

Dehydrogenation tuning of ammine borohydrides using double-metal cations

Yanhui Guo,^a Hui Wu,^{b,c} Wei Zhou,^{b,c} Xuebin Yu^{*a}

^a Department of Materials Science, Fudan University, Shanghai 200433, China;

^b NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102;

^c Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115

E-mail: yuxuebin@fudan.edu.cn

Experimental Section

The source materials, LiBH₄ 95% (Sigma-Aldrich, USA),¹ AlCl₃ 99.99%, Al powder (345 mesh), and NH₃ (Alfa Aesar, China), were obtained commercially. LiBH₄ and AlCl₃ were ball milled for 1 h before use. Al powder was used as received. NH₃ was purified by soda lime when used. Al(BH₄)₃·6NH₃ was prepared by interaction of Al(BH₄)₃ and NH₃ using an improved method described in the [literature S1](#). All handling, except for ammonia related procedures, was conducted under anaerobic and anhydrous conditions by Schlenk techniques and in a glove box filled with argon.

Approximately 0.5 g mixtures of Al(BH₄)₃·6NH₃-LiBH₄ with mole ratios of 1:1, 1:2, 1:3 and 1:4 were mechanically milled for 60 min (planetary QM-1SP2) in argon using stainless steel spheres with a ball-to-powder ratio (BPR) of 30:1 to produce Al(BH₄)₃·6NH₃/LiBH₄ composites. The milling process was carried out by alternating 6 min of milling and 6 min of rest in order to avoid increasing the temperature of the powders in the vial. Only the Al(BH₄)₃·6NH₃-LiBH₄ (1:2) crystallizes as a single phase and excessive LiBH₄ was observed in the Al(BH₄)₃·6NH₃-LiBH₄ (1:3) sample.

Thermal property measurements were performed by thermogravimetry (TG, STA 409C) /mass spectroscopy (MS, QMS 403), with a heating rate of 10 °C min⁻¹ under 1 atm argon atmosphere. Desorption properties for some samples were also evaluated using Sievert's volumetric methods with a heating rate of 5 °C min⁻¹ and at varied isothermal temperatures under argon atmosphere. Differential scanning calorimetry (DSC) was performed simultaneously on a Netzsch STA 409 PC, Germany, with highly pure Ar as the purge gas. For the DSC analysis of Li₂Al(BH₄)₅·6NH₃ at 120 °C, the sample was heated to 110 °C at heating rate of 5 °C min⁻¹, then to 120 °C at a heating rate of 2 °C min⁻¹ in case of overheat and finally hold at 120 °C for 2.5 h.

High-resolution X-ray powder diffraction data of the samples were collected on the Powder Diffraction Beamline, Australian Synchrotron by using a Mythen detector. For phase identification and structure determination, samples were loaded into pre-dried 0.7 mm glass capillary tubes inside the argon atmosphere glove box and sealed with vacuum grease for X-ray

¹ Certain commercial suppliers are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

diffraction measurements. For in-situ high temperature measurements, the sample was heated from 30 °C to 130 °C at temperature intervals of 10 °C. The heating rate was 6 °C min⁻¹, and data were collected for 8 min at each point. The wavelength for the in-situ measurements was 0.86523 Å. The reflections in the diffraction pattern of Li₂Al(BH₄)₅·6NH₃ were indexed to a hexagonal unit cell. Evaluation of the systematic absences in the XRD pattern and the Le Bail fit indicated the possible space group P3c1 and P-3c1. The structure was then solved by direct-space methods using simulated annealing, and P-3c1 symmetry gives a reasonable atomic arrangement. Al, Li, rigid BH₄ and NH₃ groups were defined as the main building units, and the favorable orientations of BH₄ and NH₃ were derived using the first-principles molecular dynamic simulations. Rietveld refinement was then performed on the resulting model using GSAS package.^{S2} The final fit to the diffraction pattern is presented in Figure S1, and the detailed crystallographic parameters are listed in Table S1. The sample of Li₂Al(BH₄)₅·6NH₃ is a nearly pure single-phase. Given the difficulty in obtaining precise hydrogen positions using X-ray powder diffraction, constrained BH₄⁻ and NH₃ geometries were used in the Rietveld refinement. The BH₄ unit was defined as tetrahedral group with B-H distances of 1.23 Å and H-B-H bond angles of 109.5°. While the NH₃ group was defined using the NH₃ molecule geometry with N-H bond length of 1.034 Å and H-N-H bond angle of 105°. The cell parameters for the P-3c1 structure are: a=7.79779(5) Å, c=15.9693(1)Å, and V=840.93(1) Å³. The agreement factors are: R_{wp}=0.0184, R_p=0.0138, χ^2 =1.795.

