Decomposition of lithium magnesium aluminum hydride

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Abstract

The quaternary aluminum hydride LiMg(AlH₄)₃ contains 9.7 wt% hydrogen, of which 7.2 wt% can be released in a two-step decomposition reaction via first formation of LiMgAlH₆ and then the binary hydrides MgH₂ and LiH. In-situ synchrotron radiation powder X-ray diffraction and thermal desorption spectroscopy measurements were performed to analyze the product distributions formed during the thermal decomposition of LiMg(AlD₄)₃. The first decomposition step occurs at about 120 °C and the second at about 160 °C for the as-milled sample, while for a purified sample of LiMg(AlD₄)₃, the decomposition temperatures involving release of hydrogen increase to 140 and 190 °C, respectively, suggesting that pure samples of LiMg(AlD₄)₃ are kinetically stabilized. Studies of the purified LiMg(AlD₄)₃ also showed that the second decomposition step can be divided into two reactions: 3LiMgAlD₆ → Li₃AlD₆ + 3MgD₂ + 2Al + 3D₂ and Li₃AlD₆ → 3LiD + Al + 3/2D₂. Addition of TiCl₃ to LiMg(AlD₄)₃ under a variety of ball milling conditions consistently led to decomposition of LiMg(AlD₄)₃ during milling. Correspondingly, all attempts to rehydrogenate the (completely or partially) decomposed samples at up to 200 bar hydrogen pressure failed. Decomposition of MgD₂ was observed at relatively low temperatures. This is ascribed to thermodynamic destabilization due to the formation of different AlₓMgᵧ phases, and to kinetic destabilization by addition of TiCl₃. A thermodynamic assessment was established for the calculation of phase stability and decomposition reaction relationships within the Li–Mg–Al–H system. The calculations confirmed the metastability of the LiMg(AlH₄)₃ phase and the irreversibility of the Li–Mg alanate phase decomposition reactions. The Li–Mg alanate decomposition pathways followed experimentally could be explained by the endothermicity of the calculated decomposition enthalpies, in that an impure or catalyzed LiMgAlH₄ intermediate phase could more directly access an endothermic decomposition reaction at lower temperatures, while a kinetically-hindered, purified LiMgAlH₄ would require higher temperatures to initiate the two-step decomposition through an exothermic reaction.

1. Introduction

Hydrogen storage in solid compounds is considered to be the only storage method that will meet the long-term goals for hydrogen storage for mobile applications [1]. One of the most attractive groups of materials is that of the lightweight, high gravimetric capacity aluminum-based hydrides (alanates), some of which have a theoretical capacity of up to 11 wt%.

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H_2 [2]. The reversibility and improved kinetics found in Ti-enhanced sodium alanate NaAlH_4 by Bogdanović and Schwickardi initiated a significant effort on alanates [3]. The theoretical gravimetric density of NaAlH_4 is 5.6 wt% H_2, which is considered too low for transportation purposes. A potential alternative is lithium magnesium tetra-alanate LiMg(AlH_4)_3, which contains 9.7 wt% H_2, whereof 7.2 wt% is released upon decomposition to the binary hydrides. LiMg(AlH_4)_3 can be synthesized mecanochemically by mixing LiAlH_4 and MgCl_2 [4–6], followed by removal of co-produced LiCl by extraction with organic solvents (Eq. (1)).

3 LiAlH_4 + MgCl_2 → LiMg(AlH_4)_3 + 2 LiCl

A two-step pathway was found for the decomposition of LiMg(AlH_4)_3. In the first decomposition reaction (Eq. (2)), 4.8 wt% H_2 is released, and in the second decomposition reaction (Eq. (3)) 2.4 wt% H_2 is released from the intermediate lithium magnesium hexa-alanate LiMgAlH_6 [5,6].

LiMg(AlH_4)_3 → LiMgAlH_6 + 2 Al + 3 H_2

LiMgAlH_6 → LiH + MgH_2 + Al + 3/2H_2

An additional 2 wt% H_2 can be released from the decomposition of MgH_2 to Mg and H_2 at 250 °C and above. The crystal structures of the corresponding deuterides, LiMg(AlD_4)_3 and LiMgAlD_6, have been determined recently [7,8]. The LiMg(AlD_4)_3 structure consists of isolated AlD_6 octahedra connected through octahedral Mg- and Li-ions, while the LiMgAlD_6 structure consists of isolated AlD_6 octahedra connected through octahedral Mg- and Li-ions. Recently the effect of graphic nanofibres for improving the desorption kinetics of LiMg(AlD_4)_3 has been studied [9].

The scope of this work was to investigate the thermodynamic stability of the Li–Mg alanates and their decomposition reactions, by application of both experimental and theoretical methods. Temperature programmed desorption (TPD) was performed to characterize the Li–Mg alanate dehydrogenation profiles, and in-situ synchrotron radiation X-ray diffraction studies (SR–PXD) were performed for additional phase analyses. The potential enhancement of the Li–Mg alanate kinetics was investigated by the addition of TiCl_3 via mecanochemical milling at room temperature, at liquid nitrogen temperature, and at high H_2 pressure. Rehydrogenation was attempted using H_2 pressures up to 200 bar. Thermodynamic modeling was used to interpret the experimentally observed phase behavior, and a thermodynamic assessment of the Li–Mg–Al–H quaternary order system was made using published experimental data. This assessment was evaluated by comparison with thermodynamic properties predicted by first principles atomic modeling. The experimental assessment parameters were used to model the energetics and equilibrium H_2 pressures of the possible decomposition reactions within the Li–Mg–Al–H system.

