A New Complex Borohydride LiAl(BH4)2Cl2

Oleksandr Dolotko
Ames Laboratory

Takeshi Kobayashi
Ames Laboratory, takeshi@ameslab.gov

Ihor Hlova
Ames Laboratory, ihlova@ameslab.gov

Shalabh Gupta
Ames Laboratory

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

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

Part of the Materials Science and Engineering Commons

Recommended Citation
Dolotko, Oleksandr; Kobayashi, Takeshi; Hlova, Ihor; Gupta, Shalabh; and Pecharsky, Vitalij K., "A New Complex Borohydride LiAl(BH4)2Cl2" (2021). Ames Laboratory Accepted Manuscripts. 897.
https://lib.dr.iastate.edu/ameslab_manuscripts/897

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 digrep@iastate.edu.
A New Complex Borohydride LiAl(BH4)2Cl2

Abstract
A new mixed alkali metal–aluminum borohydride LiAl(BH4)2Cl2 has been prepared via mechanochemical synthesis from the 2LiBH4–AlCl3 mixture. Structural characterization, performed using a combination of X-ray powder diffraction and solid-state NMR methods, indicates that the LiAl(BH4)2Cl2 phase adopts a unique 3D framework and crystallizes in an orthorhombic structure with the space group C2221, a = 11.6709(6) Å, b = 8.4718(4) Å, c = 7.5114(3) Å. The material shows excellent dehydrogenation characteristics, where hydrogen evolution starts at Tons = 70 °C, releasing approximately 2 wt.% of nearly pure (99.8 vol.%) hydrogen and a very small amount (~0.2 vol.%) of diborane. When compared to halide-free mixed alkali metal–aluminum borohydrides, the presence of Al–Cl bonding in the LiAl(BH4)2Cl2 structure likely prevents the formation of Al(BH4)3 upon decomposition, thus suppressing the formation of diborane.

Keywords
hydrides, X-ray diffraction, crystal structure, solid-state NMR, hydrogen storage

Disciplines
Materials Science and Engineering
A New Complex Borohydride LiAl(BH$_4$)$_2$Cl$_2$

Oleksandr Dolotko $^{1, *}$, Takeshi Kobayashi $^{1, *}$, Ihor Z. Hlova $^{1}$, Shalabh Gupta $^{1}$ and Vitalij K. Pecharsky $^{1, 2}$

$^1$ U.S. DOE Ames Laboratory, Iowa State University, Ames, IA 50011, USA; takeshi@iastate.edu (T.K.); ihlova@iastate.edu (I.Z.H.); shalabhhiitd@gmail.com (S.G.); vitkp@ameslab.gov (V.K.P.)
$^2$ Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA
* Correspondence: sdotkot@yahoo.com

Abstract: A new mixed alkali metal–aluminum borohydride LiAl(BH$_4$)$_2$Cl$_2$ has been prepared via mechanochemical synthesis from the 2LiBH$_4$–AlCl$_3$ mixture. Structural characterization, performed using a combination of X-ray powder diffraction and solid-state NMR methods, indicates that the LiAl(BH$_4$)$_2$Cl$_2$ phase adopts a unique 3D framework and crystallizes in an orthorhombic structure with the space group C222$_1$, $a = 11.6709(6)$ Å, $b = 8.4718(4)$ Å, $c = 7.5114(3)$ Å. The material shows excellent dehydrogenation characteristics, where hydrogen evolution starts at $T_{ons} = 70{ }^\circ$C, releasing approximately 2 wt.% of nearly pure (99.8 vol.%) hydrogen and a very small amount (~0.2 vol.%) of diborane. When compared to halide-free mixed alkali metal–aluminum borohydrides, the presence of Al-Cl bonding in the LiAl(BH$_4$)$_2$Cl$_2$ structure likely prevents the formation of Al(BH$_4$)$_3$ upon decomposition, thus suppressing the formation of diborane.

Keywords: hydrides; X-ray diffraction; crystal structure; solid-state NMR; hydrogen storage