FTIR (Magna-IR 550 II, Nicolet) analysis was conducted to determine the chemical bonding. During the IR measurements (KBr pellets), samples were loaded into a closed tube with KBr.

The solid-state ¹¹B NMR experiments were performed on a Bruker DSX 300 spectrometer operating at 12 kHz, using 4 mm ZrO₂ rotors filled up in a purified argon atmosphere glove box. A 0.55 μ s single-pulse excitation was employed, with repetition times of 1.5 s.

Attempts to recharge the dehydrogenated sample were carried out under 6.9 MPa of H₂ at 170 and 350 °C for 10 h was unsuccessful.

First-principles calculations based on density-functional theory (DFT) were performed by using the PWSCF package.^{S3} We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 544 eV was found to be enough for the total energy to converge within 0.5 meV/atom. Car-Parrinello molecular dynamics simulations^{S4} were used to help in searching for the most likely crystal structures. The conventional unit cells were used, with the cell dimensions fixed at the experimental values. The initial system temperature was set to 600 K. The system was first allowed to evolve and equilibrate for 20 ps, and then the system temperature was slowly decreased to 0 K in a period of 20 ps. Structure optimizations on the resulting candidate structures at 0 K were further performed with respect to atomic positions, with the lattice parameters fixed at the experimental values. Lattice dynamics calculations were then performed on the relaxed structures using the supercell method with finite displacements,^{S5} to rule out unstable candidates. A 2×2×2 supercell was used. The total energies of the stable candidate structures at 0 K, including corrections for the zero-point motion, were also evaluated. This information was used in combination with XRD pattern matching to derive the best crystal structure solutions of the ammine borohydride compound.

Table S1. Experimental and calculated structural parameters of Li₂Al(BH₄)₅·6NH₃ (Space group*P*-3*c*1, No. 165, *a*=7.79779(5) Å, *c*=15.9693(1)Å, *V*=840.93(1) Å³, *Z*=2)

Atom	Site	x		y		z	
		Exp	Cal.	Exp.	Cal.	Exp.	Cal.
N	12 <i>g</i>	0.17060(9)	0.17699	0.9318(1)	0.93523	0.57508(3)	0.57266
H1	12 <i>g</i>	0.12053(9)	0.10887	0.8678(1)	0.84734	0.63328(3)	0.62438
H2	12 <i>g</i>	0.21046(9)	0.23435	0.8397(1)	0.86085	0.54468(3)	0.53970
H3	12 <i>g</i>	0.30276(9)	0.30027	0.0605(1)	0.06028	0.58675(3)	0.59528
B2	6 <i>f</i>	0.6251(1)	0.60919	0.6251(1)	0.60919	0.25	0.25
H4	12 <i>g</i>	0.5822(9)	0.57203	0.4821(7)	0.46464	0.2956(3)	0.29361
H5	12 <i>g</i>	0.6636(7)	0.64948	0.7706(4)	0.75159	0.2932(3)	0.29566
B1	4 <i>d</i>	0.33333	0.33333	0.66667	0.66667	0.9544(1)	0.95465
H6	4 <i>d</i>	0.33333	0.33333	0.66667	0.66667	0.0314(1)	0.02639
H7	12 <i>g</i>	0.3692(4)	0.35633	0.5392(4)	0.53108	0.9287(1)	0.92345
Li	4 <i>d</i>	0.33333	0.33333	0.66667	0.66667	0.2864(2)	0.28516
Al	2 <i>b</i>	0.0	0.0	0.0	0.0	0.5	0.5

