Hydrogen release from amminelithium borohydride, $LiBH_4 \cdot NH_3$

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1. Experimental

General considerations:

The source materials were obtained commercially, $LiBH_4$ 95% (Sigma-Aldrich, USA) and $MgCl_2$ 99.999%, $ZnCl_2$ 99.99% $AlCl_3$ 99.99%, and NH_3 (Alfa Aesar, China). $LiBH_4$, $MgCl_2$, $ZnCl_2$ and $AlCl_3$ were used without further purification. NH_3 was purified by soda lime when using. All handling except ammonia related procedures were conducted under anaerobic and anhydrous condition by Schlenk techniques and glove box filled with argon.

Thermal property measurements were performed by thermogravimetry (TG, STA 409C) /mass spectrometer (MS, QMS 403) with heating rate of 10 °C/min under 1 atm argon atmosphere. The sample cell was vacuumized and then filled with argon three times before measurement to avoid oxidation during heating. Meanwhile, desorption properties for some samples were also evaluated using Sievert's volumetric methods with heating rate of 5 °C/min under argon and ammonia atmosphere with a pressure of 1 bar.

High-resolution X-ray powder diffraction with transmission optics (X'Pert PRO MPD, PANalytical, Netherlands) and powder X-ray diffraction (XRD, Rigaku D/max 2400) measurements were conducted to confirm the phase structure. During the High-resolution X-ray powder diffraction measurement, samples were sealed by Mylar foil (6μm) then loaded on transmission sample holder in argon glove box to avoid oxidation and hydrolysis during the measurement. And during the XRD measurement amorphous polymer tape was used to cover the surface of the powder to avoid oxidation.

For high-resolution X-ray powder diffraction, the data were collected from 5 to 70 （2θ）degrees with 0.005 stepsize. Space group of Pnma was determined by matching amplitudes of extracted structure factor with Le bail method. Direct phasing by charge flipping was aided by superflip program, which helped identifying atomic positions of Li, B and N. A full geometry optimization of $Li_4B_4N_4H_{28}$ in a unit cell as suggested by elemental analysis was then offered by refining BH_4 tetrahedral (initial B-H distance of 1.2 Å) and NH_3 (initial N-H distance of 1.0 Å) pyramid moieties with Lenard-Jones repulsion potential weighted Rietveld methods in Maud program.

FT-IR (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bond. Samples were pressed with KBr then loaded in sealed chamber filled with argon for the measurement.

Solid-state MAS NMR spectra were measured using a Bruker Avance 300 MHz spectrometer, employing a boron-free Bruker 4 mm CPMAS probe. The resonance frequency was 96.30 MHz for the ^{11}B nucleus. The powder samples collected after decomposition reaction was spun at 5 kHz, using 4mm ZrO_2 rotors filled up in purified argon atmosphere glove boxes. The one-dimensional (1D) ^{11}B MAS NMR spectra were acquired after a 1 μm single pulse.

The contents of H_2 and NH_3 in the emission gas were determined using gravimetric and volumetric results. Firstly, the mass percent (W_p) and mole per gram (M_p) of gas released from the sample were calculated from the weight of the samples and volumetric results, then the mole proportion of H_2 (C_{H2}) and NH_3 (C_{NH3}) can be calculated from the below two equations,

$C_{H2}+C_{NH3}=1$ (1)

$(C_{H2}*2.02+C_{NH3}*17.03)*\ M_p= W_{p.}$ (2)

Synthesis of ammonia complexes of $LiBH_4$ and their composites:

1) Synthesis of ammonia complexes of $LiBH_4$

$LiBH_4·xNH_3$ was prepared by exposing $LiBH_4$ to NH_3 atmosphere at room temperature. $LiBH_4$ was loaded in a Schlenk tube. Then the tube was evacuated by a rotary vacuum pump. Subsequently, purified NH_3 with 1.0 bar pressure was introduced into the tube and kept for 20 min, then the tube was evacuated for 3h to get sample S1. If the tube was filled by 1.0 bar NH_3 and kept for about 30min without pumping or shaking, a liquid sample S2 can be obtained. Further shaking and spreading the liquid around the tube wall, the liquid will change to solid to produce sample S3. The value for x is calculated by the following formula: x= (weigh gain/ initial weigh of $LiBH_4$)×21.8/17.03.

