# IV.A.4c Lightweight Intermetallics for Hydrogen Storage

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Contract Number: DE-FC3605GO15062

Start Date: March 1, 2005
Projected End Date: May 29, 2009

## Introduction

The key challenges for metal hydrides are to simultaneously satisfy the high gravimetric density, high volumetric density, low desorption temperature, and fast hydriding and dehydriding kinetics. Among these requirements, the high gravimetric density and low reversible temperature are the most difficult to satisfy simultaneously.

## Approach

As a partner for the DOE Metal Hydride Center of Excellence (MHCoE), GE Global Research in Niskayuna, NY developed a robust approach for metal hydride discovery as schematically shown in Figure 1. The approach is used on a daily basis at GE and it has streamlined the metal hydride discovery process. Our research allows us to investigate large numbers of compositions simultaneously, quickly screen their hydrogen storage properties, and gain a detailed understanding of the critical hydrogen storage performance characteristics. The key features of our approach is a robust combinatorial/high-throughput screening (HTS) methodology and a unique apparatus for in situ x-ray diffraction (XRD) to "watch" the hydrogen absorption and desorption process in real time with varying temperature and/or hydrogen pressure. The integrated approach with up-front theoretical analysis, HTS methodology, and mechanistic understanding will allow us to effectively discover new hydrides to meet the DOE 2010 targets.

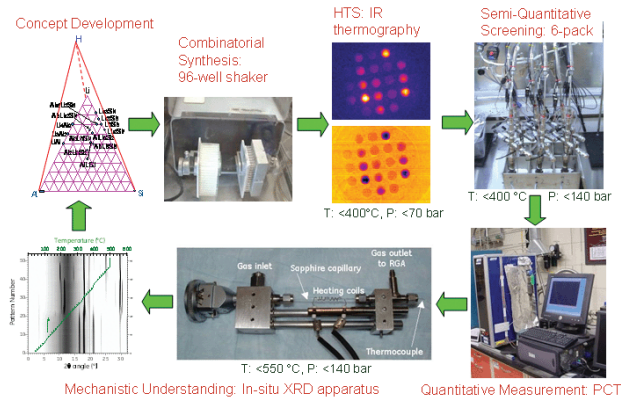


**FIGURE 1.** Schematic Illustration of GE's Approach for Metal Hydride Discovery

## Results

The project initially has a significant focus on the development of a combinatorial/HTS methodology. Validation of this methodology was accomplished using benchmark systems, and by finding new hydrides in the aluminides and silicides compositional space. Materials identified by HTS were further validated by confirming hydrogen storage in these compositions using a standard pressure-composition-temperature (PCT) apparatus. The PCT confirmation of HTS observations in several systems serves as a great testament to the robust approach developed at GE Global Research.

We first applied the methodology to screen for reversible metal hydrides in aluminides and silicides with the expectation of finding some moderate capacity and low desorption temperature hydrides. Approximately 10 ternary systems were screened using our approach, however the few compositions we found to be reversible all have very high operating temperatures (>250°C) and low weight percent hydrogen capacity. Based on the results, we decided to move away from the aluminides and silicides.

Using the unique in situ XRD apparatus, we studied the reaction pathway of the mixture of 2 $LiNH_2$ + $MgH_2$ (developed by Weifang Luo at Sandia), including the ammonia formation. Employing both high resolution synchrotron XRD and neutron diffraction, we identified four different crystal structures of $Li_2Mg(NH)_2$. The crystal structure understanding, especially the formation and ordering of compositional vacancies led us to design a family of compositions with a general formula of $Li_{4-2x}Mg_x\square_x(NH)_2$ ($\square$ denotes vacancies) with slightly

higher capacity than the original mixture, but with essentially the same desorption temperatures. Our limited exploration of catalysts did not find any effective ones to reduce the desorption temperatures. Since the MHCoE have formed a sizable team on amide-imide systems, we decided to put GE's work in this area on hold while remaining available for mechanistic understanding work when needed by the MHCoE team.

