 Mechanochemistry of the LiBH4–AlCl3 System: Structural Characterization of the Products by Solid-State NMR

Takeshi Kobayashi  
Ames Laboratory, tkobayashi@ameslab.gov

Oleksandr Dolotko  
Ames Laboratory, dolotko@ameslab.gov

Shalbh Gupta  
Ames Laboratory, shalabh@ameslab.gov

Vitalij K. Pecharsky  
Iowa State University and Ames Laboratory, vitkp@ameslab.gov

Marek Pruski  
Iowa State University and Ames Laboratory, mpruski@iastate.edu

Follow this and additional works at: https://lib.dr.iastate.edu/ameslab_manuscripts

Part of the Materials Chemistry Commons, Materials Science and Engineering Commons, and the Nanoscience and Nanotechnology Commons

Recommended Citation
Kobayashi, Takeshi; Dolotko, Oleksandr; Gupta, Shalbh; Pecharsky, Vitalij K.; and Pruski, Marek, "Mechanochemistry of the LiBH4–AlCl3 System: Structural Characterization of the Products by Solid-State NMR" (2018). Ames Laboratory Accepted Manuscripts. 130.
https://lib.dr.iastate.edu/ameslab_manuscripts/130

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Mechanochemistry of the LiBH4–AlCl3 System: Structural Characterization of the Products by Solid-State NMR

Abstract
The double-cation metal borohydride, Li₄Al₃(BH₄)₁₃, mechanochemically produced from a 13:3 mixture of lithium borohydride (LiBH₄) and aluminum chloride (AlCl₃), has a low hydrogen desorption temperature; however, the material’s decomposition is accompanied by a large emission of toxic diborane (B₂H₆). We found that a decrease of the LiBH₄:AlCl₃ ratio in the starting mixture yields increased amounts of partially chlorinated products that also dehydrogenate at low temperature, but release negligibly small amounts of diborane. Extensive characterization by solid-state NMR spectroscopy (SSNMR) and powder X-ray diffraction (XRD) found that the 11:3 ratio product maintains the Li₄Al₃(BH₄)₁₃-like structure, with additional anions substituting for [BH₄]⁻ compared to the 13:3 mixture. Further decrease of relative LiBH₄ concentration in the starting mixture to 9:3 results in a different product composed of tetrahedral [Al(BH₄)₄]⁻ and [Al(BH₄)₂Cl₂]⁻ complexes, in which two hydrogen atoms of each borohydride group are bridged to aluminum sites. Additionally, SSNMR revealed the covalent character of the Al-H bonds, which is not observed in Li₄Al₃(BH₄)₁₃. These findings suggest that the Al-Cl bonding present in the chlorinated complexes prevents the formation of Al(BH₄)₃, which is a known intermediate leading to the formation of diborane during thermal dehydrogenation of the nearly chlorine-free Li₄Al₃(BH₄)₁₃.

Disciplines
Materials Chemistry | Materials Science and Engineering | Nanoscience and Nanotechnology

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/ameslab_manuscripts/130
Mechanochemistry of the LiBH₄-AlCl₃ System: 

Structural Characterization of the Products by Solid-State NMR

T. Kobayashi*,1, O. Dolotko1, S. Gupta1, V.K. Pecharsky,*1, 2, M. Pruski,*1, 3

1U.S. DOE Ames Laboratory, Iowa State University, Ames, Iowa 50011, USA
2Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA
3Department of Chemistry, Iowa State University, Ames, IA 50011, USA

ABSTRACT: The double-cation metal borohydride, Li₄Al₃(BH₄)₁₃, mechanochemically produced from a 13:3 mixture of lithium borohydride (LiBH₄) and aluminum chloride (AlCl₃), has a low hydrogen desorption temperature; however, the material’s decomposition is accompanied by a large emission of toxic diborane (B₂H₆). We found that a decrease of the LiBH₄:AlCl₃ ratio in the starting mixture yields increased amounts of partially chlorinated products that also dehydrogenate at low temperature, but release negligibly small amounts of diborane. Extensive characterization by solid-state NMR spectroscopy (SSNMR) and powder X-ray diffraction (XRD) found that the 11:3 ratio product maintains the Li₄Al₃(BH₄)₁₃-like structure, with additional Cl⁻ anions substituting for BH₄⁻ compared to the 13:3 mixture. Further decrease of relative LiBH₄ concentration in the starting mixture to 9:3 results in a different product composed of tetrahedral [Al(BH₄)₄]⁻ and [Al(BH₄)₂Cl₂]⁻ complexes, in which two hydrogen atoms of each borohydride group are bridged to aluminum sites. Additionally, SSNMR revealed the covalent character of the Al–H bonds, which is not observed in Li₄Al₃(BH₄)₁₃. These
findings suggest that the Al–Cl bonding present in the chlorinated complexes prevents the formation of Al\((BH_4)\)₃, which is a known intermediate leading to the formation of diborane during thermal dehydrogenation of the nearly chlorine-free Li₄Al₃\((BH_4)\)₁₃.
INTRODUCTION