By weighting the products, the x value for the prepared sample S1, S2, S3 are 1.02, 2.02 and 2.99, respectively. So, the main composition for sample S1, S2 and S3 are recorded as $LiBH_4·NH_3$, $LiBH_4·2NH_3$ and $LiBH_4·3NH_3$.

2) Preparation of $LiBH_4·NH_3$ composites

$LiBH_4·NH_3/MgCl_2$, $LiBH_4·NH_3/ZnCl_2$ and $LiBH_4·NH_3/AlCl_3$ composites were prepared by mixing $LiBH_4·NH_3$ with the additives, after hand milling for 5 min, the mixtures were heated to 65 °C for 5 min in sealed bottle then cooled down to get the composites. Heat release was detected when preparing these mixtures, so additives should be added very carefully to prevent the rapid increase of temperature during preparation.

$LiBH_4 \cdot NH_3$ $LiBH_4 \cdot 2NH_3$ $LiBH_4 \cdot 3NH_3$

Figure S1. The views of $LiBH_4 \cdot xNH_3$. These samples are enclosed in transparent glass bottles in argon glove box and then took out for photographing at room temperature.

2. Crystallographic data and structure refinement for $LiBH_4·NH_3$

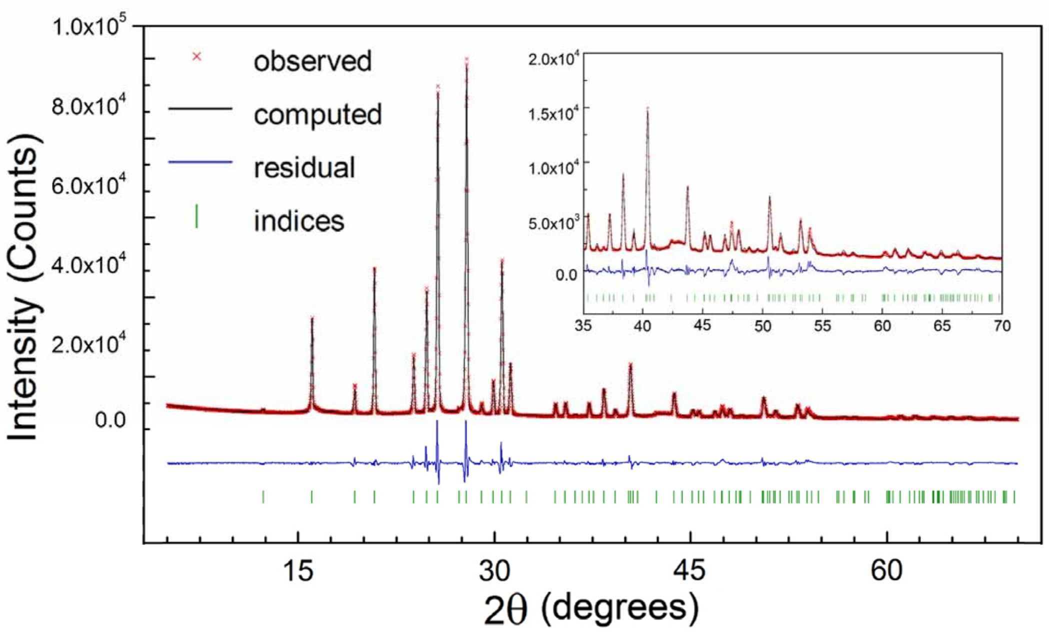


Figure S2 Rietveld fitting results, observed (cross), calculated (line), and residual (line below observed and calculated patterns) XRD profiles for $LiBH_4·NH_3$ at 298 K. Vertical bars indicate the calculated positions of Bragg peaks for $LiBH_4·NH_3$.