Our search for high weight-percent hydrides pointed us to borohydrides. We quickly narrowed our selection to $Mg(BH_4)_2$ due to its high gravimetric density (14.8 wt% theoretical) and attractive thermodynamic stability (heat of formation ~53 kJ/mole of $H_2$). We synthesized Mg borohydride and studied its decomposition kinetics and mechanism. The results are very promising. By teaming with Profs. Karl Johnson, Duane Johnson and David Sholl at MHCoE to select promising doping elements and focusing our future combinatorial/HTS effort on dopants and catalysts, we hope to make $Mg(BH_4)_2$-based materials reversible. More detailed descriptions of these results are provided in the following.

## Development and Validation of the Robust Approach

Selection of materials concepts and compositional systems was guided by thermodynamic and atomistic modeling (density functional theory) together with an extensive search of literature and phase diagrams. Multiple compositions were then synthesized using high-energy multi-well reactive ball-milling. HTS of hydrogen storage properties were performed using infrared (IR) thermography which images the heat of evolution during hydriding and dehydriding processes to assess the hydrogen interactions with the metals. The versatility of this technique allows for the differentiation of surface hydrogen absorption, irreversible hydride formation and reversible hydride formation. When reversible hydriding and dehydriding behavior was observed for particular compositions, the materials were scaled up to gram-quantities and semi-quantitative PCT measurements were performed using a home-built 6-pack system (six samples at a time – each tests independently with different temperature and pressure conditions). The promising compositions from this intermediate screening then go to more quantitative PCT tests with gas sampling capability to obtain accurate gravimetric density and kinetics. Mass spectrometry is used to sample the desorbed gas to check whether there are other by-product gases, such as ammonia or diborane. Once storage properties were confirmed by PCT analysis, mechanistic phase formation during hydriding and dehydriding conditions were elucidated using an in situ XRD technique. This technique utilizes a unique apparatus to observe in situ hydriding and dehydriding reactions using synchrotron XRD at Brookhaven National Laboratory. The understanding of mechanism and crystal structures serve as input again to help us to define new concepts/compositions for future exploration with the aim of finding a metal hydride to meet the DOE 2010 targets.

## HTS of Hydrogen Storage Materials in Aluminides and Silicides

To explore the compositional space of Al, Si, Li, Mg, and Na, we employed the HTS methodology to quickly search through the intermetallic compounds of among these elements. These elements were chosen for their lightweight, low price, wide availability and rich unexplored compound space. Ternary compositions were synthesized using a diffusion-multiple approach and screened for hydrogen sorption with either time-of-flight secondary ion spectroscopy or IR imaging (thermography). Several diffusion multiples were screened which include: LiAlM, NaAlM where M = (Cu,Mn,Mg,Zn,Ga,Ge,Si,Ti,B,C,Ni) and LiSiM, NaSiM, LiNaSiM where M = (Al,Mg). Areas that indicated hydrogen sorption were analyzed by μ-XRD and the active phase for the LiAlM and LiSiM experiments were identified as AlLi and $Li_{12}Si_7$ respectively. However, the reactive nature of these materials with oxygen and water, along with the small domain of the phase of interest proved to be a major challenge during phase characterization. Due to these constraints a multi-sample reactive ball milling technique was developed (up to 96 samples at a time). This technique produced bulk samples for both reversible hydrogen sorption testing and phase identification. The entire synthesis and IR reactor loading was contained in a glove box minimizing oxidation products that can severely limit hydrogen sorption properties.

Several ternary compounds were reported in the literature for the Al-Li-Si system. These phases were originally studied as anode materials for lithium ion batteries, however their hydrogen storage properties were unknown. To explore this area, several known and unknown binary and ternary compositions were synthesized by reactive ball milling of the elements. Several of the phases were confirmed by XRD, however the samples usually contained unreacted elements or disproportionated binaries. The compositions were screened in parallel for reversible hydrogen sorption properties using IR imaging. The results showed that many of the ternary compositions demonstrated reversible hydrogen storage as low as 150°C with 55 bar $H_2$. From the IR imaging results, the best candidate materials were studied at Brookhaven using an in situ XRD-hydriding technique coupled to a residual gas analyzer. The in situ XRD results showed a general trend that included the disproportionation of the ternary phase followed by the formation of AlLiSiH during hydriding. The remaining elements form several

different phases as a function of temperature that include $Li_7Si_3$, $Li_{12}Si_7$ and two different AlLi phases. The hydrogen storage properties were confirmed by PCT measurement which showed a reversible 1.2 wt% hydrogen storage capability with a hydrogen sorption onset at 150°C with 55 bar $H_2$ and desorption at ~300°C. Although these results are significantly lower than the literature values for AlLiSi ↔ AlLiSiH (535°C, 82 bar $H_2$), due to the low storage content and disproportionation characteristics, subsequent study of the Al-Li-Si compositional space has been halted.