1. Introduction

Complex borohydrides continue to attract significant attention as potential hydrogen storage materials due to their large gravimetric hydrogen contents, for example, 10.5 wt.% hydrogen in NaBH$_4$, 14.8 wt.% in Mg(BH$_4$)$_2$, and 18 wt.% in LiBH$_4$. Borohydrides are, however, thermodynamically stable and they release hydrogen in successive steps, some of which require rather high temperatures [1–4]. One of the most effective approaches to tailor the hydrogen desorption properties of borohydrides is through the synthesis of mixed-cation or mixed-anion borohydrides with weakened B–H bonds. Consequently, modifications of the structure and properties of metal borohydrides by anion substitutions when alkali or alkali earth halide salts form solid solutions with the corresponding borohydrides, such as LiBH$_4$–LiX and Ca(BH$_4$)$_2$–CaX$_2$ systems, where X = F, Cl, Br or I, were recently demonstrated [5–9]. Further, when mixed-cation borohydrides are formed, hydrogen desorption onset temperatures decrease with increasing Pauling electronegativity ($\chi_P$) of the partner cation [10], as has been demonstrated by the syntheses and characterizations of LiK(BH$_4$)$_2$, LiSc(BH$_4$)$_4$, NaSc(BH$_4$)$_4$, LiZn$_2$(BH$_4$)$_3$, and Li$_4$Al$_3$(BH$_4$)$_3$ [11–16]. These materials also show enhanced hydrogen desorption kinetics compared to pristine LiBH$_4$. Functionality of these mixed complex borohydrides, however, remains impeded by either or both high desorption temperatures and emissions of gaseous products other than hydrogen, one of which is often diborane [17]. Further, hydrogen reversibility remains a major challenge because extreme pressures and high temperatures are required, and the hydrogen absorption rates are usually very low.

On the other hand, some of the mixed-cation mixed-anion borohydrides, such as NaY(BH$_4$)$_2$Cl$_2$, release no measurable amounts of diborane during their decomposition, retaining boron in the solid, which is a prerequisite for reversible hydrogen storage [18]. Further, synthesized via mechanochemical reactions in the LiBH$_4$–SiS$_2$ system, mixed-cation mixed-anion Li$_x$(SiS$_2$)$_y$(BH$_4$)$_z$, where x and y depend upon the ratio of the starting materials, demonstrate improved kinetics of hydrogen desorption when compared to pure...
LiBH₄ [19]. Recently, we also reported suppression of diborane release in the LiBH₄–AlCl₃ system via simultaneous cation and anion substitutions in LiBH₄ [20]. Here, the covalent character of the Al–H bonds and the presence of Al–Cl bonds in the resultant borohydride materials are responsible for the purity of the released hydrogen. Samples reported at that time were, however, multiphase mixtures. In this work, we report the successful synthesis, crystal structure, and hydrogen desorption properties of a new mixed-cation mixed-anion complex borohydride LiAl(BH₄)₂Cl₂.

2. Results and Discussions

2.1. Initial Phase Analysis

LiBH₄ reacts with AlCl₃ upon ball milling over a short period of time. After 3 h of milling, the reaction is completed. Depending on the ratio of the starting materials in the mixture, the formation of different phases was observed, as listed in Table 1. As earlier reported by Lindemann et al., when the system is LiBH₄-rich, one of the phases in this system corresponds to the Li₄Al₃(BH₄)₁₃ compound [15]. The stoichiometry of this compound requires a molar LiBH₄/AlCl₃ ratio of 4.33:1 (or 13:3) to complete the following metathesis reaction:

$$13\text{LiBH}_4 + 3\text{AlCl}_3 \rightarrow \text{Li}_4\text{Al}_3(\text{BH}_4)_{13} + 9\text{LiCl}.$$  (1)

Table 1. Results of the phase analysis based on XRD data of the LiBH₄–AlCl₃ system obtained after 3 h of ball milling of the mixtures with different molar ratios of the starting materials. Lattice parameters of LiAlCl₄ (Sp. Gr. P2₁/c; a = 7.050(1) Å, b = 6.499(1) Å, c = 13.076(2) Å, β = 93.1(1)°) and LiCl (Sp. Gr. Fm-3m, a = 5.146(1) Å) are constant. Lattice parameters of stoichiometric Li₄Al₃(BH₄)₁₃ and LiAlCl₂(BH₄)₂ are for the 4.3:1 and 2.1 reactions, all other represent Li₄Al₃(BH₄)₁₃-xClₓ and LiAlCl₂±y(BH₄)₂±y stoichiometries.

<table>
<thead>
<tr>
<th>LiBH₄:AlCl₃ Molar Ratio</th>
<th>Li₄Al₃(BH₄)₁₃</th>
<th>LiAlCl₂(BH₄)₂</th>
<th>LiAlCl₄</th>
<th>LiCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3:1</td>
<td>a = 11.390(1) Å</td>
<td>not present</td>
<td>not present</td>
<td>present</td>
</tr>
<tr>
<td>4:1</td>
<td>a = 11.367(1) Å</td>
<td>not present</td>
<td>not present</td>
<td>present</td>
</tr>
<tr>
<td>3.65:1</td>
<td>a = 11.350(1) Å</td>
<td>not present</td>
<td>not present</td>
<td>present</td>
</tr>
<tr>
<td>3:1</td>
<td>a = 11.291(2) Å</td>
<td>a = 12.159(4) Å, b = 8.493(4) Å, c = 7.377(3) Å</td>
<td>not present</td>
<td>present</td>
</tr>
<tr>
<td>2:1</td>
<td>not present</td>
<td>a = 11.6698(5) Å, b = 8.4724(4) Å, c = 7.5116(3) Å</td>
<td>not present</td>
<td>present</td>
</tr>
<tr>
<td>1.3:1</td>
<td>not present</td>
<td>a = 11.577(1) Å, b = 8.436(1) Å, c = 7.553(1) Å</td>
<td>present</td>
<td>present</td>
</tr>
<tr>
<td>1:1</td>
<td>not present</td>
<td>a = 11.575(2) Å, b = 8.417(1) Å, c = 7.541(1) Å</td>
<td>present</td>
<td>not present</td>
</tr>
</tbody>
</table>