2. Methodology

2.1. Synthesis and Instruments

All chemicals were purchased from commercial sources: LiAlD_4 (>98 atom% D and chemical assay >95%; Sigma–Aldrich), MgCl_2 (99.9% Sigma–Aldrich), TiCl_3 (>99.99, Sigma–Aldrich), and used as received. The deuterated lithium alanate, LiAlD_4, was used since high purity LiAlH_4 is not commercially available. Toluene was dried over Na/anthracene and distilled under argon, and Et_2O was dried over Na/benzophenone and distilled under argon.

LiMg(AlD_4)_3 was synthesized by milling LiAlD_4 and MgCl_2 (ratio 3:1) in a Fritsch P6 planetary rotary ball mill at 300 rpm for 3 h, using a ball:powder ratio of 200:1, and was recrystallized and purified as described earlier [7]. All handling of the samples was performed under argon, using a glove box with less than 1 ppm O_2 and H_2O. Four different milling procedures were used for the addition of TiCl_3: high intensity, low intensity, cryogenic, and high-pressure milling. The former two were performed using the Fritsch P6 planetary ball mill, with a 250 ml grinding bowl and a GTM sensor lid measuring the pressure during milling (certified up to 5 bar). The typical sample mass was 2 g. High intensity (HI) ball milling was performed at 300 rpm for several hours, with excess pressure released during milling. Low intensity (LI) ball milling was done at 150 rpm with a repeated series of 15 min milling interrupted by 5 min pauses. Cryogenic milling (cryomilling, CM) was performed in an SPEX 6750 freezer mill where liquid nitrogen is used to cool a steel container with the sample and a stainless steel cylindrical impactor. The impact frequency was 30 Hz, and the impactor mass was 32 g. CM was performed using 6 min milling time with subsequent cooling time of 3 min to prevent heating of the system. This was repeated 9 times, giving an effective milling time of 54 min. High-pressure (HP) ball milling was performed using an in-house built milling vial, at 70–75 bar H_2 pressure. The speed was 300 rpm and the milling time was 15 min with 5 min pauses. Variable total milling times were used, and the typical ball:powder ratio was 24:1. Details of the syntheses of the different samples studied are available in the Supporting Information.

TPD was performed with an in-house built setup. Different quantities (0.1–0.5 g) and heating rates (0.25–5 K/min) were used depending on the sample. The experiments were generally performed under dynamic vacuum, in some experiments samples were desorbed into a constant volume. Pressure–Composition–Temperature (PCT) experiments were performed using an in-house built Sieverts apparatus equipped with a pressure sensor from Presens [10] and is operable up to 200 bar and 600 °C.

Initial powder X–ray diffractometer (PXD) data for inspecting phase compositions were obtained with an INEL XRG 3000 with Cu Kα radiation (\( \lambda = 1.540598 \) Å), Ge crystal monochromator, and Inel CNS 120, a curved position sensitive detector. Time resolved in-situ SR–PXD data were collected at the Swiss-Norwegian beamline (SNBL, station BM1A) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Two-dimensional data with an exposure time of 30 s were collected with an imaging plate (MAR345) detector. Wavelengths between 0.7 and 0.8 Å were used. The samples were packed in boron-silica-glass capillaries and connected to a vacuum pump using Swagelok fittings. The samples were heated using a hot air blower with heating rates in the range 0.25–4 K/min from room temperature (RT) up to 400 °C, and data were collected every second minute. The temperatures were calibrated using an Ag-standard and by determining the
The description of the Li—Mg—H in Ternary Alloys [28] does not include any stable ternary compounds. The Mg(AlH₄)₂ compound with a P-3m1 structure [29] is metastable. The Mg(AlH₄)₂ dehydrogenation reaction

\[ \text{Mg(AlH}_4\text{)}_2 \rightarrow \text{MgH}_2 + 2 \text{Al} + 3 \text{H}_2 \]  

has been evaluated by differential scanning calorimetry (DSC) [5] to have an enthalpy of 0.56 kJ/mol H₂ over the temperature range 110–130 °C. Earlier reaction enthalpies extrapolated from calorimetric measurements [30] were also taken into consideration.

The only known quaternary compounds in the Li—Mg—Al—H system are LiMg(AlH₄)₃ and LiMgAlH₆, in which the various elements occupy discreet sublattices [7,8]. The decomposition reactions of these compounds were characterized by DSC. The enthalpy of the LiMg(AlH₄)₃ decomposition (Eq. (2)) was measured to be −5.00 [5] and −5.50 kJ/mol H₂ [31], and the enthalpy of the LiMgAlH₆ decomposition (Eq. (3)) was measured to be 8.67 [5] and 13.05 [31] kJ/mol H₂.

