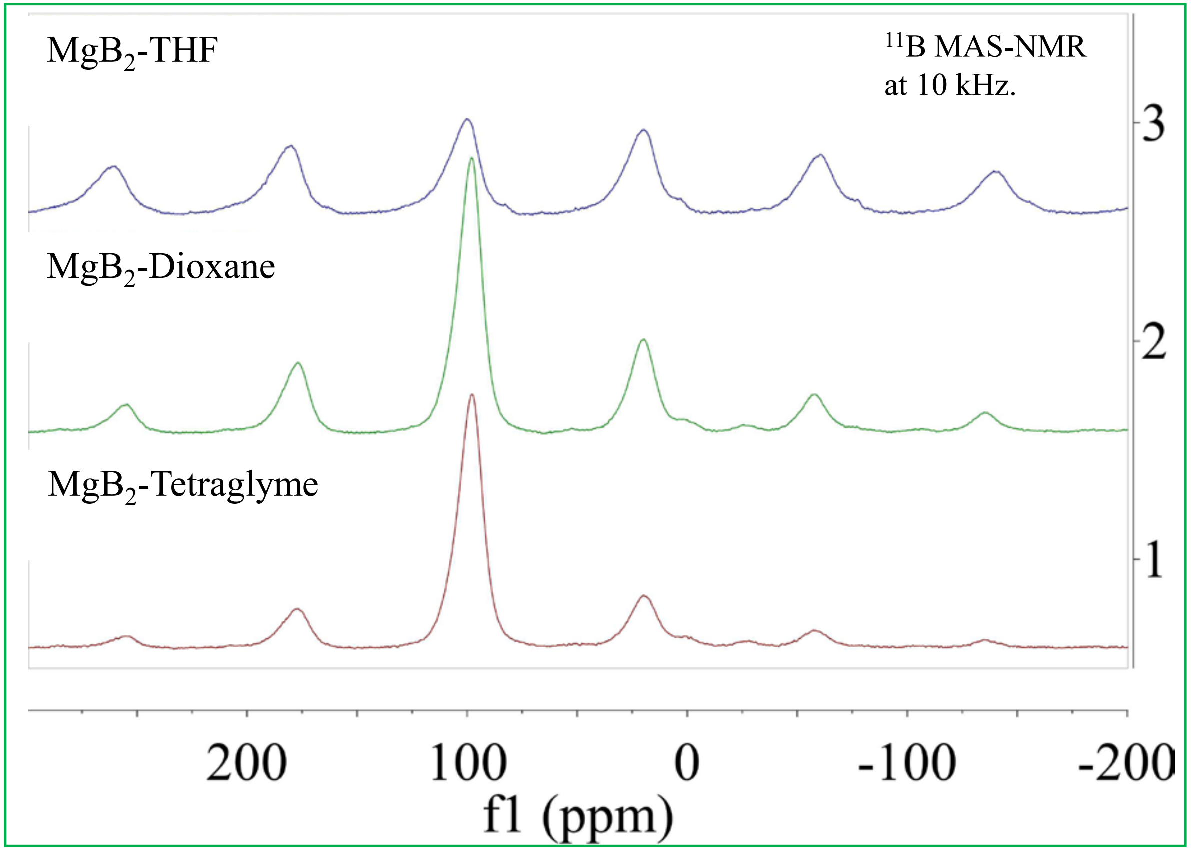
- Complete studies on dehydrogenated forms of magnesium borohydride etherates.

- **Towards search of novel ether coordinated MgB_2 for practical hydrogen storage?**

Accomplishments and Progress

2. MgB_2 Etherates Syntheses from MgB_2

A. Synthesis By Heat Treatment



NMR shows minimum changes in ^{11}B chemical shifts of MgB_2 etherate samples

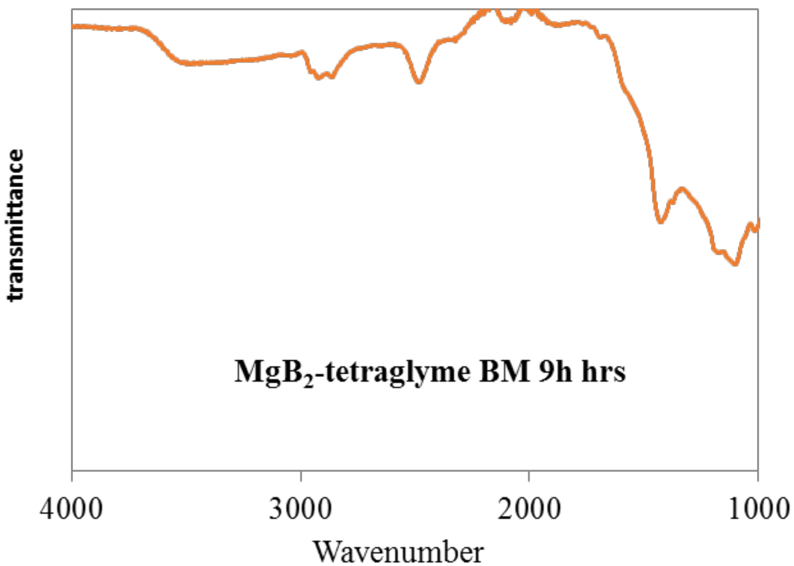
Accomplishments and Progress

2. MgB_2 Etherates Syntheses from MgB_2

B. Synthesis By Ball Milling Approach

$$MgB_2 + THF \xrightarrow[\text{400 rpm}]{\text{9 hrs total, 4 hrs in ether}} MgB_2(THF)_x$$

Characterization of synthesized products.



- Ether stretches observed only in washed and dried glymes (MgB_2 triglyme and tetraglyme) samples.
- No ether peaks in THF, Dioxane and Dioxalane BM samples.

Accomplishments and Progress

Comparison of MgB_2-THF BM 9hr and Pure MgB_2 hydrogenated Samples