When the concentration of LiBH₄ in a system is reduced below the ideal stoichiometric ratio of 4.33:1, minor shifts in Bragg reflections corresponding to this compound are observed, as illustrated in Figure 1. Bragg reflections are highlighted with pink rectangles. The reduction in the unit cell parameter of the cubic Li₄Al₃(BH₄)₁₃ compound can be explained by partial substitutions of BH₄⁻ anions with Cl⁻ due to an excess of AlCl₃ over the stoichiometry of reaction 1. These substitutions were also reported by Lindemann et al. when the reaction products of the 4:1 mixture (instead of the ideal 4.33:1 stoichiometry as in reaction 1) were characterized by Rietveld refinement [15]. A further increase in the AlCl₃ concentration leads to progressive shifts of the Bragg reflections of the Li₄Al₃(BH₄)₁₃-xClₓ phase, which continues down to the 3.65(or slightly lower):1 stoichiometry. When the LiBH₄/AlCl₃ ratio is lowered to 3:1, the Li₄Al₃(BH₄)₁₃-xClₓ phase coexists with a new phase and LiCl (Figure 1 and Table 1).
Figure 1. (a) Powder XRD patterns of samples with different LiBH$_4$/AlCl$_3$ ratios ball-milled for 3 h; (b) details between 12 and 33° of 2θ, where the Bragg reflections of the Li$_4$Al$_3$(BH$_4$)$_{13}$ phase are highlighted by the pink rectangles and those of the LiAlCl$_2$(BH$_4$)$_2$ phase are highlighted by the blue rectangles. Locations of the Bragg’s peaks of the reaction products are shown as the vertical markers at the bottom of the plot; for Li$_4$Al$_3$(BH$_4$)$_{13}$ and LiAlCl$_2$(BH$_4$)$_2$ the locations are for the ideal stoichiometries observed at 4.3:1 and 2:1 molar LiBH$_4$/AlCl$_3$ ratios, respectively.

When the molar LiBH$_4$/AlCl$_3$ ratio becomes 2:1, only a new phase that coexists with LiCl is observed with no detectable traces of Li$_4$Al$_3$(BH$_4$)$_{13-x}$Cl$_x$. Considering the as-weighed stoichiometry, the underlying metathesis reaction can be described as the following:

$$2\text{LiBH}_4 + \text{AlCl}_3 \rightarrow \text{LiAl(BH}_4\text{)}_2\text{Cl}_2 + \text{LiCl}. \quad (2)$$

The stoichiometry of this new mixed-cation mixed-anion phase, that is, LiAl(BH$_4$)$_2$Cl$_2$, is also confirmed by the Rietveld refinement of the XRD data described in the next section. In addition to 3:1 and 2:1 stoichiometries, mixtures with 1.3:1 and 1:1 molar component ratios after ball milling show the presence of the same phase as in the 2:1 reaction but with slightly shifted Bragg reflections. Similar to the Li$_4$Al$_3$(BH$_4$)$_{13-x}$Cl$_x$ compound, partial substitutions between the BH$_4^-$ and Cl$^-$ anions in the structure of the new phase are responsible for these lattice parameter variations. When the LiBH$_4$/AlCl$_3$ ratio is reduced below 2:1 in the starting mixture, the new LiAl(BH$_4$)$_2$Cl$_2$ phase coexists with LiAlCl$_4$ in addition to LiCl. LiAlCl$_4$ forms as a result of the reaction of excess AlCl$_3$ with the newly formed LiCl via the following reaction:

$$\text{LiCl} + \text{AlCl}_3 \rightarrow \text{LiAlCl}_4. \quad (3)$$

Hence, the mechanochemical reaction at the 1:1 stoichiometry can be described by the following overall scheme:

$$2\text{LiBH}_4 + 2\text{AlCl}_3 \rightarrow \text{LiAl(BH}_4\text{)}_2\text{Cl}_2 + \text{LiAlCl}_4. \quad (4)$$

2.2. Crystal Structure Refinement

The LiAl(BH$_4$)$_2$Cl$_2$ phase that forms when LiBH$_4$ and AlCl$_3$ are ball-milled in a 2:1 molar ratio is a bimetallic halide-containing borohydride, which crystallizes in a C222$_1$ space group with the lattice parameters ($a = 11.6698(5)$ Å, $b = 8.4724(4)$ Å, $c = 7.5116(3)$ Å). The atomic positions, bond distances, and bond angles determined from the Rietveld refinement are listed in Tables 2 and 3. The best fit (Figure 2) was obtained for random (within two standard deviations) occupancy of the two available 4a sites with Al and Li atoms. The Rietveld refinement was performed with the application of additional constraints, where the overall occupancies of the 4a sites were fixed to 1 and the overall
Al to Li ratio was 1:1. The refinements of the models where Al and Li are ordered in M1 and M2 positions lead to an increase in $R_p$ and $R_{wp}$ from 4.8 and 6.5% to $\sim$5.8 and $\sim$8.5%, respectively, in both of the ordered models.