### 2.2. Thermodynamic modeling

#### 2.2.1. Review and selection of thermodynamic data

The description of the Li—Mg—Al—H quaternary system was built up from the progressive assessment of increasingly higher order subsystems. Elemental and gas phase data was obtained from the SGTE SSUB3 database [13]. Established assessments were used for the Li—Mg (version 1) [14], Al—Mg [14], Al—H [15,16], Mg—H [17], Al—Li [14], Li—H [18], and Al—Li—Mg [14] systems. The Al—Li—Mg data was checked with experimental data [19]. There are no known ternary Li—Mg—H phases to require an assessment of the Li—Mg—H system. Development of the remaining Al—Li—H and Al—Mg—H system descriptions was required to prepare for the assessment of the Li—Mg—Al—H system.

The Al—Li—H system was recently assessed by Jiang et al. [20], who accepted the STGE description of the LiH and LiAlH₄ phases [13], but could not reach consensus on the description of the diverging Li₃AlH₆ pressure composition data reported in the literature [21,22]. In particular, the decomposition pressures reported by Chen et al. [21] for ball-milled nanocrystallites were much lower than those reported by Brinks et al. [22]. A new description of the Li₃AlH₆ phase was established from the thermal analysis measurements of Claudy et al. [23], the data compilation of Dymova et al. [24] and first principles predictions [25–27]. Decomposition pressure calculations based on this description were in reasonable agreement with the experimental values of Chen et al. [21].

The description of the Al—Mg—H system [28] does not include any stable ternary compounds. The Mg(AlH₄)₂ compound with a P-3m1 structure [29] is metastable. The Mg(AlH₄)₂ dehydrogenation reaction

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#### 2.2.2. Thermodynamic models

The Gibbs energy per mole of formula for stoichiometric line compounds are typically modeled with the polynomial equation

\[ G_m^o = a + bT + cT \ln T + dT^2 + eT^3 + \frac{f}{T} \]  

over the temperature range of 298.15–2000 K, where \( a, b, c, \ldots \) are constants. The compound enthalpy, entropy, and heat capacity values are derived from this equation using standard thermodynamic relations. Since only enthalpy experimental data were available for the unassessed LiMg(AlH₄)₃, LiMgAlH₆, and Mg(AlH₄)₂ phases, the Neumann-Kopp rule was invoked to derive their Gibbs energy relations instead. Here the Gibbs
energy was determined to be a constant plus the sum of the Gibbs energies of assessed lower order compounds equivalent in stoichiometry to the formula of the compound being assessed, for example

$$G_{\text{LiMgAlH}_6} = \text{Constant} + G(\text{LiH}) + G(\text{MgH}_2) + G(\text{AlH}_3)$$

(6)

The constant values for the LiMg(AlH₄)₃, LiMgAlH₆, and Mg(AlH₄)₂ were determined by setting the reaction enthalpies for Eqs. 2-4, respectively, in the assessment to be equal to those measured by Mamatha et al. [5].

2.3. Atomic modeling

First principles thermodynamic property predictions of the ternary and quaternary phases within the Li–Mg–Al–H system [7,8,25,31] were made for comparison with those modeled from the thermodynamic assessment of experimental data. The periodic atomic structures of bulk phases in the Li–Mg–Al–H system were predicted with the density functional theory Vienna ab initio simulation package (VASP) code [32,33] full minimizations using regular projector augmented wave potentials [34] with generalized gradient PW91 exchange correlation corrections [35]. All calculations were made with 0.3 Å⁻¹ spacing of the k-point meshes, a planewave cutoff of 750 eV, and Gaussian smearing with a broadening of 0.3 eV. The criteria for convergence of the atomic forces in the full bulk minimization of the lattice parameters and atomic positions were 0.005 eV/Å. The thermodynamic properties of selected relaxed phases were predicted with direct method lattice dynamics using the Materials Design MedeA Phonon module [36,37] with the harmonic approximation. The zero point energy and other thermodynamic functions were determined from the integration of the vibrational density of states over the Brillouin zone following established methodology [38,39].

3. Results and discussion

3.1. Synthesis of LiMg(AlD₄)₃

LiMg(AlD₄)₃ (1) was synthesized by HI ball milling with a 3:1 LiAlD₄ : MgCl₂ ratio [40]. The gray product was stable for several months. As-milled 1 diffracted poorly, indicating a small grain size and/or the presence of amorphous phases. In addition to LiCl, other unidentified trace impurities were present. A purification/recrystallization step from Et₂O and toluene, as described previously [7], reduced the amount of LiCl, removed the unidentified impurities, and increased the crystallinity of 1. The purified sample was fluffy, white, and diffracted strongly.

3.2. Addition of TiCl₃ to LiMg(AlD₄)₃

The catalyst TiCl₃ was added to as-milled 1 under different milling conditions and in different amounts. High intensity ball milling was used to mix first 2 mol% TiCl₃ with in-situ synthesized 1 (3 LiAlD₄ + 1 MgCl₂) and, second, to mix 2 mol% TiCl₃ with as-milled 1. In both cases, the pressure developed during milling was consistent with the decomposition of 1 to MgD₂ and LiD. Furthermore, PXD patterns of material from both of these syntheses showed LiCl and Al. The weight ratio between LiCl and Al was determined by QPA to be close to 1:1, as expected after a complete decomposition of 1 to MgD₂ and LiD. This clearly indicates the catalytic effect of TiCl₃ and the low stability of the alanates. The Bragg peaks from MgD₂ were weak and broad, indicating the presence of amorphous or nanocrystalline MgD₂.