Note: $U_{Al}=1.54(3)$, $U_{Li}=3.2(1)$, $U_{B1}=2.38(8)$, $U_{B2}=2.24(8)$, $U_N=3.55(4)$, $U_{H(N)}=4.5(1)$, $U_{H(B2)}=6.6(1)$ and $U_{H(B1)}=6.2(1)$ ($\times 100$ Å²). The isotropic thermal parameters (U_{iso}) of H in the same rigid body were constrained to be identical. [NH3] (rigid body): Center of the body (N) (0.17060(9), 0.9318(1), 0.57508(3)). Orientation angle about *a*, *b*, *c*-axis: -24.9(4)°, 7.8(2)°, 50.2(4)°. N-H distance: 1.034 Å; [BH2] (rigid body): Center of the body (B2) (0.6251(1), 0.6251(1), 0.25). Orientation angle about *a*, *b*, *c*-axis: 0.6(3)°, 1.7(4)°, -14.1(3)°. B-H distance: 1.23 Å; [BH2] (rigid body): Center of the body (B1) (0.3333, 0.6667, 0.9544(1)). Orientation angle about *a*, *b*, *c*-axis: 0°, 0°, -42.0(5)°. B-H distance: 1.23 Å.

Table S2. Interatomic distances (Å) and Angles (°) for Apparent Dihydrogen Bonds

Distance		Angle		Angle	
H1...H5	2.06(1)	N-H1...H5	148.9(1)	B2-H5...H1	94.8(1)
H2...H6	2.02(1)	N-H2...H6	156.9(1)	B1-H6...H2	96.0(1)
H2...H7	2.24(1)	N-H2...H7	140.4(1)	B1-H7...H2	85.2(1)
H3...H7	2.19(1)	N-H3...H7	158.0(1)	B1-H7...H3	96.9(1)
H3...H7	2.26(1)	N-H3...H7	137.2(1)	B1-H7...H3	93.2(1)

Table S3. Calculated capacity and purity of H₂.

Samples ^[a]	wt. H ₂ capacity [b]	% mol % H ₂ [b]	Mole H ₂
			Mole Al(BH ₄) ₃ ·6NH ₃
Al(BH ₄) ₃ ·6NH ₃ ^{S1}	11.8	94.6	10.2
Li ₂ Al(BH ₄) ₅ ·6NH ₃	15.5	97.0	16.8
Li ₂ Al(BH ₄) ₅ ·6NH ₃ at 110 °C	10.6	99.3	11.5
Li ₂ Al(BH ₄) ₅ ·6NH ₃ at 120 °C	10.8	99.0	11.7
Li ₂ Al(BH ₄) ₅ ·6NH ₃ at 130 °C	10.0	97.3	10.8
Al(BH ₄) ₃ ·6NH ₃ at 130 °C	4.3	97.0	3.7

[a] Non-isothermal and isothermal heat treatment of the samples corresponding to [Figure 2](#) and [Figure S4](#). The capacity and purity of H₂ emission gas were determined using gravimetric and volumetric results, with the assumption that the impurity was only NH₃ to facilitate calculation.