Several binary Al-Ti intermetallic compounds and two Al-Mg compounds are known from the literature, while the Mg-Ti binary system forms no compounds and has limited solubility between Mg and Ti. One ternary composition was reported in the literature as $Al_{18}Mg_3Ti_2$, leaving a large area of unexplored compositional space. Several formulations were ball milled using mixtures of the elemental hydrides. Screening of the materials for hydrogen storage properties was accomplished using the HTS IR imaging and several of the compositions showed reversible hydrogen storage properties at 300°C, 55 bar $H_2$. Further analysis of promising candidates using PCT measurements showed an onset of hydrogen sorption at 230°C, 55 bar $H_2$, with a total reversible hydrogen content of 4.4 wt%. Using the in situ synchrotron XRD technique, the active phase was identified as an $Mg_{17}Al_{12}$ alloy that cycles to $MgH_2$ and Al when hydrided. In all the samples, the Ti did not alloy under the conditions used and remained in elemental form, however a catalytic role cannot be ruled out as the alloy's kinetics were significantly faster than un-catalyzed $MgH_2$

A surprising finding was a mixture of $AlH_3$ and Si with Ti. The Ti was found to remain as elemental powders. HTS experiment found hydriding and dehydriding behavior, but no hydride with both Al and Si was experimentally reported in the literature and an Al-Si-H compound is not intuitive either. The HTS experiment was, however, confirmed in the PCT test with gram quantity samples and multiple (up to six) cycles. The result clearly shows the power of combinatorial/HTS approach we developed. Only very recently, we found a theoretical prediction of molecules such as $AlH_3Si$ and $AlH_5Si_2$. Again, since the low capacity (~3 wt% H) and high temperature (400-460°C), we decided to halt the effort in this general area of aluminides and silicides.

## Mechanistic Understanding of Imide-Hydride System

As mentioned earlier, we have developed a unique approach to look "inside" reactions in order to study the hydrogen storage reaction pathway under operational conditions. Such ground-level knowledge is critical to understanding the behavior of potential storage materials and optimizing their properties. We have applied this capability to study the hydrogen desorption and absorption reactions of mixture of lithium amide ($LiNH_2$) and magnesium hydride ($MgH_2$). This material system was first reported by Luo at Sandia National Lab [1]. Luo found that a 2:1 mixture of $LiNH_2$ and $MgH_2$ releases 5.6 wt% hydrogen at approximately 200°C. At the time, Luo speculated that, after discharge, the mixture formed a mixed Li-Mg imide with a formula like $Li_2Mg(NH)_2$ but they did not report a structure at the time. We set out to determine the reaction pathway using combined time-resolved synchrotron x-ray diffraction and mass spectrometry (performed at the X7B Beamline of the National Synchrotron Light Source, Brookhaven National Laboratory), and determine the structure of $Li_2Mg(NH)_2$ at temperatures up to 500°C using high resolution synchrotron x-ray diffraction (performed at beamline X3B1 of the NSLS, BNL) and neutron powder diffraction (performed at the BT-1 high-resolution powder diffractometer at the NIST Center for Neutron Research). Given the much improved hydrogen desorption temperatures and equilibrium pressures of the Li-Mg-N-H system, a more profound knowledge of the imide structure and reactivity should help optimize the characteristics of this interesting system.