The decomposition of 1 during milling may have been caused by the high milling rate and the accompanying increase in temperature (up to 40 °C). Since reduction of the ball milling speed reduces the mechanical energy and the

![Fig. 3](image-url) Relative weight ratios versus temperature for different phases in purified 1 refined from SR–PXD data during heating to 220 °C. NaCl and LiCl are present in constant amounts, and they are therefore excluded from the analysis. LiD is excluded from the calculations [40].

![Fig. 4](image-url) Relative weight ratios versus temperature for different phases in purified 1 refined from SR–PXD data during heating from about 200 to 400 °C. NaCl and LiCl are present in constant amounts and are therefore excluded from the analysis.
Introduction of pauses during milling reduces the heating effect. Li ball milling of as-milled $\text{LiAlD}_4$ with 1 mol% TiCl$_3$ was investigated as a means to prevent the decomposition of $\text{LiAlD}_4$. The PXD pattern showed the presence of Al, which also indicates decomposition. However, QPA gave an approximate LiCl:Al weight ratio of 3:2. This is a lower Al content than expected from a complete decomposition, and it is also lower than expected for the decomposition to LiMgAlD$_6$, which should give a weight ratio of about 4:3. Thus, the low intensity ball milling reduced the amount of decomposition during the milling, but not completely.

Cryomilling is an effective method to obtain metastable phases. The low temperature prevents decomposition of the sample and furthermore decreases the particle size because of increased brittleness. A mixture of LiAlD$_4$ and MgCl$_2$ (3:1) with 1.5 mol% TiCl$_3$ was thus cryomilled (sample #1). The PXD pattern showed only traces of Al, indicating that no significant decomposition of $\text{LiAlD}_4$ had occurred. The presence of LiCl indicated that the synthesis reaction had taken place, according to Eq. (1). As a check, as-milled 1 was cryomilled together with 3 mol% TiCl$_3$. The same features were found, but the peaks were somewhat broader than in sample #1.

High-pressure mechanochemical synthesis was also used to introduce TiCl$_3$. As-milled 1 was ball-milled at 75 bar H$_2$ pressure together with 5 mol% TiCl$_3$. Analysis of the PXD pattern showed that a minor amount of Al had been produced, confirming that only a small amount of 1 had decomposed. The presence of Al was also inferred by the change in colour from light to dark gray. These observations are consistent with the reaction in Eq. (7).

$$3 \text{LiMgAlD}_6 + \text{TiCl}_3 \rightarrow 3 \text{LiCl} + 3 \text{MgD}_2 + \text{Al}_2\text{Ti} + 6 \text{Al}^+ + 15 \text{D}_2 \tag{7}$$

This is similar to what is seen when TiCl$_3$ is added to NaAlH$_4$ [41], upon which NaCl and various Al$_{1-x}\text{Ti}_x$ compositions are formed. Based on the present data it has not been possible to analyze the details of the composition of the Al–Ti phases that have been formed, and thus “Al$_2\text{Ti} + 6\text{Al}$” is used as a symbolic representation of these compounds. Notice that the theoretically released amount of Al is larger than in the corresponding reaction with NaAlH$_4$. The reason for the observation of more Al in the HP-milled sample than in the cryomilled samples is probably the higher concentration of TiCl$_3$ (5 mol%) in this sample, compared to 1.5 and 3 mol% in the cryomilled samples.

3.3. Synthesis and stability of LiMgAlD$_6$

As-milled 1 was carefully decomposed to LiMgAlD$_6$ (2) at about 120 °C [40]. The temperature was chosen from inspection of the decomposition curve (vide infra), such that Eq. (2) can occur without the decomposition of 2 according to Eq. (3). Analogous to 1, ball-milling of a mixture of 1.5 mol% TiCl$_3$ and as-milled 2 led to a pressure increase consistent with the formation of MgD$_2$ and LiD (Eq. (3)). This shows that 2 also has decreased stability after addition of TiCl$_3$.

In an attempt to prevent decomposition of 2 when mixed with TiCl$_3$, as-milled 2 was mixed with 5 mol% TiCl$_3$ and cryomilled as described above. The PXD pattern of the resulting product material showed that the LiMgAlD$_6$ phase was intact, but some Al was formed. As discussed above for the high-pressure milling of 1 and TiCl$_3$, this can most readily be explained by a reaction between TiCl$_3$ and 2 (Eq. (8)).

$$3 \text{LiMgAlD}_6 + \text{TiCl}_3 \rightarrow 3 \text{LiCl} + 3 \text{MgD}_2 + \text{Al}_2\text{Ti} + 6 \text{H}_2 \tag{8}$$

As in Eq. (7), the “Al$_2\text{Ti}” term simply represents the Al$_{1-x}\text{Ti}_x$ phases present in the sample; no further analysis was performed.