Among various classes of potential solid-state hydrogen storage media, metal borohydrides, $M(BH_4)_n$, consisting of alkali or alkaline earth metal cations ($M^{n+}$) and borohydride anions ($BH_4^-$), have attracted considerable interest due to their high gravimetric density of hydrogen.\textsuperscript{1} Despite their high hydrogen content, many borohydrides release hydrogen at temperatures much higher than 100 °C. For example, LiBH$_4$ contains ~18 wt.% of hydrogen but hydrogen desorption initiates at around 400 °C.\textsuperscript{2} To enhance the decomposition kinetics of metal borohydrides, doping by various additives, including transition metals,\textsuperscript{3-4} metal oxides,\textsuperscript{5-6} hydrides,\textsuperscript{7-8} amides,\textsuperscript{9-11} halides,\textsuperscript{12-14} or graphite\textsuperscript{15-16} has been widely explored. Nakamori et al. reported that the dehydrogenation temperature ($T_d$) correlates with the Pauling electronegativity ($\chi_P$) of metal cations in the borohydrides.\textsuperscript{17} Since the manipulation of $T_d$ in single-cation borohydrides is limited by the nature of the individual metal, they introduced a second metal cation to tune the dehydrogenation process. For example, the $T_d$ value of the products obtained from the ball-milled mixture of zirconium chloride and lithium borohydride ($ZrCl_4 + nLiBH_4, n = 4-6$) is related to the average value of $\chi_P$ for ZrLi$_{n-4}$, and thus can be altered by changing $n$.\textsuperscript{18} Subsequent studies achieved more precise and extensive tuning by the mechanochemical synthesis of double-cation borohydrides\textsuperscript{19-24} via metathesis or double-substitution reactions.

Among the double-cation borohydrides, Li$_4$Al$_3$(BH$_4$)$_{13}$ is an attractive compound with a high hydrogen content (17.1 wt.% and low $T_d$ (70-80°C). The compound can be synthesized at room temperature in 3 hours by ball milling, which effects a simple mechanochemical reaction between LiBH$_4$ and aluminum chloride (AlCl$_3$):\textsuperscript{25-26}

\begin{equation}
13\text{LiBH}_4 + 3\text{AlCl}_3 \rightarrow \text{Li}_4\text{Al}_3(\text{BH}_4)_{13} + 9\text{LiCl}.
\end{equation}

Upon heating to 70-80°C, Li$_4$Al$_3$(BH$_4$)$_{13}$ decomposes into LiBH$_4$ and Al(BH$_4$)$_3$, whereas the latter decomposes into elemental aluminum releasing hydrogen and diborane according to eqs 2 and 3:

\begin{equation}
\text{Li}_4\text{Al}_3(\text{BH}_4)_{13} \rightarrow 3\text{Al}(\text{BH}_4)_3 + 4\text{LiBH}_4
\end{equation}

\begin{equation}
3\text{Al}(\text{BH}_4)_3 \rightarrow 3\text{Al} + 9\text{H}_2 + 6\text{B}_2\text{H}_6.
\end{equation}
The formation of the volatile Al(BH$_4$)$_3$ (b.p. $\sim$45°C) results in the loss of aluminum from the reaction mixture during thermal dehydrogenation, which precludes the potential reversibility of this system.

In the present work, we found that a decrease of relative LiBH$_4$ concentration in the starting LiBH$_4$:AlCl$_3$ mixture from the stoichiometric 13:3 (eq 1) to 11:3 and 9:3 suppresses diborane formation during thermal dehydrogenation, without affecting the T$_d$. Solid-state (SS)NMR techniques combined with powder XRD analysis revealed a discontinuous change in the structure of the ball-milled products upon reduction of the LiBH$_4$ content. In particular, the 9:3 mixture yields a partially chlorinated aluminum borohydride [Al(BH$_4$)$_2$Cl$_2$]$^-$ complex in which, unlike in the Li$_4$Al$_3$(BH$_4$)$_{13}$ structure, the non-hydrogen atoms (Al, B, Cl) form a tetrahedral AlB$_2$Cl$_2$ skeleton with two hydrogen atoms of each borohydride group being covalently bridged between the aluminum and boron. We note that our study is focused solely on the chemical composition and structure of the ball-milled materials, whereas local motions were important to us only to the extent that they affected the SSNMR spectra. The reorientation of [BH$_4$]$^-$ anions or the translational diffusion of Li$^+$ cations in metal borohydrides can be studied by NMR via the temperature dependence of spin-lattice relaxation rates.$^{27-28}$