In situ x-ray diffraction during hydrogen desorption of the 2 $LiNH_2$ + $MgH_2$ mixture was performed on heating from 50 to 500°C while the evolved gases were monitored by RGA (Figure 2 left). Diffraction patterns were collected once a minute at 10°C increments. The dark streaks represent peaks indicative of particular structures present in the reaction mixture. Up to 220°C only peaks associated with the starting materials are observed. At approximately 220°C, additional peaks indicative of LiH and $Mg(NH_2)_2$ are observed. These are quickly followed by peaks associated with the $Li_2Mg(NH)_2$ imide, while the peaks of the starting materials fade. The reaction cell is equipped with a gas analyzer to identify the gases desorbed during the diffraction measurement. Although not shown in the figure, the gas analysis shows that hydrogen is evolved beginning as low 180°C and reaches a maximum at about 230°C, just ahead of the change to the imide seen in the diffraction pattern. Aside from hydrogen, a significant (although unquantified) amount of ammonia is released as well. The presence of ammonia during desorption has been reported previously [2,3], and has been implicated in the hydrogen release mechanism [4]. However, ammonia is detrimental to the proton exchange membrane (PEM) fuel cell expected to be downstream in a real hydrogen storage system and its emission is a significant drawback of this $H_2$ storage medium. For convenience in subsequent discussions, this structure will be referred to as $\alpha$-$Li_2Mg(NH)_2$ to distinguish it from its structural variants observed at higher temperatures.

Upon heating beyond 300°C, other structural transitions were observed. Beginning around 400°C

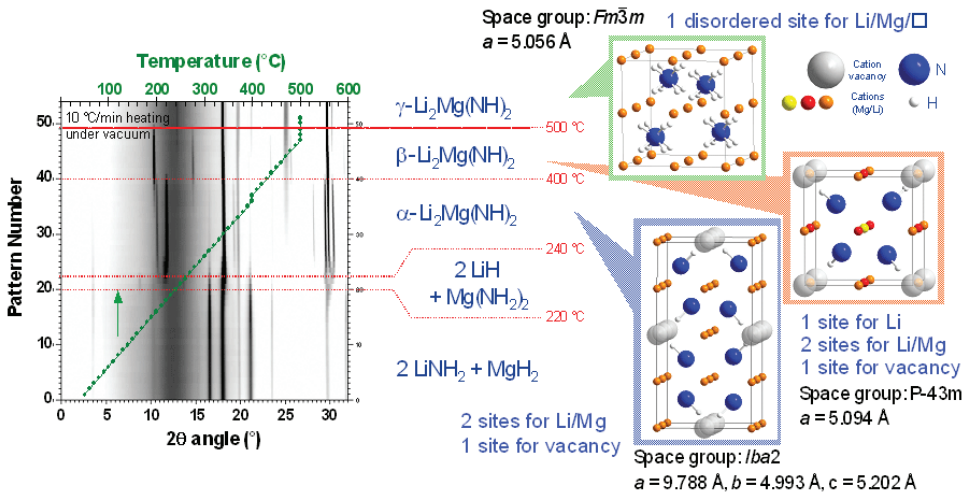


**FIGURE 2.** Reaction Pathway and Crystal Structures of $Li_2Mg(NH)_2$

the diffraction patterns change indicating a structural transformation. Simultaneous gas analysis suggests that the structure change is not associated with a significant compositional change and we have dubbed this structure β-$Li_2Mg(NH)_2$. At 500°C, another structural change is observed to γ-$Li_2Mg(NH)_2$. The fact that the main peak at 18° in 2θ remains constant throughout indicates that the three structures are closely related.

Although the in situ diffraction data were adequate to determine the approximate nature of the structural changes, an accurate determination of the individual crystal structures required high-resolution x-ray and neutron diffraction data. It was necessary to collect both kinds of data because x-ray diffraction is only weakly sensitive to hydrogen atoms while the neutron technique is insensitive to the cations (at this particular ratio). Analysis of these data yielded the three structures shown on the right of Figure 2. Nitrogen atoms are in blue, Li is in yellow, Mg in red and when the two are mixed on the same site they are orange. Hydrogen atoms are white and empty sites, known as vacancies, are shown in grey. The cation vacancies arise because two lithium atoms are replaced by only one magnesium atom, leaving behind an empty site.