Table 2. Crystallographic data for LiAl(BH$_4$)$_2$Cl$_2$ compound determined from Rietveld refinement of the structure model obtained using FOX: space group C222$_1$ (No. 20), $a = 11.6698(5)$ Å, $b = 8.4724(4)$ Å, $c = 7.5116(3)$ Å. Fit residuals (not corrected for background) $R_p = 4.78$%; $R_{wp} = 6.49$%.  

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$, Å$^2$</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 (Al1)</td>
<td>4a</td>
<td>0.633(2)</td>
<td>0</td>
<td>0</td>
<td>0.081(2)</td>
<td>0.45(2)</td>
</tr>
<tr>
<td>M1 (Li1)</td>
<td>4a</td>
<td>0.633(2)</td>
<td>0</td>
<td>0</td>
<td>0.081(2)</td>
<td>0.55(2)</td>
</tr>
<tr>
<td>M2 (Al2)</td>
<td>4a</td>
<td>$-0.119(2)$</td>
<td>0</td>
<td>0</td>
<td>0.081(2)</td>
<td>0.55(2)</td>
</tr>
<tr>
<td>M2 (Li2)</td>
<td>4a</td>
<td>$-0.119(2)$</td>
<td>0</td>
<td>0</td>
<td>0.081(2)</td>
<td>0.45(2)</td>
</tr>
<tr>
<td>Cl</td>
<td>8c</td>
<td>0.752(1)</td>
<td>0.8070(2)</td>
<td>0.0306(3)</td>
<td>0.098(1)</td>
<td>1</td>
</tr>
<tr>
<td>B1</td>
<td>4b</td>
<td>0</td>
<td>0.479(1)</td>
<td>$\frac{1}{4}$</td>
<td>0.052(3)</td>
<td>1</td>
</tr>
<tr>
<td>H11</td>
<td>8c</td>
<td>0.063</td>
<td>0.401(1)</td>
<td>0.327</td>
<td>0.052(3)</td>
<td>1</td>
</tr>
<tr>
<td>H12</td>
<td>8c</td>
<td>0.050</td>
<td>0.558(1)</td>
<td>0.152</td>
<td>0.052(3)</td>
<td>1</td>
</tr>
<tr>
<td>B2</td>
<td>4b</td>
<td>0</td>
<td>0.983(1)</td>
<td>$\frac{1}{4}$</td>
<td>0.052(3)</td>
<td>1</td>
</tr>
<tr>
<td>H21</td>
<td>8c</td>
<td>0.065</td>
<td>1.061(1)</td>
<td>0.175</td>
<td>0.052(3)</td>
<td>1</td>
</tr>
<tr>
<td>H22</td>
<td>8c</td>
<td>0.048</td>
<td>0.904(1)</td>
<td>0.350</td>
<td>0.052(3)</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3. Bond distances (Å) and angles (°) in the LiAl(BH$_4$)$_2$Cl$_2$ compound. (M1 and M2 atoms consist of Li or Al, partially occupied the 4a positions.). Since only the centers of gravity of two symmetrically independent (BH$_4$)$^-$ groups were refined, the M–H bond lengths are tentative.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1–H11</td>
<td>2.7202(1)</td>
<td></td>
</tr>
<tr>
<td>M1–H11</td>
<td>2.7628(1)</td>
<td></td>
</tr>
<tr>
<td>M1–H12</td>
<td>1.5758(1)</td>
<td></td>
</tr>
<tr>
<td>M1–B1</td>
<td>2.4411(1)</td>
<td></td>
</tr>
<tr>
<td>M1–Cl</td>
<td>2.1613(1)</td>
<td></td>
</tr>
<tr>
<td>M2–H21</td>
<td>2.5683(1)</td>
<td></td>
</tr>
<tr>
<td>M2–H21</td>
<td>2.5715(1)</td>
<td></td>
</tr>
<tr>
<td>M2–H22</td>
<td>1.6158(1)</td>
<td></td>
</tr>
<tr>
<td>M2–B2</td>
<td>2.3385(1)</td>
<td></td>
</tr>
<tr>
<td>M2–Cl</td>
<td>2.2337(1)</td>
<td></td>
</tr>
<tr>
<td>M1–Cl–M2</td>
<td>82.515(4)</td>
<td>2x</td>
</tr>
<tr>
<td>B1–H11</td>
<td>1.1503(1)</td>
<td>2x</td>
</tr>
<tr>
<td>B1–H12</td>
<td>1.1508(1)</td>
<td>2x</td>
</tr>
<tr>
<td>H–B1–H11</td>
<td>109.1(1)–109.8(1)</td>
<td>2x</td>
</tr>
<tr>
<td>B2–H21</td>
<td>1.1502(1)</td>
<td>2x</td>
</tr>
<tr>
<td>B2–H22</td>
<td>1.1502(1)</td>
<td>2x</td>
</tr>
<tr>
<td>H–B2–H</td>
<td>109.4(1)–109.6(1)</td>
<td>2x</td>
</tr>
</tbody>
</table>