**EXPERIMENTAL**

**Sample preparations.** The starting materials LiBH$_4$ (>95 wt.% purity) and AlCl$_3$ (99.99 wt.% purity) were purchased from Sigma-Aldrich and used as such. Due to the sensitivity of the starting materials and the products to moist air, all manipulations were carried out in a glove box under a continuously purified and monitored argon atmosphere. For synthesis, mixtures with various molar ratios of starting components weighing $\sim$1 g total were individually loaded in a 65 ml hardened-steel vial and ball-milled for 3 hours, as per the earlier report,$^{25}$ in an 8000 M SPEX mill containing two 8 g and four 1 g balls. Each synthesis was repeated at least 3 times and the reproducibility of the products was confirmed by subsequent analyses.
**Hydrogen desorption.** The kinetics of hydrogen desorption was measured using an automated Sievert’s-type pressure-composition-temperature (PCT) apparatus (PCTPro-2000, SETARAM-HyEnergy LLC), which enables experiments in the temperature region from 25°C to 400°C and up to 200 bar of hydrogen pressure. While still in the glove box, the investigated samples were pressed into pellets and placed in the sealed autoclave, which was then connected to the instrument and evacuated. Volume calibration using high-purity helium gas was performed at room temperature before the kinetic measurements. The samples were heated from 25 °C to 390 °C with a heating rate of 1 °C/min under continuously monitored pressure and held at this temperature until the pressure in the system was stable, or up to 80 hours for reactions with slow kinetics. Qualitative analysis of the released gas was carried out using a residual gas analyzer (RGA, RGAPro-2500, SETARAM-HyEnergy LLC), connected to the autoclave. Following dehydrogenation, the samples were cooled to room temperature using forced air cooling, evacuated and removed in a glove box for further analyses. However, due to the highly amorphous nature of dehydrogenated materials, XRD did not yield any discernable patterns other than one attributable to LiCl. The SSNMR spectra, although detectable, were very broad and uninformative, and thus will not be further discussed.

**XRD.** The products were characterized by powder XRD analysis at room temperature on a PANaytical powder diffractometer using Cu Kα1 radiation with a 0.02° 2θ step, with Bragg angles (2θ) ranging from 10° to 80°. During the measurements, a polyimide (Kapton) film was used to protect the sample from moisture and oxygen, which resulted in a weak amorphous-like background in the XRD patterns between 13° and 20°.

**Solid-state NMR.** The $^{11}$B and $^{27}$Al SSNMR experiments were performed at room temperature ($\sim$295 K) on a Varian 600 MHz (14.1 T) NMR spectrometer, equipped with a 3.2-mm triple-resonance magic-angle spinning (MAS) probe, and an Agilent 400 MHz (9.4 T) spectrometer equipped with a 3.2-mm double-resonance MAS probe. The samples were packed in MAS zirconia rotors in a glove box under argon atmosphere and sealed with double O-ring caps to avoid possible reaction with oxygen and
moisture. The following one- and two-dimensional (1D and 2D) experiments were carried out: 1D $^{11}$B and $^{27}$Al direct polarization (DP)MAS, 2D $^{27}$Al triple-quantum (3Q)MAS, $^{29}$-$^{30}$ $^{27}$Al{$^{11}$B} REDOR, $^{31}$-$^{32}$ 1D $^{27}$Al{$^{1}$H} MAS-$J$-HMQC, $^{33}$ and $^{27}$Al{$^{1}$H} $J$-modulated spin-echo experiment $^{34}$. All spectra were acquired using SPINAL64 $^{1}$H decoupling. $^{35}$ Detailed experimental conditions are given in the figure captions, where $B_0$ denotes the strength of the external magnetic field, $v_R$ is the MAS rate, $v_{RF}(X)$ is the magnitude of the radio frequency magnetic field applied to X spins, $\tau_{rec}$ is the REDOR recoupling time, $\tau_{max}$ is the optimum $J$ evolution time, $\Delta t_1$ is the increment of $t_1$ during the 2D experiment, $\tau_{RD}$ is the recycle delay, and NS is the number of scans. The $^{11}$B and $^{27}$Al shifts were referenced to the diethyl ether-boron trifluoride complex (BF$_3$·OEt$_2$) at $\delta$ $^{11}$B = 0 ppm and 1.0 M aqueous solutions of Al(NO$_3$)$_3$ at $\delta$ $^{27}$Al = 0 ppm, using methyl proton signal of sodium-3-(trimethylsilyl)propanesulfonate (DSS) at $\delta$ $^{1}$H = 0 ppm as a secondary external reference. $^{36}$

RESULTS AND DISCUSSION

Characterization of the ball-milled products of LiBH$_4$-AlCl$_3$ mixtures; PCT, RGA and XRD analyses. The results of thermal dehydrogenation of products obtained with LiBH$_4$:AlCl$_3$ ratios of 13:3, 11:3 and 9:3 are shown in Figure 1A and Table 1. The 13:3 ratio product, i.e. Li$_4$Al$_3$(BH$_4$)$_{13}$, started desorption at around ~80°C, $^{25}$ and released 2.8 wt% of hydrogen below 390°C in 80 h. The amount of released hydrogen was much lower than the available hydrogen contained in the initial mixture (7.6 wt.%), which is attributed to the decomposition of some of the Li$_4$Al$_3$(BH$_4$)$_{13}$ to a more stable LiBH$_4$ (eq 2) and the formation of diborane. $^{25}$ Indeed, the RGA of the gaseous product showed release of 16 vol.% of B$_2$H$_6$ and 84 vol.% of H$_2$. Note that our PCT-RGA apparatus is not set for real-time monitoring of the gaseous decomposition products and the hydrogen desorption curves were normalized based on the hydrogen content in the overall gaseous products. Thus, due to the release of B$_2$H$_6$, these curves may not represent the exact kinetics of hydrogen desorption.