The alpha structure (in blue) closely resembles that of lithium imide, $Li_2NH$ [5,6], however the unit cell is twice as large. This doubling of the unit cell is the result of ordering of the cation vacancies. Although the cations are ordered with respect to the vacancies, the cations themselves (Li & Mg) are randomly mixed on each site (orange atoms in the (blue) alpha structure). We also found that the hydrogen atoms (white) are always "pointing" towards the vacant sites (grey). This is logical given the electrostatic and steric repulsion the imide proton would experience if it were oriented towards a filled cation site. This is an important feature that is a hallmark of these types of materials and can be seen as well in lithium amide ($LiNH_2$), magnesium imide (MgNH), lithium imide ($Li_2NH$), etc.

Above 400°C, entropy drives a different cation-vacancy ordering scheme which results in a primitive cubic structure for β-$Li_2Mg(NH)_2$ (orange). In this structure the vacancies reside at the corners and the cations have partially segregated themselves on different sites. Again, the imide protons (white) point towards the vacancies. The high temperature γ-$Li_2Mg(NH)_2$ (green) appears above 500°C and does not show any cation-vacancy ordering, and has a structure which is identical to $Li_2NH$. The vacancies are still present in this case, but are randomly mixed on the same site with the cations. The hydrogen atoms now also look disordered since they are "tied" to the now-disordered vacancy. Thus the vacancy ordering determines the hydrogen position and ordering. Since hydrogen mobility is an important factor in many hydrogen storage materials, understanding the inter-atomic forces acting on the imide protons will help to explain the energetics and kinetics of hydrogen release and absorption.

For recharging, similar experiments were carried out up to 2,000 psi (135 bar) of hydrogen pressure to observe the recharging of $Li_2Mg(NH)_2$ (Figure 3). The recharged product is a mixture of lithium hydride (LiH) and magnesium amide ($Mg(NH_2)_2$) in a 2:1 ratio, which forms at temperatures above 230°C. This proves that the cycling does not return the starting materials, but that the 2 LiH + $Mg(NH_2)_2$ mixture is more stable than 2 $LiNH_2$ + $MgH_2$. This is also evident from the fact that LiH and $Mg(NH_2)_2$ are formed around 220°C before hydrogen desorption occurs (Figure 2). Further heating above 300°C causes hydrogen desorption even under 2,000 psi of hydrogen pressure. The product of this hydrogen release is δ-$Li_2Mg(NH)_2$, another distinct structural variant of $Li_2Mg(NH)_2$.

In summary of the imide-hydride work, we have developed a unique reaction cell to rapidly determine the reaction pathway of hydrogen storage materials using simultaneous x-ray diffraction and desorbed gas analysis. This cell can achieve the high temperatures and pressures required to study a wide range of hydrogen storage materials. The cell gives us an unmatched ability to look "inside" reactions by correlating evolved gases with structural changes during hydrogen uptake and release. Through this study, we have discovered that $Li_2Mg(NH)_2$ is only one member of a much larger mixed-metal imide family with general formula $Li_{4-2x}Mg_x(NH)_2$ - all of which absorb and desorb hydrogen near 240°C and whose lightest members store up to 6 wt% hydrogen. Using a combination of diffraction techniques, we have determined the structure of $\alpha$-$Li_2Mg(NH)_2$ along with three high-temperature structural variants. It is clear that defects such as the vacancies found in $Li_2Mg(NH)_2$ will play a significant role in determining the hydrogen storage properties of these and other systems. The in situ reaction cell described here is a perfect tool to study such processes in great detail while they occur.