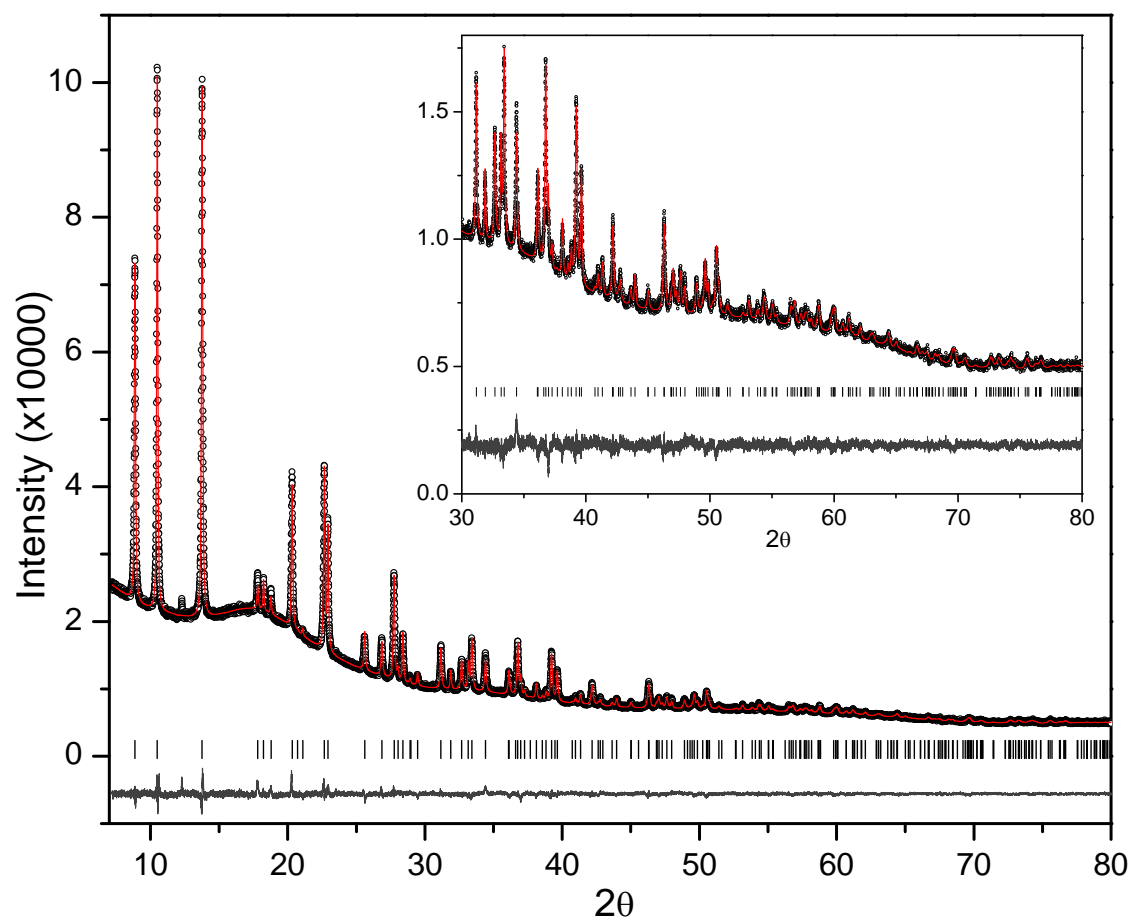
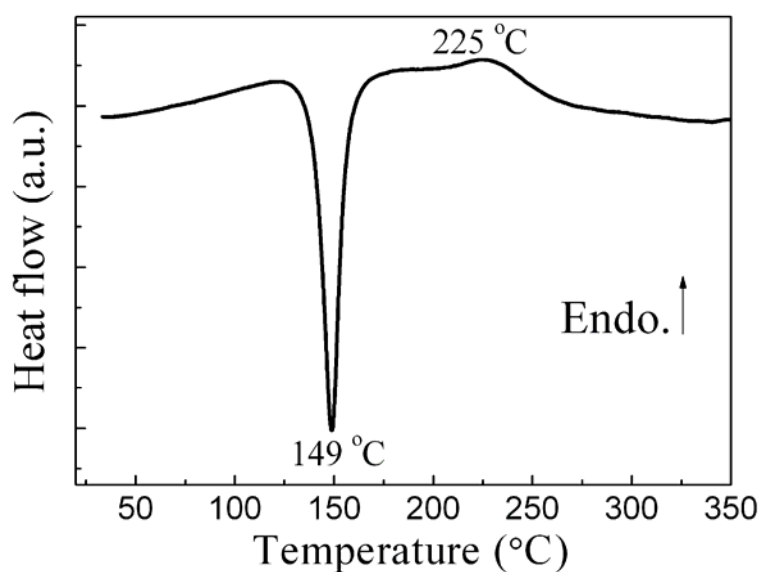
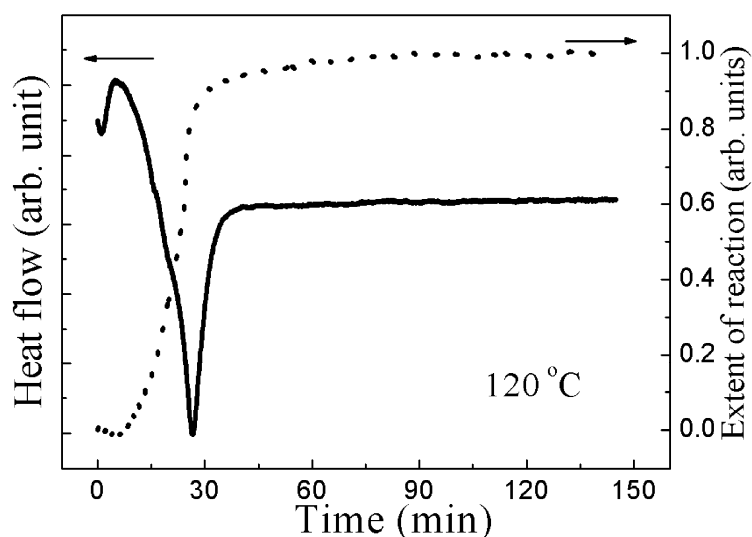