3.4. Dehydrogenation reactions

Dehydrogenation reactions of as-milled and purified 1 were studied using in-situ SR–PXD and TPD. The TPD measurements were performed under vacuum with a heating rate of 0.5 K/min, as shown in Figs. 1 and 2 for as-milled and purified 1, respectively. The corresponding in-situ SR–PXD studies of the decompositions are also reported in Figs. 1 and 2. The heating rate was in this case 2 K/min for the as-milled 1, while...
the purified 1 was heated in two experiments: from room temperature to 220 °C with a heating rate of 0.5 K/min, and from 200 to 400 °C at 4 K/min. Analysis of each diffraction pattern from the in-situ SR–PXD measurement was performed for the decomposition of purified 1, which provided a thermal profile of the compositional changes during decomposition, this is shown in Figs. 3 and 4. The analyses do not include LiD [42].

The first decomposition step, from 1 to 2 (Eq. (2)), took place at 130 and 140 °C for the as-milled and purified samples, respectively. The slightly higher onset temperature of decomposition for the purified sample is most probably due to kinetic stabilization. The decomposition from 2 is more complicated. The non-purified as-milled sample proceeded directly from 2 to LiD and MgD2 (Eq. (3)) at 160 °C during the TPD experiment and at 180 °C in the SR–PXD experiment – the difference was likely due to the different heating rates. Decomposition of 2 from the purified sample also started at about 170 °C, in accordance with Eq. (3). However, the decomposition of 2 in this case accelerated at around 190 °C, with the concomitant production of MgD2 and Li3AlD6 (3). This indicated that the purified sample decomposed through 3 as an intermediate phase as described by Eqs. 9 and 10.

$$\begin{align*}
3 \text{LiMgAlD}_6 & \rightarrow 3 \text{MgD}_2 + \text{Li}_2\text{AlD}_6 + 2 \text{Al} + 3 \text{D}_2 \\
\text{Li}_2\text{AlD}_6 & \rightarrow 3 \text{LiD} + \text{Al} + 3/2 \text{D}_2
\end{align*}$$

A closer analysis of the decomposition path of the purified sample shows that 2 is starting to decompose long before the main decomposition peak appears. This can be seen in Fig. 3, where the maximum amount of 2 was reached slightly below 140 °C, when decomposition of 1 was finished. At this point, the weight ratio of Al to 2 was 1.33:1, which is higher than expected from Eq. (2) (1.08:1). Thus, decomposition of 2 must have started well below 140 °C. Furthermore, the amounts of 3 and MgD2 were respectively less than and greater than that expected from Eq. (9), the two decomposition pathways for 2, i.e., Eqs. 3 and 9, must have occurred simultaneously. The TPD shoulder between 220 and 250 °C in Fig. 2 was due to decomposition of Li3AlD6 (Eq. (10)). After complete decomposition of 2, the calculated MgD2:Al molar ratio from the diffraction patterns was close to the theoretical one of 1:3.

Decomposition of MgD2 proceeded through two steps. The as-milled (pure) sample exhibited two TPD peaks at 260 (280) and 340 °C, in agreement with previous measurements [43].

No Mg phases could be seen from SR–PXD during the decomposition of MgD2 formed from as-milled 1, indicating the formation of amorphous Mg-phase(s). Furthermore, the observed decomposition temperature for the in situ-formed MgD2 was lower than that for pure MgD2 [1], which can be attributed to the formation of Al–Mg phases contributing to a thermodynamic destabilization of the Mg hydride. This was confirmed by quantitative analysis of the in-situ SR–PXD data for purified 1 at high temperatures (Fig. 4). Ten phases were included in the Rietveld refinements: LiCl, NaCl, Al, Mg, MgO, Li2O, MgD2, Al0.65Mg0.35, Al6Mg27, and Al12Mg17. When small amounts were present, only the scale parameters of the phases were refined. No new crystalline phases appeared during the decomposition until 300 °C, indicating that MgD2 decomposed into amorphous phase(s). The peaks in the SR–PXD patterns from the Al-phase were constant between 200 and 300 °C, and thus the calculated increased wt% of Al was an artifact. As the decomposition of MgD2 neared completion, two new phases appeared: a main phase, Al6Mg27, and a minor phase, Al0.65Mg0.35. The Al6Mg27 phase reached a maximum of 20 wt% at about 320 °C. If all Mg was present as Al6Mg27, as proposed by Feuerbacher et al. [44], the wt% should have been about 60%; the lower observed value is thus consistent with the presence of amorphous Mg phases.

The formation of MgO and Li2O from about 330 to 370 °C, respectively, will probably influence the decomposition process at higher temperatures.

In order to study how the addition of TiCl3 influenced the decomposition of the Li-Mg alanates, several different experiments were performed. Sample #1 (cryomilled LiAlD4 and MgCl2 (3:1) with 1.5 mol% TiCl3) was heated, and with release of D2 into a constant volume. As-milled 1 was cryomilled together with 2 mol% TiCl3 (sample #2) and heated under dynamic vacuum with a heating rate of 0.5 K/min. Finally, HP-milling of 1 and 1 mol% TiCl3 was performed (sample #3), followed by SR–PXD one week later.