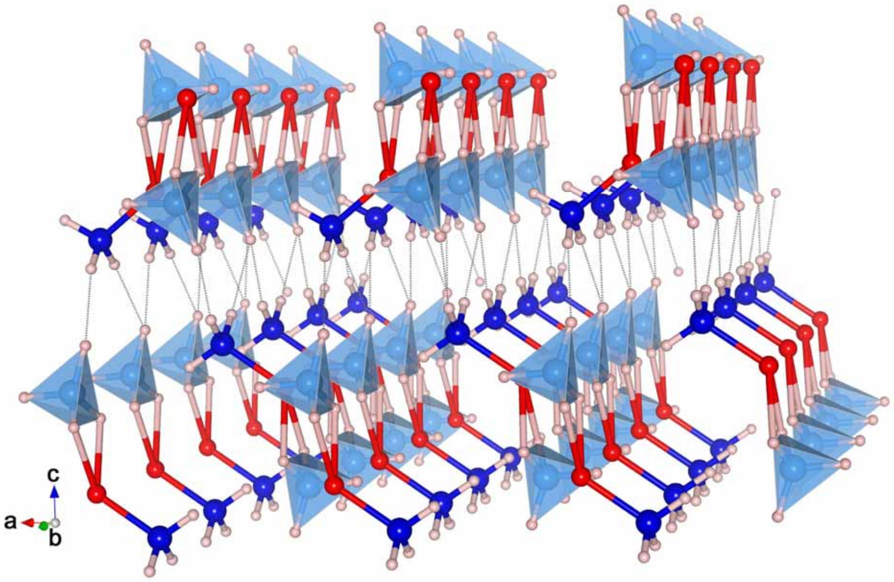


Figure S3 3-dimensional crystal structure of $LiBH_4·NH_3$. H, Li and N atoms are in pink, red and deep blue as well as BH_4^- light blue tetrahedral building blocks. Dashed lines show closely interacting hydrogen pairs

Table S1 Main crystallographic data and the parameters of data collection and structure refinement

Empirical formula	LiBNH7	
Formula weight	38.82	
Crystal system	Orthorhombic	
Sp. gr.	P n m a	
Unit cell dimensions	a= 5.97213(2) Å	α= 90°
	b=4.46432(1) Å	β= 90°
	c=14.34875(0) Å	γ =90°
Volume	382.6 Å^3	
Z	4	
Density (calculated)	0.6748 g/cm^3	
$2\theta_{max}$, deg	70	
Diffractometer*	X'Pert PRO MPD	
Scan mode	ω/2θ□	
N_a**	101	
N_o**	95	
N_p**	44	
R1	0.05119	
wR2	0.07716	
Gof	1.6762	

** *Na* is the number of reflections with $F > 0$, *No* is the number of reflections with $F > 4\sigma(F)$, and *Np* is the number of parameters in the refinement.

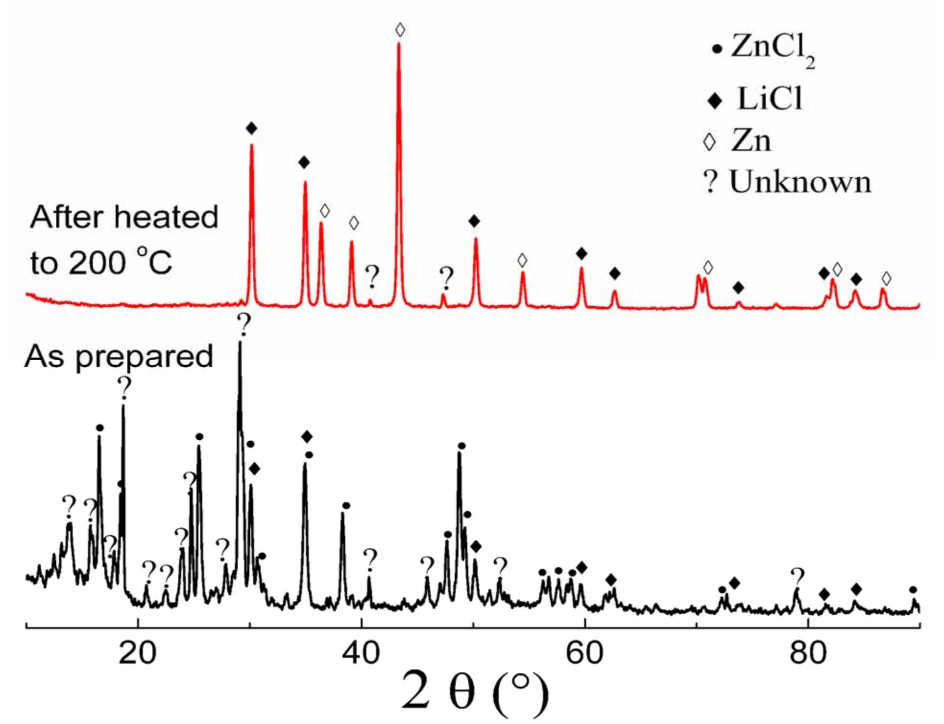
Table S2 Atomic coordinates and thermal parameters