Figure S1. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) synchrotron XRD profiles for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ at 298 K. Vertical bars indicate the calculated positions of Bragg peaks for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$. $\lambda = 1.2372 \text{ \AA}$. $R_{\text{wp}} = 0.0184$, $R_p = 0.0138$, $\chi^2 = 1.795$.



(a)



(b)

Figure S2. (a) DSC profile for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in argon; (b) DSC curves for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ at $120\text{ }^\circ\text{C}$. The dotted line shows the time-dependent release of hydrogen from composite I.

The non-isothermal DSC (Figure S2 a) curve indicates an exothermic events peaked at $149\text{ }^\circ\text{C}$, demonstrating that the first dehydrogenation step of $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ is an exothermic reaction, which is similar to most of the other reported BN-related hydride systems. However, the second dehydrogenation peaked at $225\text{ }^\circ\text{C}$ is weakly endothermic, indicating a possible reversibility.

As thermal decomposition of $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ suffers from ammonia release during the non-isothermal DSC, a rigorous conclusion regarding the thermodynamics of hydrogen release could not be made. Therefore, an isothermal DSC at $120\text{ }^\circ\text{C}$, in which the hydrogen release purity is over 99%, was carried out as shown in Figure S2 b, and the enthalpy was calculated to be -5.8 kJ/mol H_2 .

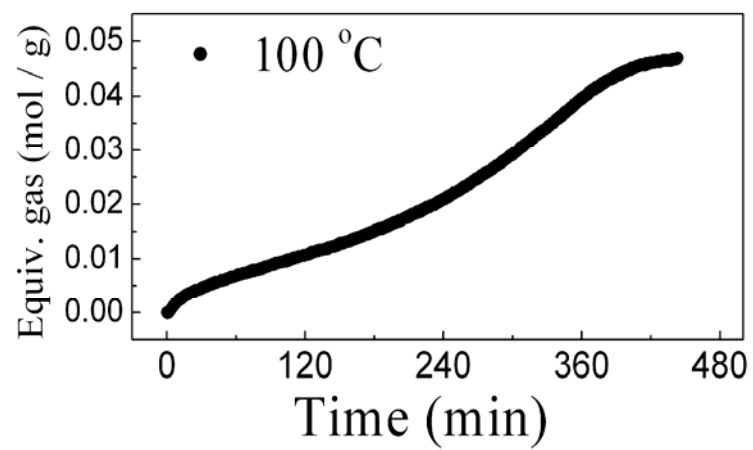


Figure S3. Isothermal TPD curves for the decomposition of $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ at 100 °C.