In the thermal treatment of the 11:3 ratio product, gas was released with a lower onset temperature of ~61°C. The concentration of diborane in the released gas was suppressed to 3 vol.%, whereas the
release of hydrogen was higher (3.5 wt.%), which corresponds to 51 % of all hydrogen available in the mixture (6.8 wt.%). Finally, the 9:3 ratio product initiated hydrogen desorption at an even lower temperature (~50°C) and released 3.0 wt.% of hydrogen in 80 h. Similar to the 11:3 stoichiometry, the gaseous product contained ~50 % of the available hydrogen in the starting mixture (6.1 wt.%), with very small contamination of diborane of 0.3 vol.%.

Table 1. Hydrogen desorption characterization and RGA analysis of decomposition products of LiBH₄-AlCl₃ mixtures of different molar ratios, ball milled for 3 hours.

<table>
<thead>
<tr>
<th>LiBH₄:AlCl₃ ratio</th>
<th>H₂ release (wt.%)*</th>
<th>H₂ (vol.%)</th>
<th>B₂H₆ (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:3</td>
<td>2.8</td>
<td>84.0</td>
<td>16.0</td>
</tr>
<tr>
<td>11:3</td>
<td>3.5</td>
<td>97.0</td>
<td>3.0</td>
</tr>
<tr>
<td>9:3</td>
<td>3.0</td>
<td>99.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* wt.% of hydrogen released during 80 h of thermal treatment.

The XRD pattern of the 13:3 ratio product displays Bragg peaks assigned to a mixture of Li₄Al₃(BH₄)₁₃ (a = 11.390(1) Å) and LiCl (first two major peaks at 2θ = 30.0° and 34.8°)²⁵. The XRD pattern of the 11:3 ratio product is similar, except that the set of Bragg peaks corresponding to the Li₄Al₃(BH₄)₁₃ phase is shifted towards slightly larger Bragg angles (Figure 1C), indicating a smaller size of the cubic unit cell (a = 11.351(1) Å). As will be shown later, the decreased cell size results from a partial substitution of the BH₄⁻ unit with Cl⁻, i.e. Li₄Al₃(BH₄)₁₃₋ₓClₓ (vide infra). The 9:3 ratio product also yielded Bragg peaks characteristic of LiCl and a new set of Bragg reflections that could not be assigned to any known structure, and thus was extensively studied by SSNMR.
Figure 1. (A) Hydrogen desorption curves versus time and versus temperature (inset) of the LiBH$_4$:AlCl$_3$ mixtures taken at 13:3, 11:3 and 9:3 molar ratios and ball-milled for 3 hours. The desorption curves were obtained during heating from room temperature to 390°C at a heating rate of 1°C/min. (B) The XRD powder patterns of the ball-milled products before the desorption. Asterisks (*) represent the Bragg reflections assigned to Li$_4$Al$_3$(BH$_4$)$_{13}$. The peaks representing LiCl at 2\(\theta\) = 30.0° and 34.8° are truncated to reveal low-intensity details. (C) Expanded XRD powder patterns of the 13:3 and 11:3 ratio products illustrate the shift of the Bragg peaks and, therefore, the smaller-size of the unit cell in the latter.

**Characterization of the ball-milled products of LiBH$_4$:AlCl$_3$ mixtures; SSNMR.** The discussion of SSNMR results is organized as follows. We first use the $^{11}$B DPMAS, $^{27}$Al DPMAS and $^{27}$Al 3QMAS results, in concert with the DFT calculations of NMR parameters, to identify the $^{11}$B and $^{27}$Al sites present in the 3-hr ball-milled LiBH$_4$:AlCl$_3$ mixtures taken in the molar ratios of 13:3, 11:3 and 9:3. Since the structural analysis of the 9:3 sample proved to be challenging not only for XRD, but also for routine SSNMR, we carried out three additional experiments to fully characterize this sample. First, we demonstrated the existence of covalent Al–H bonds by applying the 1D version of the $^1$H–$^{27}$Al MAS-J-HMQC scheme. Second, we quantified the number of BH$_4$ units that coordinate with each of the Al
cations by using the $^{27}$Al($^{11}$B) rotational double echo resonance (REDOR) experiment.\textsuperscript{31-32} Finally, we validated the multiplicity of such covalent bonds by $J$-modulated spin-echo measurements.\textsuperscript{34}

$^{11}$B DPMAS, $^{27}$Al DPMAS, $^{27}$Al 3QMAS and DFT calculations. The $^{11}$B and $^{27}$Al DPMAS spectra of ball-milled products are shown in Figures 2A and 2B, respectively. As in the case of XRD, the 13:3 and 11:3 ratio products yielded similar spectra, which differ significantly from those observed for the sample prepared using the lowest LiBH$_4$ content. Based on the crystallographic structure of Li$_4$Al$_3$(BH$_4$)$_{13}$,\textsuperscript{25} we assigned the $^{11}$B signal at -36 ppm to the dominant BH$_4^-$ unit bridging the Al and Li atoms and the minor signal at -44 ppm to the BH$_4^-$ unit surrounded by four Li atoms. The signal at -42 ppm corresponds to unreacted LiBH$_4$ (see Figure S1 in Supporting information). The 9:3 ratio product showed two signals at -36 and -37 ppm, which are also characteristic of the BH$_4^-$ units. We attribute these signals to the Al(BH$_4$)$_{4-x}$Cl$_x$ species as discussed below.