Atom	Wyckoff site	x / a	y / b	z/ c
Li1	4 c	0.1429(8)	0.25	0.0764(6)
B1	4 c	0.9306(8)	0.75	0.0956(8)
N1	4 c	0.3981(1)	0.25	0.1548(2)
H1	4 c	0.3620(1)	0.25	0.5916(9)
H2	8 d	0.6048(9)	0.9425(97)	0.7987(7)
H3	4 c	0.4536(2)	0.75	0.8824(1)
H4	8 d	0.6244(5)	0.0414(2)	0.5440(7)
H5	4 c	0.6409(8)	0.25	0.6750(1)

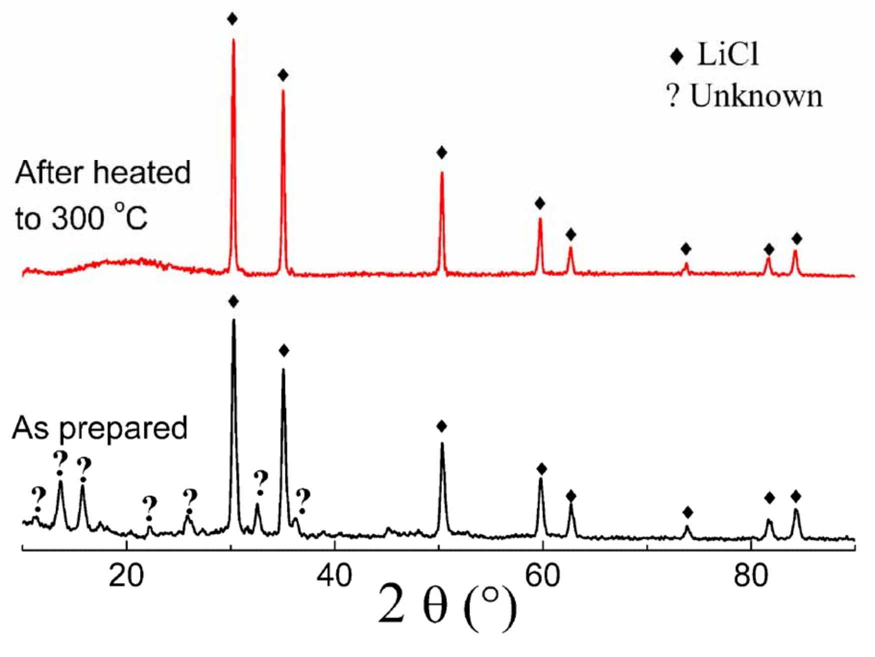
TableS3 Selected interatomic distances (*d*, Å) and angles (ω, deg)

	d		d
N(1)-H(2)	1.08(8)	H(2)-H(5)	2.25(4)
N(1)-H(3)	1.03(4)	H(3)-H(1)	4.76(4)
B(1)-H(1)	1.24(0)	H(3)-H(4)	2.58(3)
B(1)-H(4)	1.23(4)	H(3)-H(5)	3.02(5)
B(1)-H(5)	1.21(7)	Angle	□□
Li(1) - N(1)	1.89(4)	B(1)-H(5)-H(2)	134.73(5)
H(2)-H(1)	2.59(3)	N(1)-H(2)-H(5)	164.86(1)
H(2)-H(4)	3.67(7)/ 3.68(3)/ 3.86(2)		

3. Results metal chlorides / $LiBH_4 \cdot NH_3$ mixtures



(a)