The structure of the LiAl(BH$_4$)$_2$Cl$_2$ compound consists of layers of M(BH$_4$)$_2$ groups, separated by 2Cl atoms along the $a$-direction (Figure 3), where the M atoms consist of Li and Al, randomly occupying the 4a positions (also see Table 1). The coordination environment of the Li and Al atoms consists of two BH$_4$ units and two Cl atoms (i.e., M(BH$_4$)$_2$Cl$_2$), with the interatomic M–Cl distances of 2.1613(1) Å and 2.2337(1) Å. The M1 atoms are bridged to the M2 via two chlorine atoms, while two M2 atoms are connected through BH$_4$ units (Figure 3d). The chlorine atoms are coordinated to two M atoms (M1 and M2), while the coordination of each BH$_4$ unit is made of two M atoms. The structure can also be described as a network of tetrahedral (M(BH$_4$)$_2$Cl$_2$) complexes connected along the $a$-axis via alternating bridging of M–BH$_4$–M and M–Cl–M units.
Figure 2. Rietveld-refined XRD pattern of the 2:1 (molar) mixture of LiBH$_4$ and AlCl$_3$ after 3 h of milling. Short vertical bars mark calculated positions of the Bragg peaks of LiAl(BH$_4$)$_2$Cl$_2$ and LiCl.

Figure 3. Unit cell of the LiAl(BH$_4$)$_2$Cl$_2$ compound (a) in a–c (b) and a–b (c) directions. Representation of the coordination of atomic groups in unit cell(d) (M1 and M2 atoms represent cation, which consists of Li and Al atoms, partially occupying the 4a positions (Table 2)).
Considering the Bragg peak shifts discussed above, LiAl(BH$_4$)$_2$Cl$_2$ should also contain mixed-anion sites, effectively making it LiAl(BH$_4$)$_2$±$\delta$Cl$_2$±$\delta$, which is also common for the earlier known Li$_4$Al$_3$(BH$_4$)$_{13-x}$Cl$_x$. The unusual feature of the LiAl(BH$_4$)$_2$Cl$_2$ compound is the mixed occupancy of the same sites by Al and Li atoms. Despite the difference in their ionic radii, the structural model, which has identical (within experimental errors, see Table 2) concentrations of Al and Li atoms in both 4a positions, converges to the lowest residuals during the Rietveld refinement.

2.3. NMR Characterization

To identify the species formed in the ball-milled products of the 2LiBH$_4$–1AlCl$_3$ mixture, we used $^{11}$B and $^{27}$Al ssNMR. In both spectra, practically one predominant signal is observed, as follows: the $^{11}$B signal at −37 ppm assigned to the (BH$_4$)$^-$ unit (Figure 4a), and the $^{27}$Al signal at 74 ppm attributed to Al(BH$_4$)$_2$Cl$_2$ (Figure 4b) [20]. Most likely, the latter species are the same as those found in the final products from the 3:1 and 3.67:1 mixtures and as an intermediate in the formation of Li$_4$Al$_3$(BH$_4$)$_{13}$ from the 4.33:1 mixture. Indeed, the corresponding $^{27}$Al signal in the 2:1 mixture appears in the $^{27}$Al$^{[1H]}$ J–HMQC spectrum (Figure 4c), which relies on a through-bond correlation, indicating the covalent character of the Al-H bonding [20]. More importantly, however, all boron and aluminum configure a single compound in the ball-milled product of the 2:1 mixture, further confirming the chemical makeup of the title material. The minor $^{27}$Al signal at 60 ppm was also identified to Al(BH$_4$)$_2$Cl$_2$, whose coordination geometry is slightly different from that yielding the main $^{27}$Al signal at 74 ppm, suggesting the presence of a disordered phase as an impurity [21].