![Figure 2](image.png)

Figure 2. $^{11}$B (A) and $^{27}$Al (B) DPMAS spectra of the products of LiBH$_4$-AlCl$_3$ mixture ball-milled for 3h. The spectra were acquired at $B_0 = 14.1$ T with a single pulse excitation, using flip angles of 10°, $v_R = 12.5$ kHz, $v_{RF}(^{11}$B) = 50 kHz, $v_{RF}(^{27}$Al) = 50 kHz, $v_{RF}(^{1}$H) = 50 kHz for SPINAL64 $^1$H decoupling, and $\tau_{RD} = 0.5$ s. The spectra were normalized to a constant height.

The interpretation of $^{27}$Al spectra proved to be more intricate, but provided structural insights unobtainable with other methods. We first note that the $^{27}$Al DPMAS spectrum of the 13:3 ratio product
is dominated by the MAS-averaged second-order quadrupolar powder pattern centered at around 38 ppm, which is assigned to Li₄Al₃(BH₄)₁₃. Based on the analysis of the corresponding 3QMAS spectrum shown in Figure 3, the isotropic chemical shift $\delta_{cs,iso}$ and the second-order quadrupolar effect parameter $P_Q$ were estimated to be 46 ppm and 5.8 MHz, respectively. The DFT calculations of the NMR parameters carried out for the Li₄Al₃(BH₄)₁₃ structure²⁵ yielded very similar values (Table 2; see Supporting Information for the calculation details), thereby unambiguously confirming the assignment. Note that the same signal is also dominant in the 11:3 ratio product; however, it is also accompanied by a weaker signal (by a factor of ~5) centered at ~55 ppm. Again, by combining the results of $^{27}$Al 3QMAS and DFT calculations, we assign this weaker resonance to an Al(BH₄)₃Cl unit in the Li₄Al₃(BH₄)₁₃₋ₓClₓ structure. Indeed, the experimental line shape parameters obtained for this sample from the $^{27}$Al 3QMAS spectrum in Figure 3, $\delta_{cs,iso} = 59$ ppm and $P_Q = 4.2$ MHz, agree well with the DFT calculations for such a structure, $\delta_{cs,iso} = 61.8$ ppm and $P_Q = 4.7$ MHz (see Table 2). Evidently, the substitution of a single BH₄⁻ with Cl⁻ in the 11:3 ratio product resulted in the smaller size of the unit cell observed by XRD (Figure 1C). We also calculated the NMR parameters for a similar Al site with two Cl atoms, Al(BH₄)₂Cl₂, but in this case the results were inconsistent with the experimental values (see Table S2 in Supporting Information). We finally note that a small amount of partially chlorinated product(s) was already discernable in the 13:3 sample (Figure 2B), suggesting an incomplete metathesis of the mechanochemical reaction product. In fact, the signal attributed to Al(BH₄)₃Cl features prominently in the $^{27}$Al 3QMAS NMR spectrum of the intermediates from the 13:3 mixture obtained after 15-min ball-milling (See Figure S2 in Supporting Information).
Figure 3. 2D $^{27}$Al 3QMAS spectra of the products of LiBH$_4$-AlCl$_3$ mixtures ball-milled for 3h. The spectra were obtained at $B_0 = 9.4$ T using $\nu_R = 16$ kHz, $\nu_{RF}(^{27}\text{Al}) = 200$ kHz and 12.5 kHz for hard and soft pulses, and $\nu_{RF}(^1\text{H}) = 64$ kHz for SPINAL64 $^1$H decoupling. The data were acquired in 128 rows with $\Delta t_1 = 8.33$ $\mu$s, $NS = 96$ per row, and $\tau_{RD} = 1$ s. The spectra were sheared and scaled as described elsewhere.$^{37}$

Table 2. The experimentally and computationally obtained quadruple coupling parameters of $^{27}$Al spectra for ball-milled samples of LiBH$_4$-AlCl$_3$ mixtures.

<table>
<thead>
<tr>
<th>LiBH$_4$:AlCl$_3$ molar ratio</th>
<th>Phase</th>
<th>Al sites</th>
<th>$\delta_{cs,iso}$ (ppm)</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>$P_Q$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13:3</td>
<td>Li$_4$Al$_3$(BH$<em>4$)$</em>{13}$</td>
<td>Al(BH$_4$)$_4$</td>
<td>46$^b$</td>
<td></td>
<td></td>
<td>5.8$^c$</td>
</tr>
<tr>
<td></td>
<td>calc</td>
<td>Al(BH$_4$)$_4$</td>
<td>46.0</td>
<td>5.7</td>
<td>0.01</td>
<td>5.7$^d$</td>
</tr>
<tr>
<td>11:3</td>
<td>Li$_4$Al$_3$(BH$<em>4$)$</em>{13-x}$Cl$_x$</td>
<td>Al(BH$_4$)$_4$</td>
<td>46$^b$</td>
<td></td>
<td></td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al(BH$_4$)$_4$Cl</td>
<td>59$^b$</td>
<td></td>
<td></td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>calc</td>
<td>Al(BH$_4$)$_4$</td>
<td>46.6</td>
<td>5.6</td>
<td>0.10</td>
<td>5.6$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al(BH$_4$)$_4$Cl</td>
<td>61.8</td>
<td>4.7</td>
<td>0.25</td>
<td>4.7$^d$</td>
</tr>
<tr>
<td>9:3</td>
<td>New phase</td>
<td>Al(BH$_4$)$_4$</td>
<td>46$^b$</td>
<td></td>
<td></td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>Al$_1$</td>
<td>Al(BH$_4$)$_2$Cl$_2$</td>
<td>77$^b$</td>
<td></td>
<td></td>
<td>2.4$^c$</td>
</tr>
<tr>
<td></td>
<td>Al$_2$</td>
<td>Al(BH$_4$)$_2$Cl$_2$</td>
<td>65$^b$</td>
<td></td>
<td></td>
<td>3.1$^c$</td>
</tr>
<tr>
<td></td>
<td>Al$_3$</td>
<td>Al(BH$_4$)$_4$</td>
<td>51$^b$</td>
<td></td>
<td></td>
<td>2.1$^c$</td>
</tr>
</tbody>
</table>