For sample #1, Fig. 5 shows the pressure increase during heating. The behavior was consistent with faster kinetics for Eq. (2) than Eq. (3), and that decomposition according to Eq. (3) seemed to be starting as soon as 2 was formed. For sample #2, the TPD data (Fig. 6) showed one strong desorption peak at about 90 °C, corresponding to Eq. (2). Several weaker peaks between 95 and 160 °C corresponded to the decomposition of
There was also a very weak peak at around 230 °C that could be ascribed to the decomposition of MgD₂.

Decomposition of samples containing TiCl₃ took place even at room temperature, as evidenced by several observations. Sample #1 was studied by in-situ SR–PXD approximately one week after synthesis. As seen in Fig. 7, this sample consisted almost entirely of Al and small amounts of 2 at RT, while no 1 could be observed. When sample #1 was examined after several weeks of storage at room temperature, only the binary deuterides were observed. Further, sample #3 was studied by SR–PXD one week after synthesis. In this instance, sample #3 was decomposed more slowly than cryomilled sample #1, which is most probably due to a smaller grain size for the cryomilled sample. This gives a larger surface area and a better mixing of the TiCl₃ with the hydride, and thus faster decomposition. Upon heating of sample #3, 1 decomposed into 2 at 110 °C, followed by decomposition of 2 at about 150 °C, and MgD₂ at 250 °C.

Finally, sample #2 was desorbed into a constant volume after storage at RT for one month (see Fig. 5). A significantly smaller amount of D₂ was desorbed than for fresh sample #1, and the first decomposition step seemed to have almost disappeared. Taken together, these experiments demonstrated that addition of TiCl₃ to LiMg(AlD₄)₃ led to significant destabilization. The desorption peaks were moved to lower temperatures and significant decomposition occurred within a few days.

3.5. Attempts to demonstrate reversible desorption

Since an applicable hydrogen storage material must show reversibility after H₂ desorption, the rehydrogenation of the decomposition products from both 1 and 2 has been tested. First, mixtures of the final decomposition products MgH₂, Al, and LiH in a 1:1:1 ratio were ball-milled under H₂ pressure, both alone and in the presence of 5 mol% TiCl₃. However, PXD patterns of the resulting powders showed only the starting reactants and no evidence of H₂ absorption. Subsequently, sample #1 was heated to 160 °C for 5 h to produce a mixture of LiD, MgD₂ and Al, and this mixture was then ball-milled under 75 bar H₂ pressure. The PXD pattern of the resulting powder showed no peaks from MgD₂, indicating Mg is present in amorphous phases. The TPD analysis of the sample exhibited a weak peak at 240 °C consistent with decomposition of MgD₂. No evidence for the formation of 1 or 2 was observed.

In addition to HP ball milling, PCT experiments were also performed on a sample consisting of LiD and MgD₂ and Al (and LiCl), which was formed from the decomposition of as-milled 1 in the presence of 2 mol% TiCl₃. At 90 °C no absorption was observed at 100 bar H₂. Similarly, no absorption was observed after increasing the pressure to 130 bar and the temperature to 110 °C. The PXD pattern of the material after heating showed increased intensities in the MgD₂ peaks, but no indication of any new phases. This indicated a more crystalline sample, due to the heating during PCT experiment. Similarly, PCT-experiments exposed as-milled 2 to H₂ pressure. The pressure and temperature combinations of 185 bar at 80 °C and 200 bar at 100 °C, 110 °C, and 120 °C were tested, but no absorption was observed in any of the experiments.

Finally, the PXD pattern of the material resulting from the high-pressure milling of as-milled 1 with 5 mol% TiCl₃ showed the presence of 2, but not of 1. Some desorption was detected from the TPD measurement of this sample at 160 °C, confirming the presence of at least some of 2. Additionally, MgD₂ was present, with increased Bragg peak intensities. Thus, even the presence of H₂ cannot inhibit the decomposition of 1, nor promote its formation from its decomposition products.

3.6. Thermodynamic modeling

3.6.1. Comparison of thermodynamic modeling with first principles calculations

The enthalpies of formation at 298 K and 1 bar ΔHformation of the Li–Mg–Al–H ternary and quaternary phases calculated with the thermodynamic assessment of experimental data, are compared to values predicted with first principles atomic modeling results in Table 1. The first principles calculations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Thermodynamic Assessment</th>
<th>First Principles Atomic Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlH₄</td>
<td>-117.2</td>
<td>-113.4</td>
</tr>
<tr>
<td>Li₄AlH₆</td>
<td>-321.5</td>
<td>-310.9</td>
</tr>
<tr>
<td>MgAlH₄</td>
<td>-82.8</td>
<td>-65.6</td>
</tr>
<tr>
<td>LiMg(AlH₄)₂</td>
<td>-166.7</td>
<td>-179.4</td>
</tr>
<tr>
<td>LiMgAlH₆</td>
<td>-186.4</td>
<td>-186.2</td>
</tr>
</tbody>
</table>

a This work.
b Reference [25].
c Reference [45].
were in moderate agreement and provided an alternate means of confirming the reasonableness of the assessment. The first principles methodology for the finite temperature thermodynamic predictions has an estimated error of 5–15 kJ/mol, mainly due to the limitations of the exchange correlation analytical expression for the electronic energy determination of the ground state.