![Figure 4. (a) $^{11}$B DPMAS, (b) $^{27}$Al DPMAS, and (c) $^{27}$Al$^{[1H]}$ J–HMQC spectra of the products of the 2LiBH$_4$–1AlCl$_3$ mixture ball-milled for 3 h. The DPMAS spectra (a, b) were acquired with a single pulse excitation, using flip angle of 10°, $\nu_{RF}(^{11}B) = 50$ kHz, $\nu_{RF}(^{27}Al) = 50$ kHz, $\nu_{RF}(^{1H}) = 50$ kHz for SPINAL-64 decoupling, and $\tau_{RD} = 0.5$ s. The J–HMQC spectrum was obtained using $\nu_{RF}(^{1H}) = 100$ kHz for the FSLG decoupling and short pulses, and 50 kHz for SPINAL-64 decoupling during the acquisition, $\nu_{RF}(^{27}Al) = 50$ kHz and 20 khz for the initial $\pi/2$ pulse and the inversion $\pi$ pulses, respectively, $\tau_{max} = 2.8$ ms, and $\tau_{RD} = 1.0$ s.](image)

2.4. Dehydrogenation

The TPD characteristics of the as-milled products for the LiBH$_4$–AlCl$_3$ mixtures taken in different molar ratios of the starting materials are compared in Figure 5 and Table 4. The desorption of the reaction product obtained after ball-milling the mixture of LiBH$_4$ and AlCl$_3$ taken in the 4.33:1 ratio, that is, of the Li$_4$Al$_3$(BH$_4$)$_{13}$ compound, starts at ~80 °C, where 2.8 wt.% of hydrogen is released in 80 h (Figure 5). The RGA of the released gas shows the presence of 16 vol.% of diborane and 84 vol.% of hydrogen. The amount of released hydrogen (2.8 wt.%) is much less than its theoretical content in the Li$_4$Al$_3$(BH$_4$)$_{13}$ compound (7.6 wt.%). This is attributed to the decomposition of the Li$_4$Al$_3$(BH$_4$)$_{13}$ with
the formation of LiBH$_4$, which is stable at 385 °C, loss of materials by vaporization of intermediate products, and the formation of diborane [15].

Figure 5. (a) TPD of ball-milled LiBH$_4$–AlCl$_3$ mixtures taken in different molar ratios of starting materials. The green line represents temperature profile. The desorption curves were obtained during heating from room temperature to 385 °C with a heating rate of 1 °C/min. (b) Zoomed plot representing the TPD during the first 7 h of measurements.

Table 4. Hydrogen desorption characterization and RGA analysis of decomposition products of LiBH$_4$–AlCl$_3$ mixtures ball-milled for 3 h in different molar ratios.

<table>
<thead>
<tr>
<th>LiBH$_4$–AlCl$_3$ Ratio</th>
<th>H$_2$ Release (wt. %)</th>
<th>H$_2$ (vol. %)</th>
<th>B$_2$H$_6$ (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.33:1</td>
<td>2.8</td>
<td>84.0</td>
<td>16.0</td>
</tr>
<tr>
<td>3.67:1</td>
<td>3.5</td>
<td>97.0</td>
<td>3.0</td>
</tr>
<tr>
<td>3:1</td>
<td>3.0</td>
<td>99.7</td>
<td>0.3</td>
</tr>
<tr>
<td>2:1</td>
<td>2.0</td>
<td>99.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

1 wt.% of hydrogen released after 80 h.

The thermal decomposition of the ball-milled 3.67:1 mixture reveals the release of 3.5 wt.% of hydrogen with an onset temperature of 61 °C (Figure 5). This amount corresponds to 51% of all the available hydrogen in the mixture (6.8 wt.%), which is higher compared to the 4.33:1 stoichiometry. This increase is likely related to a lower amount of LiBH$_4$, which is stable at the highest temperature (385 °C) and forms upon the decomposition of Li$_4$Al$_3$(BH$_4$)$_{13-x}$Cl$_x$. The amount of released diborane (3 vol.%) is much smaller when compared to Li$_4$Al$_3$(BH$_4$)$_{13}$ (16.0 vol.%).

Decreasing the LiBH$_4$ content in the system with AlCl$_3$ to a 3:1 molar ratio leads to further suppression of the diborane release when heating the ball-milled mixture to 385 °C (Table 4). The RGA of the released gas from the 3:1 ratio product shows the presence of only 0.3 vol.% diborane. The hydrogen desorption, which initiates at ~50 °C, has similar kinetics compared to the two mixtures with higher starting LiBH$_4$ contents (Figure 5). In 80 h, the products of the mechanochemical reaction in the 3:1 system, which now include LiAl(BH$_4$)$_{2-6}$Cl$_{2-6}$, and in addition to Li$_4$Al$_3$(BH$_4$)$_{13-x}$Cl$_x$, release ~3.0 wt.% of hydrogen, which corresponds to ~50% of the hydrogen available in the 3:1 mixture (6.0 wt.%).