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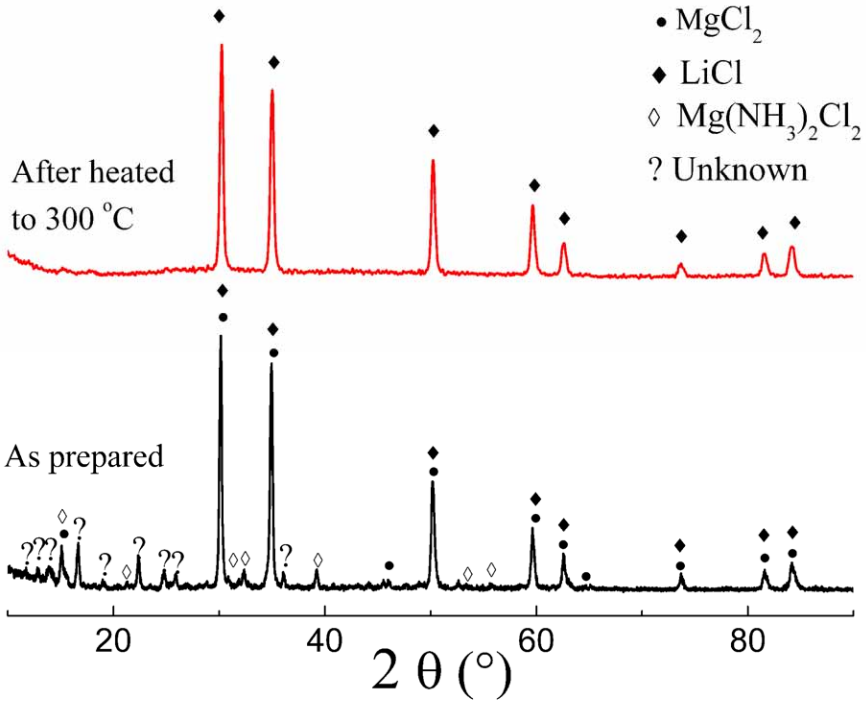
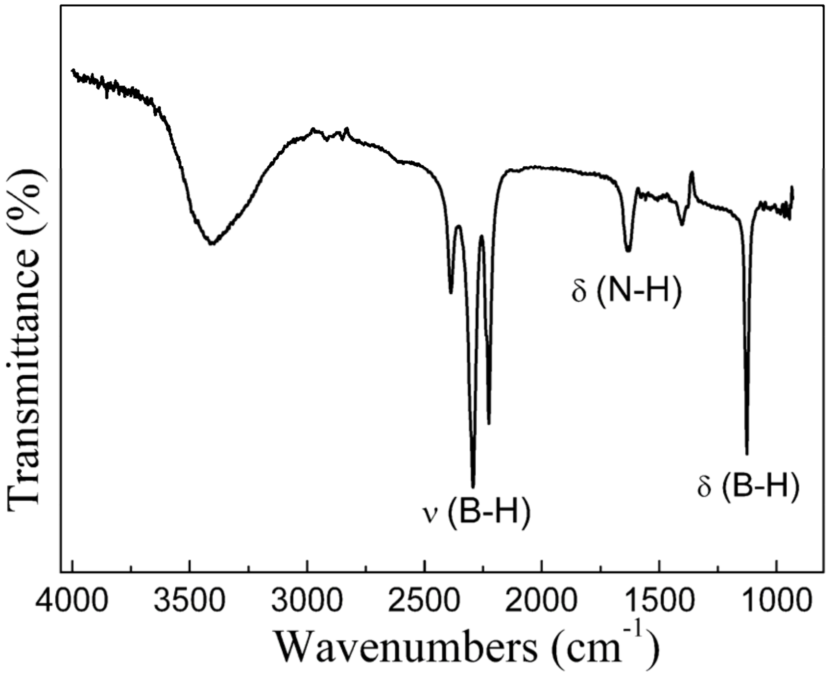
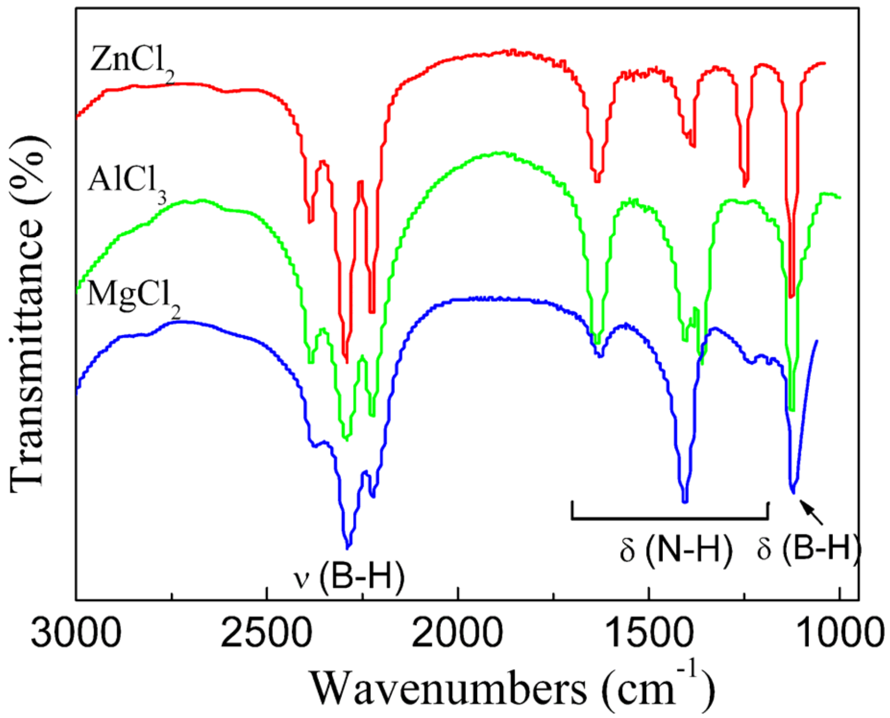