## Decomposition of $Mg(BH_4)_2$

Decomposition of magnesium borohydride started about 300°C and occurs in two stages. The studied sample of magnesium borohydride showed evolution of 13.2 wt% hydrogen beginning at 350°C. The first stage ($Mg(BH_4)_2 \rightarrow MgH_2 + 2\ B + 3\ H_2$) corresponded to 9.1 wt% (theoretical value 11.2%) and the second one ($MgH_2 \rightarrow Mg + H_2$) to 4.1% (theoretical value 3.7%) as shown in Figure 4. In situ XRD experiments showed that the crystalline phase of magnesium borohydride disappears above 300°C with the release of hydrogen. No crystalline phases were found between 300 and 350°C. Above this temperature, $MgH_2$ appears to crystallize from the mixture. Further heating promoted the decomposition of $MgH_2$ to Mg metal and hydrogen (Figure 4). It should be noted that no crystalline boron phase was detected. Analysis of the gas during decomposition (Figure 4) shows peaks with mass 2 (hydrogen evolution) that coincide with disappearance of magnesium borohydride and magnesium hydride phases in the XRD pattern. Other peaks have significantly smaller intensity. Peaks assigned to diborane (m/e 28, 27 and 26) are too small (at the noise level) to make a definite conclusion about diborane presence in the decomposition products. Differential scanning calorimetry (DSC) study of magnesium borohydride showed reproducible results and confirmed the data obtained during in situ XRD measurements (Figure 5). At 10°C/min heating rate, three peaks are observed. The first endothermic peak at 300°C corresponded to the decomposition of magnesium borohydride with formation of amorphous $MgH_2$, the second exothermic peak at 368°C corresponded to its crystallization to crystalline $MgH_2$, and the third

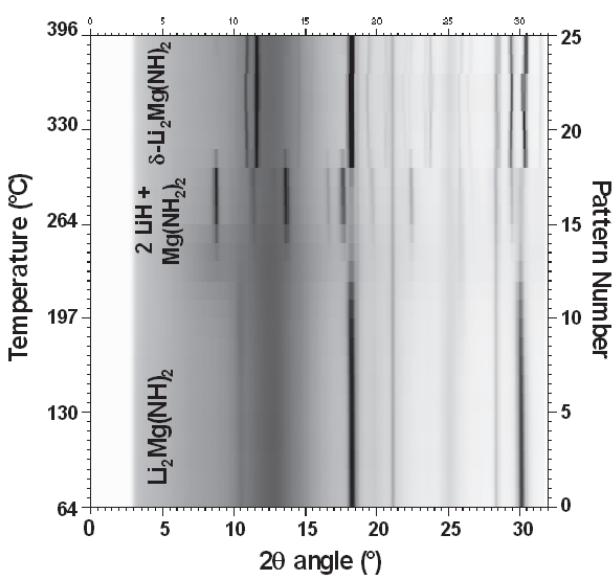


**FIGURE 3.** In Situ XRD Montage of the Decomposition Process of $Li_2Mg(NH)_2$

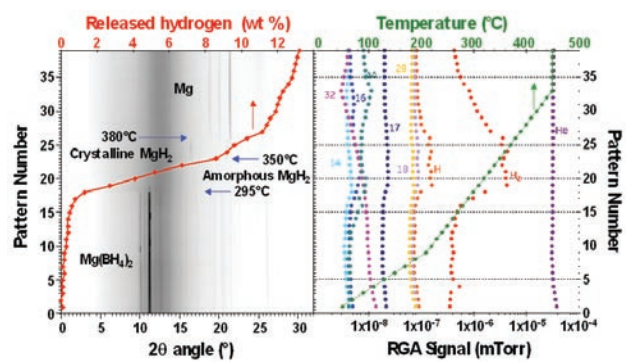


**FIGURE 4.** Decomposition Behavior of Mg borohydride

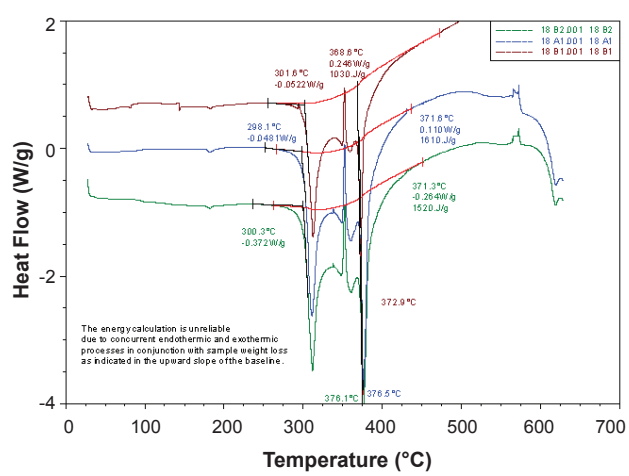


**FIGURE 5.** DSC Results of Mg Borohydride Decomposition

endothermic peak 376°C is decomposition of $MgH_2$ to Mg and $H_2$.