The TPD study of the ball-milled 2:1 mixture, which is nearly pure LiAl(BH$_4$)$_2$Cl$_2$ together with inert LiCl, shows H$_2$ desorption at a significant rate starting at 66 °C (Figure 5). The kinetics of the hydrogen desorption of this mixed-cation mixed-anion compound is much higher when compared to all other compositions. In 6 h, while the temperature in the system is ramped from ~20 to 385 °C, the mixture releases ~1.8 wt.% of hydrogen. Upon stabilization of the temperature and gas pressure in the system, the total H$_2$ release reaches ~2.0 wt.%, which corresponds to ~44% of the hydrogen available in the 2:1 mixture.
(4.5 wt.%). Improvement in the purity of the released H\textsubscript{2} is observed, with only 0.2 vol.% of B\textsubscript{2}H\textsubscript{6} detected, the remainder being pure hydrogen (Table 4).

The XRD study of the solid products after decomposition of the 2:1 system shows the formation of a mixture of different products. Among the crystalline products are LiCl and Al. However, the presence of multiple unknown Bragg reflections and the possible formation of amorphous byproducts does not allow us to make definitive conclusions about a decomposition pathway. This study requires additional efforts, and the nature of the products after temperature-induced decomposition will be described when available.

The analysis of the TPD illustrated in Figure 5 shows two-step decompositions. The first step starts at a low temperature, is relatively fast, and ends around 100 °C regardless of the LiBH\textsubscript{4}/AlCl\textsubscript{3} ratio in the starting mixture. The second step, which starts around 150–160 °C is observed for all mechanochemical reaction products in LiBH\textsubscript{4}-rich materials. This step is very slow, and it extends for a long period of time without reaching saturation after 80 h. A different behavior is clearly observed for LiAl(BH\textsubscript{4})\textsubscript{2}Cl\textsubscript{2}. The region between the first and second steps is smeared out and is not as pronounced as in all other samples. The second step of decomposition almost reaches its saturation upon heating the sample to 385 °C. Only 0.2 wt.% of additional H\textsubscript{2} is released when the sample is kept at 385 °C for an additional 14 h.

3. Materials and Methods

3.1. Sample Preparation

The starting materials, LiBH\textsubscript{4} (>95 wt.% purity) and AlCl\textsubscript{3} (99.99 wt.% purity), were used as purchased from MilliporeSigma, Inc. The precursors taken in desired molar ratios were ball-milled in a 50 mL hardened steel vial using 20 g of steel balls (two large balls weighing 8 g each and four small balls weighing 1 g each) in an SPEX 8000M mill for 3 h. All manipulations were conducted in a glovebox under inert argon atmosphere with oxygen and moisture levels below 1 ppm.

3.2. Powder X-Ray Diffraction

Powder X-ray diffraction (XRD) data for phase analysis of the reaction products and determination of the crystal structure were collected at room temperature on a PANalytical powder diffractometer using Cu K\alpha radiation with a 0.02° step, in the range of Bragg angles 10° ≤ 2θ ≤ 80°. The measurements were carried out using a sample holder covered by the polyimide (Kapton) film to protect the samples from the ambient air. Presence of the film resulted in an enhanced amorphous-like background in the XRD patterns between 13° and 20° of 2θ.

3.3. Hydrogen Desorption

The kinetics of hydrogen desorption were measured using PCTPro-2000—a fully automated Sieverts-type instrument, which enables experiments in the temperature range from 25 to 400 °C. While still in the glove box, pellets of materials to be examined were placed in a PCTPro-2000 autoclave. The closed autoclave was then connected to the PCT instrument and evacuated. Volume calibrations using high-purity helium gas were performed at room temperature before every hydrogen desorption kinetic measurement. The temperature-programmed desorption (TPD) was performed by heating the samples from ambient temperature to 385 °C with a heating rate of 1 °C/min. When the pressure caused by gas release stabilized, samples were cooled down to room temperature and evacuated. The nature and composition of gaseous products released during the heating was tracked by using the RGAPro-2500 residual gas analyzer, connected to the PCT autoclave. For more precise gas analysis, in order to avoid losing the less volatile B\textsubscript{2}H\textsubscript{6} during mass spectroscopy, the length of the connection between the autoclave and the gas analyzer was the shortest possible.
3.4. Solid-State NMR

The $^{11}$B and $^{27}$Al solid-state nuclear magnetic resonance (ssNMR) experiments were performed on a Varian spectrometer operated at 14.1 T, equipped with a 3.2 mm triple-resonance magic-angle spinning (MAS) probe. The samples were packed in a MAS zirconia rotor in a glovebox under argon atmosphere and sealed with double O-ring caps to minimize contamination of oxygen and moisture, and were spun at 12.5 kHz. One-dimensional (1D) $^{11}$B and $^{27}$Al direct polarization (DP) MAS and 1D $^{27}$Al(¹H) MAS-J-HMQC experiments were carried out. All spectra were acquired using SPINAL64 ¹H decoupling [22]. Detailed experimental conditions are given in the figure captions using the following symbols; νRF(X) is the magnitude of the radio frequency magnetic field applied to X spins, $\tau_{\text{max}}$ is the optimum / evolution time, and $\tau_{\text{RD}}$ is the recycle delay. The $^{11}$B and $^{27}$Al shifts were referenced to the diethyl ether–boron trifluoride complex (BF₃·OEt₂) and 1.0 M aqueous solutions of Al(NO₃)₃ at 0 ppm, respectively.