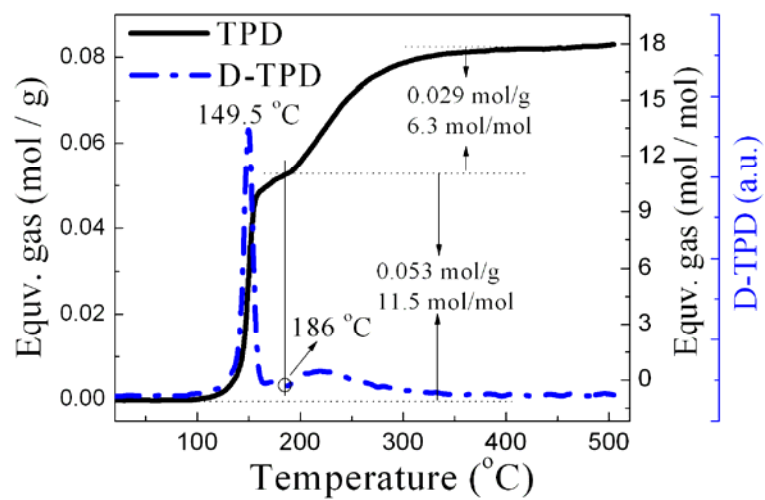


Figure S4. Non-isothermal TPD curve and its differential curve (D-TPD) with a heating rate of 5 $^{\circ}\text{C min}^{-1}$ for the decomposition of $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$.

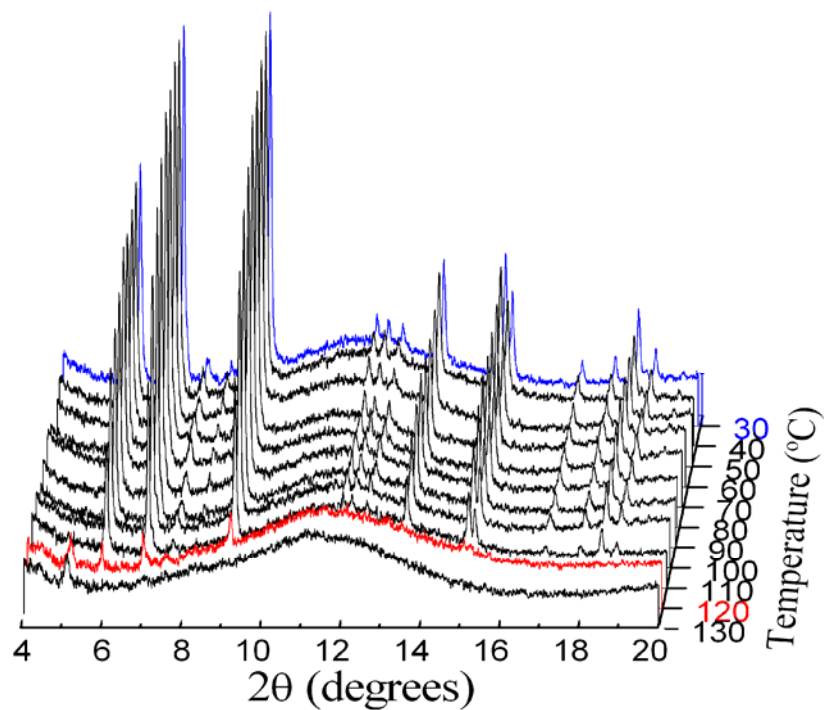


Figure S5. Selected parts of the in-situ high resolution XRD patterns for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$. The sample was heated to a scheduled temperature at a heating rate of $6^\circ\text{C}/\text{min}$ and then held for 8 min to allow collection of the data.

Compared with the TG or TPD results, lower temperature was observed for a complete phase transformation in the in-situ XRD results, which may be due to the long time holding period (8 min for each pattern) during the in-situ XRD process.