$^a$ Minor Cl substitution is expected.$^{25}$ $^b$ $\delta_{cs,iso}$ was obtained from the MQMAS spectra, as described in reference 34. $^c$ $P_Q$ was obtained from the analysis of the 2D $^{27}$Al 3QMAS spectra. $^d$ The second-order quadrupolar effect parameter $P_Q$ is given by $P_Q = C_Q \left(1 + \frac{\eta^2}{3}\right)^{1/2}$, where $C_Q$ and $\eta_Q$ are the quadrupole coupling constant and the asymmetry of the electric field gradient tensor, respectively.
As in the case of XRD and $^{11}$B SSNMR, further reduction of the LiBH$_4$ content in the LiBH$_4$:AlCl$_3$ starting mixture to 9:3 resulted in a substantial change of the $^{27}$Al DPMAS spectrum. In the reaction product, the $^{27}$Al signal centered at 55 ppm disappeared, the signal at 38 ppm significantly decreased, and three new peaks appeared at 74, 60, and 48 ppm, which will be hereafter denoted as Al$_1$, Al$_2$, and Al$_3$. Additional double-resonance SSNMR methods were used to refine our understanding of these sites, as described below.

$^1$H-$^{27}$Al MAS-$J$-HMOC. In analogy to the liquid-state HMQC experiment, the 2D MAS-$J$-HMOC sequence relies on the polarization transfer via scalar ($J$) coupling, and hence probes the heteronuclear correlations between pairs of directly bonded nuclei. Knowing that only the BH$_4$ protons are present in the studied materials, we used a simplified, 1D version of the $^1$H-$^{27}$Al HMQC experiment, in which $J$-polarized $^{27}$Al magnetization was observed with the evolution time $t_1$ set to 0. The sequence used the frequency-switched Lee-Goldburg (FSLG) homonuclear decoupling scheme$^{38}$ to remove the $^1$H-$^1$H dipolar coupling during the polarization transfer.$^{33,39}$ The MAS-$J$-HMOC spectra (Figure 4) unequivocally demonstrate that Al$_1$, Al$_2$, and Al$_3$ sites in the 9:3 ratio product are covalently bonded to the hydrogen of BH$_4$ units, or at least the Al–H bonding has some degree of covalent character. The magnitudes of the $J_{AlH}$-couplings could not be estimated from this experiment, because the maximum transfer was observed at $\tau_{max} = 2.8$ ms due to fast $T_2'$ relaxation (note that we measured the $J_{AlH}$-couplings using the $J$-modulated spin-echo experiment described below). It is interesting to note that the $^{27}$Al signal from Li$_4$Al$_3$(BH$_4$)$_{13}$ did not appear in the MAS-$J$-HMOC experiment, which suggests that the BH$_4$ units are present as isolated anions in the Li$_4$Al$_3$(BH$_4$)$_{13}$ structure.
Figure 4. 1D $^{27}\text{Al}\{^1\text{H}\}$ MAS-$J$-HMOC spectra of the 13:3 and 9:3 ratio products. The spectra were obtained at $B_0 = 14.1$ T using $v_R = 12.5$ kHz, $v_{RF}(^1\text{H}) = 100$ kHz during the FSLG decoupling and short pulses, and 50 kHz for SPINAL-64 decoupling during the acquisition, $v_{RF}(^{27}\text{Al}) = 50$ kHz and 20 kHz for the initial $\pi/2$ and the inversion $\pi$ pulses, respectively, $\tau_{\text{max}} = 2.8$ ms, $\tau_{RD} = 1$ s, and $NS = 2400$.