The thermodynamic parameter optimization was carried out using the Parrot module in the Thermo-Calc software [46], integrating already assessed parameters for the necessary lower order systems with parameter fits for the newly assessed phases. The convergence on a consistent thermodynamic description enabled phase diagrams and reaction values to be modeled for a wide range of conditions. The thermodynamic model parameters for the newly described phases are listed in the Supporting Information.

3.6.2. Thermodynamic modeling results

The thermodynamic analyses confirmed the metastable nature of LiMg(AlH4)3 and LiMgAl6 and the relationships between the various possible decomposition pathways observed experimentally. The thermodynamic assessments were used to calculate the H2 pressures of the Li–Mg–Al–H phases’ decomposition reactions as a function of reciprocal temperature, using the van’t Hoff equation

\[ P_{\text{H}_2} = \exp\left(-\Delta G_{\text{decomp}}/RT\right) = \exp\left(-\Delta H_{\text{decomp}}/RT + \Delta S_{\text{decomp}}/R\right) \]

where \(\Delta G_{\text{decomp}}, \Delta H_{\text{decomp}},\) and \(\Delta S_{\text{decomp}}\) are the free energy, enthalpy, and entropy changes for the decomposition reaction per mol of H2, respectively, and R is the ideal gas constant. This equation describes the relationship of increasing H2 pressure with the increasing favorability of the decomposition reaction, at a given temperature. The slopes of the van’t Hoff lines plotted versus 1000/T correspond to the value of \(\Delta H_{\text{decomp}}\) for the decomposition reaction, where a positive slope corresponds to an exothermic reaction and a negative slope to an endothermic reaction. For reversible H2 storage applications with polymer electrolyte membrane fuel cells operating at 100 °C and 1–100 bar, the ideal moderate hydride \(\Delta H_{\text{decomp}}\) value is close to 40 kJ/mol H2. Hydrides with lower \(\Delta H_{\text{decomp}}\) are thermodynamically unstable, and those with higher \(\Delta H_{\text{decomp}}\) are too stable for reversibly storing H2 under these conditions.

The thermodynamically calculated H2 pressures for the primary LiMg(AlH4)3 decomposition reactions are shown in Fig. 9, and those for the secondary decomposition reactions involving the intermediate products LiMgAlH6, LiAlH4, and MgH2 are shown in Fig. 10, where the thermodynamically-described AlMg8 phase had a composition of Al1.4Mg6.5, virtually identical to the experimentally identified Al6Mg37 phase. The decomposition reaction \(\Delta H_{\text{decomp}}\) values are given in Table 2. The stepwise exothermic LiMg(AlH4)3 decomposition to form LiMgAlH6, given by Eq. (2), has a high H2 pressure and was observed experimentally in 1 without the TiCl3 catalyst. The other two LiMg(AlH4)3 decomposition curves in Fig. 9 and \(\Delta H_{\text{decomp}}\) values in Table 2 correspond to the two possible overall LiMg(AlH4)3 decomposition reactions.

The thermodynamic assessment was used to probe the relationship between the two LiMgAlH6 decomposition pathways, the first given by Eq. (3), and second given by Eqs. 9 and 10. The calculated decomposition curves in Fig. 10 and \(\Delta H_{\text{decomp}}\) values in Table 2 show that LiMgAlH6 decomposition to binary hydride and elemental products via Eq. (3) is endothermic. The analogous reaction in 2 was observed to be enhanced by impurities. The other LiMgAlH6 decomposition pathway to Li3AlH6 is exothermic, nearly equivalent in \(\Delta H_{\text{decomp}}\) to that of the LiMg(AlH4)3 in Eq. (2). The subsequent Li3AlH6 decomposition reaction (Eq. (10)) is moderately endothermic. Both reactions were observed to shift to higher temperatures during the decomposition of the kinetically-hindered, purified 1.

The final MgH2 decomposition reactions in Table 2 have similar magnitude in their \(\Delta H_{\text{decomp}}\) values. Here, the

![Fig. 10 – van’t Hoff plots for LiMgAlH6, Li3AlH6, and MgH2 decomposition reactions calculated with the thermodynamic assessment.](image)

<table>
<thead>
<tr>
<th>Decomposition Reactions</th>
<th>(\Delta H_{\text{decomp}}) (kJ/mol H2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMgAlH6 = LiH + MgH2 + Al + 3H2 (Eq. (2))</td>
<td>–4.16</td>
</tr>
<tr>
<td>LiMgAlH6 = MgH2 + LiH + 3Al + 4.5H2</td>
<td>0.19</td>
</tr>
<tr>
<td>LiMgAlH6 = LiH + AlMg8 + Al + 5.5H2</td>
<td>13.33</td>
</tr>
<tr>
<td>MgMgH4 = MgH2 + 0.33 Li3AlH6 + 0.67 Al + H2 (Eq. (9))</td>
<td>–4.38</td>
</tr>
<tr>
<td>MgMgH4 = MgH2 + LiH + Al + 1.5H2 (Eq. (3))</td>
<td>8.89</td>
</tr>
<tr>
<td>0.33Li3AlH6 = LiH + 0.33 Al + 0.5H2 (Eq. (10))</td>
<td>35.4</td>
</tr>
<tr>
<td>MgH2 + 1.4Al = AlMg8 + H2</td>
<td>72.5</td>
</tr>
<tr>
<td>MgH2 = Mg + H2</td>
<td>82.7</td>
</tr>
</tbody>
</table>
formation of the AlMg₆ phase is the most accessible at elevated temperatures, but actually has a lower decomposition pressure. Experimentally MgH₂ decomposition was observed first before the formation of the Al–Mg intermetallic phases. While three Al–Mg phases were identified by SR–PXD after heating LiMg(AlH₄)₃ to around 400 °C, the experimentally observed predominance of the AlMg₆ phase was corroborated by the thermodynamic modeling.