Initial attempts to recharge magnesium borohydride at 350°C with 135 bar hydrogen was successful only for the second decomposition step, i.e. Mg + $H_2$ to $MgH_2$. The challenge is to reverse the first reaction from $MgH_2$ + B to magnesium borohydride. This will be the focus of GE team's work in the future.

## Conclusions and Future Directions

We have developed a very robust metal hydride discovery approach with a demonstrated combinatorial/HTS methodology and a unique in situ XRD apparatus. Together with up-front theoretical analysis and rigorous PCT tests and mechanistic understanding, the general approach will accelerate metal hydride discovery.

Our HTS exploration together with other experimental and mechanistic work on the aluminides and silicides of Li, Mg and Na found only hydrides with low capacity and high desorption temperatures. The knowledge gained in the exploration of this composition space led us to leave this area in favor of more promising materials.

The work on the mixed metal imides has provided an unprecedented level of understanding of the chemistry-structure-property relationships in this materials space. The flexibility of the imide superstructure allows for the incorporation of various levels of magnesium substitution and surprisingly large levels of cation vacancies. Yet, despite this malleability, the structure has so far not accepted substituents other than magnesium (e.g., Na, Ca, Al, Ti, etc.). We have also not found any catalysts that significantly reduce the hydrogen absorption and/or release temperatures. These drawbacks, in addition to the low hydrogen capacity (≤6 wt% $H_2$) and persistent ammonia release, have led us to conclude that the amide-hydrides mixtures in this system are not worth pursuing as practical hydrogen storage solutions. However, there are many interesting questions that remain to be answered, especially in relation to the exact interplay of cation vacancies, proton mobility and their effect on the hydrogen storage properties. We have suggested to the amide-imide team under the MHCoE to pursue mixtures of amide/imides with borohydrides. We will still be available for mechanistic understanding work using our in situ XRD apparatus and expertise when needed by the MHCoE team.

Mg borohydride is a very promising hydride for high-capacity on-board hydrogen storage. It has a very high capacity (14.8 wt% theoretical and 13.2 wt% observed so far) and very favorable thermodynamic stability ($\Delta H = 53$ kJ/mole of $H_2$, as compared to $LiBH_4$ and $NaBH_4$ both of which have a $\Delta H = \sim 96$ kJ/mole of $H_2$). The reversibility has previously only been demonstrated at very high temperature, 620°C and 150 bar $H_2$ [7]. The key is to use dopants and catalysts to reduce the recharging temperature to <450°C, preferably <350°C. We are working closely with the theoretical prediction team (Karl Johnson, Duane Johnson, David Sholl, etc.) to identify the potential dopants. Together with the HTS capability at GE, we expect to accomplish our goal.

## FY 2006 Publications/Presentations

**1.** Job Rijssenbeek presented a poster "Characterization of the titanium catalyst in $NaAlH_4$", at IPHE International Hydrogen Storage Technology Conference, Lucca, Italy (June '05).

**2.** John Lemmon presented a poster "High-throughput hydride discovery" at Metal - Hydrogen Gordon Conference (July '05).

**3.** Job Rijssenbeek presented a poster "Phase formation and reaction pathway of $Mg(NH_2)_2$ + 2 LiH mixtures for reversible hydrogen storage" at Metal - Hydrogen Gordon Conference (July '05).

**4.** Job Rijssenbeek gave a talk "Crystal structure determination and reaction pathway of amide-hydride mixtures" the MRS Fall Meeting, Boston (Nov '05).

**5.** J.-C. Zhao attended the IEA Task 17 meeting in Takeshita, Japan & presented talk on "Lightweight intermetallics for hydrogen storage" (Oct '05) .

**6.** J.-C. Zhao attended the TMS meeting in San Antonio and presented an invited talk on "Reversible hydrogen storage in mixtures of $Mg(NH_2)_2$ and LiH studied by X-ray and neutron diffraction" (March '06).

**7.** Job Rijssenbeek, Yan Gao, Jonathan Hanson, Qingzhen Huang, Camille Jones, and Brian Toby: "Crystal structure determination and reaction pathway of amide-hydride mixtures" to be submitted to Journal of Alloys and Compounds.

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