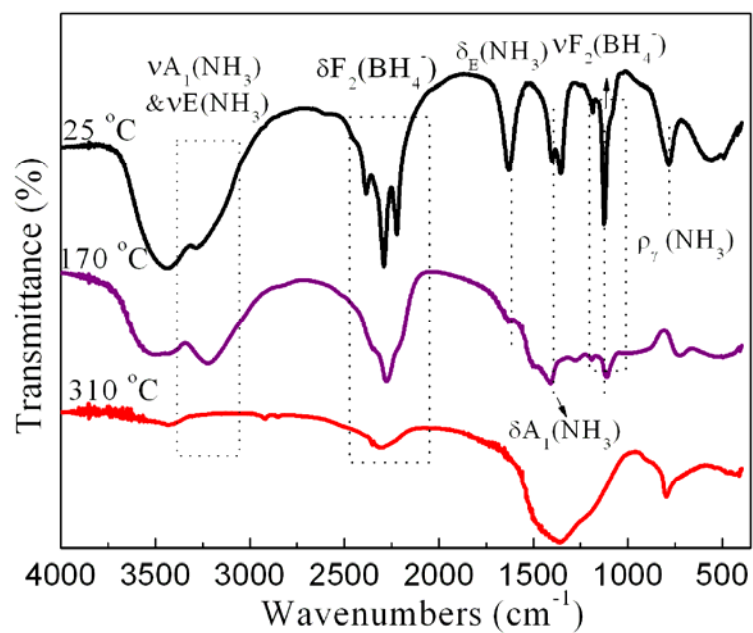


Figure S6. FTIR spectra for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ at 25 °C and its products after heating to 170 °C and 310 °C. The heating rate is 5 °C/min.

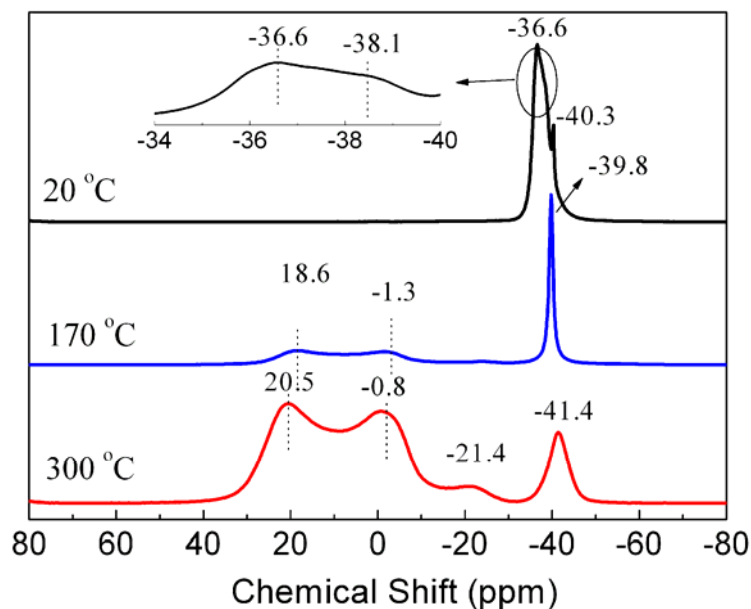


Figure S7. ^{11}B NMR results for $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ composite with mole ratio of 1:2 before and after heating to 170 °C and 300 °C. There is a small sharp peak (-40.3ppm) in the as-synthesized sample. The resonance is the same as in LiBH_4 . It may arise from a slightly partial decomposition during ball milling or from a slight amount of unreacted LiBH_4 .

On further heating $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ to 300 °C, a tricoordinate B nucleus peaks at 20.5 and three kinds of tetracoordinate B nucleus peaks at -0.8 ppm, -21.4 and -41.4 ppm were observed.^{S6} The above results indicate that the dehydrogenation mechanism in S2 may be similar to that of other B-N-H systems, i.e. hydrogen release occurs through the combination of BH and NH, resulting in the formation of amorphous BN polymer.

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