The van’t Hoff relationships shown in Figs. 9 and 10 enable the calculation of the equilibrium H₂ pressure needed to rehydrogenate the Li–Mg–Al–H dehydrogenation products to reform LiMgAlH₆ and LiMg(AlH₄)₃. The direct reformation of LiMg(AlH₄)₃ by rehydrogenation of the binary hydride and elemental products would require over \( 2.7 \times 10^6 \) bar H₂. Rehydrogenation of these products to form LiMgAlH₆ would require \( 1 \times 10^5 \) bar H₂. Reformation of LiMg(AlH₄)₃ by LiMgAlH₆ rehydrogenation would require \( 1 \times 10^6 \) bar H₂. This modeling confirms that the potentially high H₂ capacity in the Li–Mg–Al–H system is not thermodynamically accessible.

4. Conclusions

The decomposition temperature and pathway of LiMg(AlD₄)₃ depend strongly on the additional phases in the sample and the crystallinity of the product. While purified 1 is stable for more than one year, presumably because of kinetic stabilization resulting from the removal of LiCl and other, unidentified by-products, as-milled 1 decomposes during the course of a few months, and, if TiCl₃ is added, the decomposition is almost finished after a week. As well, purified 1 has a distinctly higher decomposition temperature as compared to as-milled 1, and the addition of TiCl₃ decreases the dehydrogenation temperatures even further. The effect of impurities is additionally illustrated by the observation of LiAlD₆ as an intermediate only in the decomposition of purified 1.

Thus, purified 1 decomposes to the binary deuterides by three different reactions. The first decomposition step is to LiMg(AlD₄)₃ (Eq. (2)), which thereafter decomposes by two different pathways, either directly to the binary deuterides (Eq. (3)) or by formation of 3 and then the deuterides (Eqs. 9 and 10). Decomposition of MgD₂ from purified 1 happens at relatively low temperatures usually around 260 °C. This is due to the formation of the Al–Mg phases Al₃Mg₉, Al₁₂Mg₁₁, and Al₀.₆₅Mg₀.₃₅, which decreases the hydrogenation enthalpy of the dehydrogenation of MgD₂ (“destabilization”). As with the observation of 3, these AlₓMₙ phases are only seen during heating of purified 1. There may be different reasons for this. Some of the phases may actually be present in the unpurified samples but unobservable, due to low crystallinity. It is also conceivable that the decomposition route is affected by the impurities in the as-milled and Ti-enhanced samples of 1. This has recently been demonstrated in the case of NaₓLiAlH₆, where the addition of TiF₃ led to a new reaction path [47].

The decomposition of 1 when TiCl₃ was mixed at high intensity room temperature milling is triggered by the increased temperature (up to 40 °C) during ball milling and the mechanical energy released. Attempts to reduce the amount of decomposition by reducing the ball milling rate and adding pauses, by applying H₂ pressure, or by milling at liquid nitrogen temperature significantly reduced, or prevented, the decomposition during milling. The addition of TiCl₃ through cryomilling clearly lowers the stability of 1 and 2, and the products rapidly decomposed at room temperature.

A thermodynamic assessment of the Li–Mg–Al–H system was created from experimental data and evaluated with first principles simulations. The decomposition reaction van’t Hoff relationships calculated with the assessment showed that the metastable LiMg(AlH₄)₃ phase decomposed through an exothermic reaction. The experimentally observed decomposition pathways could be explained by the endothermicity of the calculated Li–Mg alanate decomposition enthalpies, in that the impure or catalyzed LiMgAlH₆ intermediate phase could access a more direct endothermic decomposition reaction at lower temperatures, while the kinetically hindered purified LiMgAlH₆ would require higher temperatures to initiate a two-step decomposition through an exothermic reaction. Extraordinarily high H₂ pressures were calculated to be required for the reverse rehydrogenation of the Li-Mg alanate phases.

It is thus not surprising that absorption of H₂ could not be observed in any of our attempts to reverse the decomposition pathways shown in Eqs. 2 and 3, despite using both using high-pressure (up to 200 bar) and HP-milling. This was the case both for samples containing 2 and for a mixture of MgD₂ and LiD; in the cases where 2 was present, this phase decomposed further according to Eq. (3). We conclude therefore that the thermodynamic stability of the Li-Mg alanates is too low for practical reversible hydrogenation.

Acknowledgments

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Appendix. Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.ijhydene.2011.03.110.

REFERENCES