$^{27}\text{Al}\{^{11}\text{B}\}$ REDOR. In the REDOR experiment, a series of rotor-synchronized $\pi$ pulses are typically applied at the resonance frequency of non-observed nuclei (spins $I$), to reintroduce the heteronuclear dipolar coupling with the observed nuclei (spins $S$), which is otherwise fully or partially removed by MAS. Such experiments result in the so-called REDOR dephasing curve, which is constructed as a normalized difference, $\Delta S/S_0 = [S_0(\tau_{\text{rec}}) - S(\tau_{\text{rec}})]/S_0(\tau_{\text{rec}})$, between two spin-echo decays $S_0(\tau_{\text{rec}})$ and $S(\tau_{\text{rec}})$, measured as a function of the recoupling time $\tau_{\text{rec}}$ without and with the recoupling $\pi$ pulses, respectively. In the case of an isolated pair of spins with $I = S = 1/2$, $\Delta S/S_0$ can be fitted to a simple analytical formula which yields the dipole-dipole coupling constant, and thereby the internuclear distance $r_{IS}$. The interpretation of the REDOR dephasing curves becomes more complicated in the presence of multiple-spin systems, such as $SI_n$, because for long recoupling times the dipolar dephasing curves are sensitive to their geometry. It turns out, however, that in such case the initial slope of the REDOR curve, measured within the limit $0 < \Delta S/S_0 < \sim 0.2$, can be fitted to a simple analytical formula,

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2}(\tau_{\text{rec}})^2 M_{2IS}^S$$  \hspace{1cm} (4)$$

with
\[ M_2^{IS} = \frac{4}{15 \left(4\pi \right)} \gamma_I^2 \gamma_S^2 \hbar (I + 1) \sum_{i=1}^{n} \left\langle r_{i,S}^{-6} \right\rangle, \]  

(5)

where \( M_2^{IS} \) is the van Vleck’s heteronuclear dipolar second moment calculated over all spins \( I \) surrounding spin \( S, \) \( \mu_0 \) is the vacuum permeability, \( \tau_{rec} \) is given by the multiple of the rotor period \((NT_R), \) \( \gamma_x \) is the gyromagnetic ratio of spin \( x, \) and \( r_{i,S} (k = 1,2,\ldots n) \) represent the internuclear \( I-S \) distances. Accordingly, in \( SI_n \) spin systems with a single (and known) internuclear distance \( r_{IS} \) the order ‘\( n \)’ can be determined from the initial slope of the REDOR curve.

Further complications can arise if one, or both, of the spins involved are half-integer quadrupolar. However, in relatively common situations when only the central transition is effectively excited by the \( \pi \) pulses, eq. (4) can be written as

\[ \frac{\Delta S}{S_0} = \frac{f}{I(I+1)\pi^2} \left( \tau_{rec} \right)^2 M_2^{IS}, \]  

(6)

where the scaling factor \( f \) accounts for incomplete saturation of the non-observed spins and other experimental imperfections.\(^{42-43}\)

The \( ^{27}\text{Al}\{^{11}\text{B}\} \) REDOR curves for the \( \text{Al}_1, \text{Al}_2, \) and \( \text{Al}_3 \) sites in the 9:3 ratio product are shown in Figure 5. In order to use eq. (6), we first determined the scaling factor \( f, \) by measuring the \( ^{27}\text{Al}\{^{11}\text{B}\} \) REDOR curve for the known structure of \( \text{Li}_4\text{Al}_3(\text{BH}_4)_{13} \) \( (f = 0.20). \) Since we have established the presence of covalent bonds between hydrogen in \( \text{BH}_4 \) units and all three aluminum sites, we could safely assume that the Al-B pairs are approximately equidistant and are fixed in the solid structure of the 9:3 ratio product (i.e., do not undergo any motions that would affect the second moment \( M_2^{IS} \)). Finally, by using the internuclear distance \( r_{\text{Al-B}} = 2.1 \text{ Å} \) (which is a value known for \( \text{Al}(\text{BH}_4)_3 \)), the number of \( \text{BH}_4 \) units \( n \) in the first coordination sphere of each Al site becomes the sole fitting parameter in eq (6).

The resulting fits, carried out over the range \( 0 < \Delta S/S_0 < 0.2 \) (Figure 5) show that the numbers of coordinated \( \text{BH}_4 \) units are 2, 2, and 4 for \( \text{Al}_1, \text{Al}_2, \) and \( \text{Al}_3, \) respectively. With the observed \( ^{27}\text{Al} \) NMR
shifts being consistent with tetrahedral coordination, the Al₁ and Al₂ sites must be coordinated to two chlorine atoms (Al(BH₄)₂Cl₂).

**Figure 5.** $^{27}$Al{¹¹B} REDOR curves for the Al₁-Al₃ sites in the 9:3 products. The solid lines represent the analytical curve assuming two (Al₁ and Al₂) and four (Al₃) equivalent boron neighbors with an Al–B distance of 2.1 Å. The experiments were carried out at $B₀ = 14.1$ T using $v_R = 12.5$ kHz, $v_{RF}(^1H) = 100$ kHz for the $\pi$ pulse during $τ_{rec}$ and 50 kHz for SPINAL-64 decoupling during the acquisition, $v_{RF}(^{27}Al) = 50$ kHz and 20 kHz for the initial $\pi/2$ and the inversion $\pi$ pulses, respectively, $τ_{RD} = 0.5$ s, and $NS = 2400$.