3.5. Structural Characterization

The XRD data of the ball-milled 2LiBH₄–AlCl₃ mixture containing Bragg peaks of LiCl and an unknown phase were used for indexing and structure solution. A total of 11 lowest angle Bragg peaks with the highest intensities, presumably belonging to the unknown phase, were successfully indexed ab initio using TREOR [23] in a base-centered orthorhombic cell. Correctness of indexing was verified by Le Bail refinement using FullProf [24]. The initial structural model was obtained in the C222₁ space group through the global optimization in direct space using FOX [25]. During the structure solution, the positions of two cations, one Cl⁻ anion and centers of gravity of two (BH₄)⁻ groups were optimized. H-atoms were refined with 1.15(1) Å restraints on the B-H distances and with 109.5(5)° restraints on the H-B-H angles in BH₄ tetrahedra. The final structure refinement was performed by Rietveld analysis with soft restraints on interatomic bond lengths and bond angles using FullProf. The background was approximated using linear interpolations between data points selected from regions with no Bragg peaks present. The pseudo-Voigt function was used for the peak shape description. The scale factor, lattice parameters, fractional coordinates of atoms and their isotropic displacement parameters, zero shift, peak shape parameters, and half width (Caglioti) parameters were allowed to vary during the refinement.

4. Conclusions

In summary, we synthesized a new double-cation double-anion complex LiAl(BH₄)₂Cl₂ by mechanochemical synthesis from the 2LiBH₄–AlCl₃ mixture. This phase shows a unique 3D framework and crystallizes in a new orthorhombic structure with the space group C222₁ and lattice parameters $a = 11.6709(6)$ Å, $b = 8.4718(4)$ Å, $c = 7.5114(3)$ Å. The replacement of about a half of the BH₄⁻ anions with Cl⁻ in the coordination sphere of Al results in the coexistence of covalent Al–H and more ionic Al-Cl bonds in the structure, which are not present in the earlier reported Li₄Al₃(BH₄)₁₃ and are present to a much lesser extent in Li₄Al₃(BH₄)₁₃·₃Clₓ.

We also studied the hydrogen desorption properties of the mechanochemically prepared phases starting with LiBH₄–AlCl₃ mixtures taken in different molar ratios, including the 2:1 product. Temperature-programmed desorption analysis shows that despite the high theoretical hydrogen content and the low desorption temperature, all LiBH₄-rich mixtures with AlCl₃ (with more than 3 moles of LiBH₄ per 1 mole of AlCl₃) release significant amounts of diborane. Decreasing the concentration of LiBH₄ in the starting mixture suppresses diborane emission without affecting the onset temperature of hydrogen release. The 4.33:1 and 3.67:1 ratio mixtures are keeping the Li₄Al₃(BH₄)₁₃-like structures for the hydride phase and release nearly 16 and 3 vol.% of B₂H₆ respectively. The 3:1 ratio mixture contains halide derivatives of two structure types—the cubic Li₄Al₃(BH₄)₁₃ and the new orthorhombic LiAl(BH₄)₂Cl₂. The 2:1 composition contains the nearly stoichiometric LiAl(BH₄)₂Cl₂ compound, which releases almost pure hydrogen upon its decomposition.
Most likely, the formation of Al-H bonds in the (Al(BH₄)₂Cl₂)⁻ complex in the new compound weakens the B-H bonds and decreases the dehydrogenation temperature, while the ionic Al-Cl bonds prevents the formation of Al(BH₄)₃, which is a known intermediate leading to the formation of diborane.

Author Contributions: O.D. contributed to the design of experiments, performed materials synthesis, Rietveld refinements, hydrogen storage investigations, and writing the manuscript; I.Z.H. performed the material synthesis and hydrogen storage properties measurements, contributed to the manuscript writing; T.K. performed solid-state NMR characterization, contributed to interpretation of result and manuscript writing; S.G. contributed to design the experiments, interpretation of results and manuscript writing. V.K.P. guided the study, contributed to structural characterization, data interpretation, and the manuscript writing. All authors provided comments and edits during the preparation of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: 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.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data that support plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: The authors thank Yaroslav Filinchuk from the Institute of Condensed Matter and Nanosciences, and the Université Catholique de Louvain, Belgium for help in the finding the model of the crystal structure of the new LiAl(BH₄)₂Cl₂ compound using FOX.

Conflicts of Interest: The authors declare no conflict of interest.

References