(c)

Figure S4 XRD patterns for the as-prepared and dehydrogenated $ZnCl_2$/ $LiBH_4·NH_3$ (a), $AlCl_3$/ $LiBH_4·NH_3$ (b) and $MgCl_2$/ $LiBH_4·NH_3$ (c) mixtures. New phase can be found from all these as-prepared mixtures.



(a)



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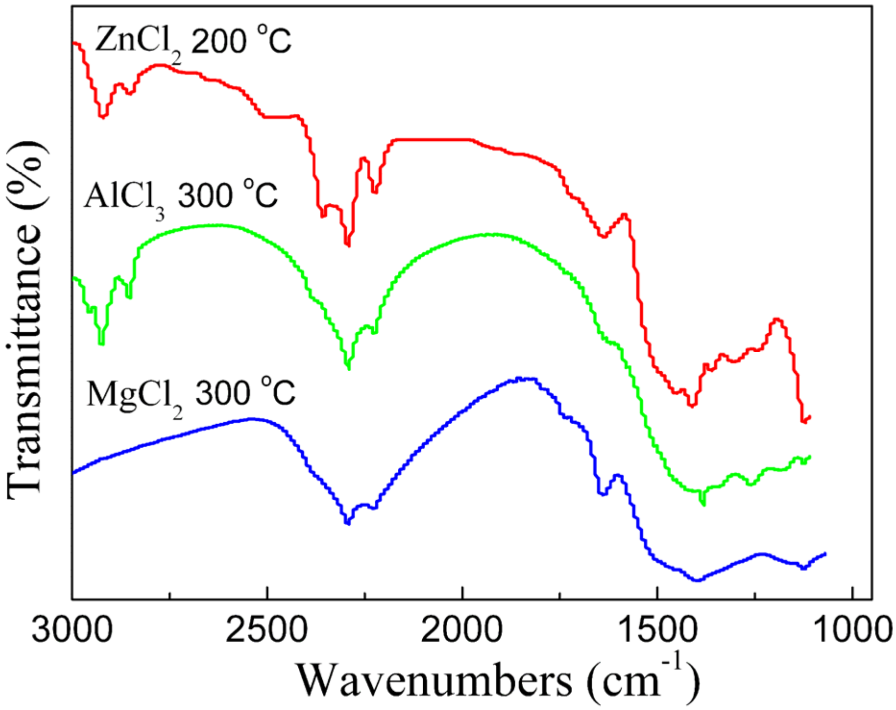

(c)

Figure S5 IR spectra for $LiBH_4 \cdot NH_3$ (a), the as-prepared chlorides / $LiBH_4 \cdot NH_3$ mixtures (b) and their dehydrogenated samples (c).