**J-modulated spin-echo.** As the final confirmation of the HMQC and REDOR results, we estimated the $J_{Al-H}$ values by measuring the evolution of $J$-modulated spin-echoes for Al₁, Al₂, and Al₃.³⁴ As in the MAS-$J$-HMQC experiment, we used $^1$H–$^1$H FSLG decoupling to extend the spin-echo evolution, which is given by

$$S(τ) = S₀ \cos^m\left(2πJ_{Al-H}^0s_fτ\right)e^{-2τ/T_2'},$$  

where $τ$ is the echo delay, $S₀$ is the signal intensity without $J$-coupling, $m$ represents the number of attached protons, $T_2'$ is the previously mentioned transverse relaxation time that is non refocusable by a $\pi$ pulse, and $s_f$ is the scaling factor introduced by homonuclear decoupling ($1/\sqrt{3}$ for FSLG). The experimental conditions and the echo decays measured for Al₁, Al₂, and Al₃ in the range $0 < τ < 5$ ms are reported in the Supporting Information (Figure S3 in Supporting Information). The experimental data were subsequently fitted to eq (7) in order to determine the value of $m$ which yields the $J_{Al-H}$ couplings that are in agreement with those observed for Al(BH₄)₃.⁴⁵-⁴⁸ For Al₂, we obtained $m = 4$. For
the remaining sites, two values of \( m \) yielded fits of similar quality: \( m = 3 \) and 4 for Al\(_1\), and \( m = 7 \) and 8 for Al\(_3\). Given that in the molecular substructures present in the 9:3 product each BH\(_4\) anion bonds to Al via two hydrogens, the even values of \( m \) appear more likely.

Taken together, our SSNMR results suggest that in each Al(BH\(_4\))\(_x\)Cl\(_{4-x}\) complex, the non-hydrogen atoms form a tetrahedral AlB\(_x\)Cl\(_{4-x}\) skeleton with two hydrogen atoms of each borohydride group being bridged between the aluminum and boron atoms, as depicted in Figure 6.\(^{21-22,25,49-51}\)

**Figure 6.** Schematic diagrams of aluminum coordination described in this study: (A) Al(BH\(_4\))\(_4\) unit in Li\(_4\)Al\(_3\)(BH\(_4\))\(_{13}\) (13:3 product), (B) Al\(_1\) and Al\(_2\) sites in Al(BH\(_4\))\(_2\)Cl\(_2\) (9:3 product), and (C) Al\(_3\) site in Al(BH\(_4\))\(_4\] (9:3 product). Al, B, Cl, and H atoms are shown in light blue, dark green, light green, and white, respectively.

4. Conclusion

In summary, the combined use of SSNMR, XRD, volumetric analysis and RGA measurements provided new insights into a series of hydrogen-containing materials mechanochemically synthesized from LiBH\(_4\) and AlCl\(_3\). While the high total hydrogen content and the low hydrogen desorption temperature of Li\(_4\)Al\(_3\)(BH\(_4\))\(_{13}\) produced from the 13:3 ratio mixture are clearly advantageous, this compound releases a significant amount of diborane. We found that a decrease of LiBH\(_4\) content in the starting mixture leads to formation of complexes in which diborane emission can be suppressed without affecting the onset temperature of hydrogen release. The 11:3 ratio mixture yields a partially chlorinated product, Li\(_4\)Al\(_3\)(BH\(_4\))\(_{13-x}\)Cl\(_x\), which preserves the Li\(_4\)Al\(_3\)(BH\(_4\))\(_{13}\) structure, albeit with a minor reduction of the phase volume due to partial replacement of the borohydride with a chlorine anion. The 9:3 ratio mixture no longer leads to the chlorinated derivative of Li\(_4\)Al\(_3\)(BH\(_4\))\(_{13}\); instead, a compound
containing \([\text{Al(BH}_4\text{)}_2\text{Cl}_2]\)^- complex was identified, in which the non-hydrogen atoms form a tetrahedral \(\text{AlB}_2\text{Cl}_2\) skeleton with two hydrogen atoms of each borohydride group being bridged between the central aluminum and boron atoms. In addition, SSNMR experiments indicate the covalent character of the Al–H bonding, which was not observed in \(\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}\). These results suggest that the insertion of Cl alters the nature of the Al–BH\(_4\) bonding and consequently affects the dehydrogenation process. Even though the majority of past efforts have been devoted to improving the dehydrogenation process of metal borohydrides by substituting various metal cations and creating double-cation borohydrides, the results of this work clearly suggest an alternative, i.e. tuning the dehydrogenation process of metal borohydrides by manipulating the anion moieties instead.

ASSOCIATED CONTENT

Supporting Information. Supporting Information is available free of charge on the ACS Publication website at DOI. The SI contains: 1D \(^{11}\text{B}\) DPMAS spectrum of \(\text{LiBH}_4\) reference, 2D \(^{27}\text{Al}\) 3QMAS NMR spectrum of the 13:3 ratio product after 15 min of ball-milling, theoretical DFT calculation details, and evolution curves of the \(^{27}\text{Al}\) signal intensities in the \(J\)-modulated spin-echo experiment.

Corresponding Authors

*T.K.: takeshi@iastate.edu.

*V.K.P.: vitkp@ameslab.gov

*M.P.: mpruski@iastate.edu

Notes

The authors declare no competing financial interests.

Acknowledgement

We would like to thank Dr. Viktor Balema and Dr. Ihor Hlova for fruitful discussions of the results. This work was supported by the U.S. Department of Energy (DOE), Office of Energy Efficiency &
Renewable Energy under the Fuel Cell Technologies Office, Award Number DE-EE-0007047. The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358.
References


TOC graphics