Supporting Information

A New Family of Metal Borohydride Ammonia Borane Complexes: Synthesis, Structures, and Hydrogen Storage Properties

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Table S1. Calculated structural parameters of $Li_2(BH_4)_2(NH_2BH_3)$ (LiBH·AB, Space group *Pnma*, No. 62, refined lattice parameters *a*=8.3118(8) Å, *b*=12.428(1)Å, *c*=6.5944(7)Å)

Atom	Site	x	y	z
Li1	*8d*	0.3318	0.9228	0.9681
B2	*8d*	0.0995	0.5736	0.7190
H3	*8d*	0.1709	0.6520	0.7861
H4	*8d*	0.1636	0.4892	0.7734
H5	*8d*	-0.03842	0.5740	0.7845
H6	*8d*	0.1020	0.5809	0.5327
H7	*8d*	0.2996	0.1705	0.6705
H8	*8d*	0.0767	0.1837	0.9487
B9	*8c*	0.7848	0.75	0.3091
H10	*8c*	0.8982	0.75	0.4280
H11	*8c*	0.7616	0.75	0.9778
N12	*8c*	0.8533	0.75	0.0830

Table S2. Calculated structural parameters of $Ca(BH_4)_2(NH_2BH_3)_2$ (CaBH·AB, Space group *Aba2*, No. 41, refined lattice parameters *a*=8.265(1) Å, *b*=13.478(2)Å, *c*=8.136(1)Å)

Atom	Site	x	y	z
B1	*8b*	0.0544	0.2092	0.7237
B2	*8b*	0.7273	0.0082	0.5747
N3	*8b*	0.0007	0.1874	0.2995
H4	*8b*	0.0674	0.3381	0.1879
H5	*8b*	0.1361	0.1655	0.8259
H6	*8b*	0.3630	0.2255	0.1029
H7	*8b*	0.0880	0.1530	0.2291
H8	*8b*	0.0940	0.3622	0.8057
H9	*8b*	0.0470	0.1941	0.4173
H10	*8b*	0.1314	0.0067	0.5362
H11	*8b*	0.3520	0.0650	0.5352
H12	*8b*	0.2875	0.4806	0.2240
H13	*8b*	0.1788	0.4165	0.5045
Ca14	*8a*	0.5	0	0.3034

Table S3. Average calculated bond lengths of $Li_2(BH_4)_2NH_3BH_3$ and $Ca(BH_4)_2(NH_3BH_3)_2$

Bond	Length (Å)		
	$Li_2(BH_4)_2NH_3BH_3$	$Ca(BH_4)_2(NH_3BH_3)_2$	NH_3BH_3
N-B	1.596	1.591	1.592
N-H(AB)	1.030	1.032	1.030
B-H(AB)	1.222	1.222	1.222
B-H(BH_4)	1.228	1.229	
H_N-H_B (in AB layer)	2.439	1.735	2.02[1]
H_N-H_{BH4}	2.248	2.036	

[1] Klooster, W.T.; Koetzle, T.F.; Siegbahn, P. E. M.; Richardson, T. B.; Crabtree, R. H. *J. Am. Chem. Soc.* **1999**, *121*, 6337.

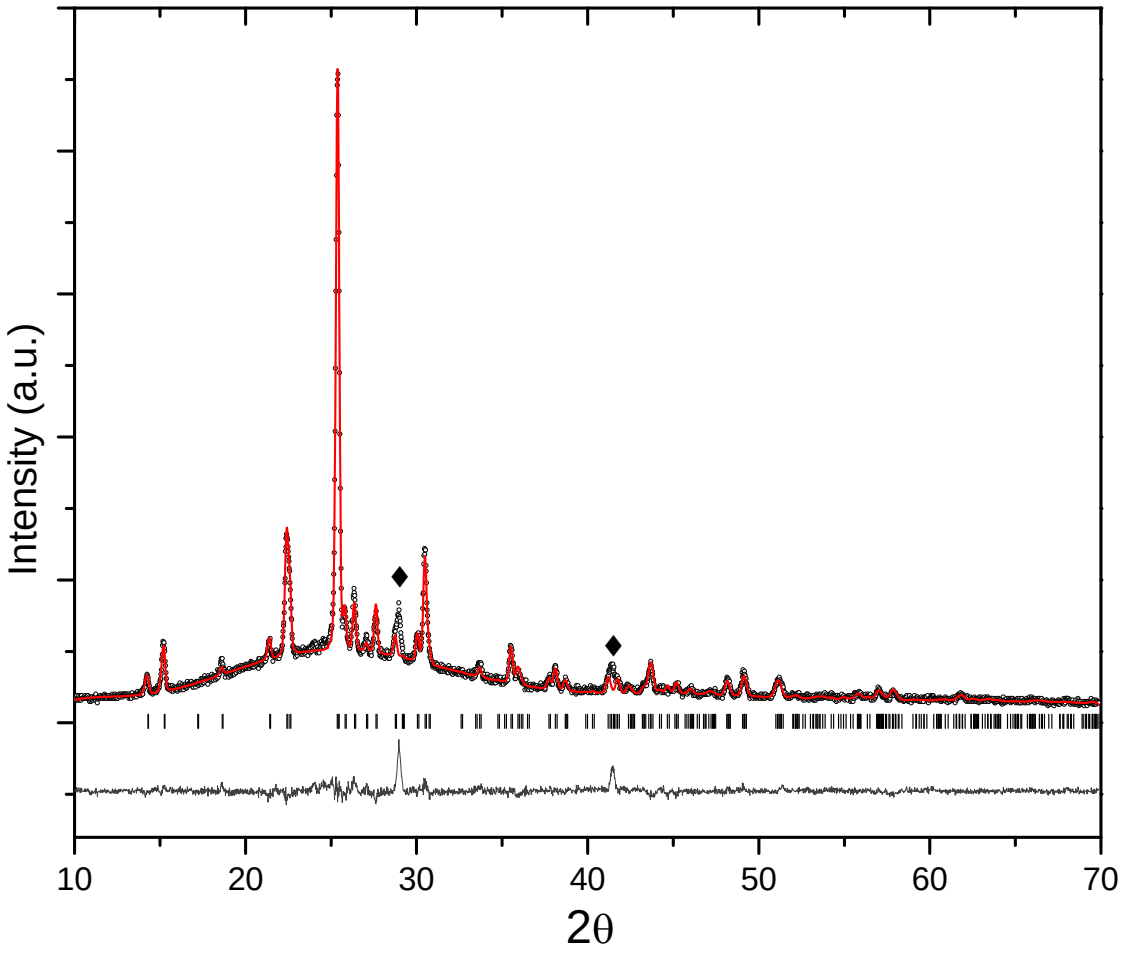

Figure S1. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) XRD profiles for $Li_2(BH_4)_2NH_3BH_3$ at 298 K. Vertical bars indicate the calculated positions of Bragg peaks for $Li_2(BH_4)_2NH_3BH_3$. The patterns also contain peaks of impurity phase from the NH_3BH_3 precursor (90% Aldrich, indicated by solid diamond) as identified in the previous study[2].

[2] Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 14834–14839.

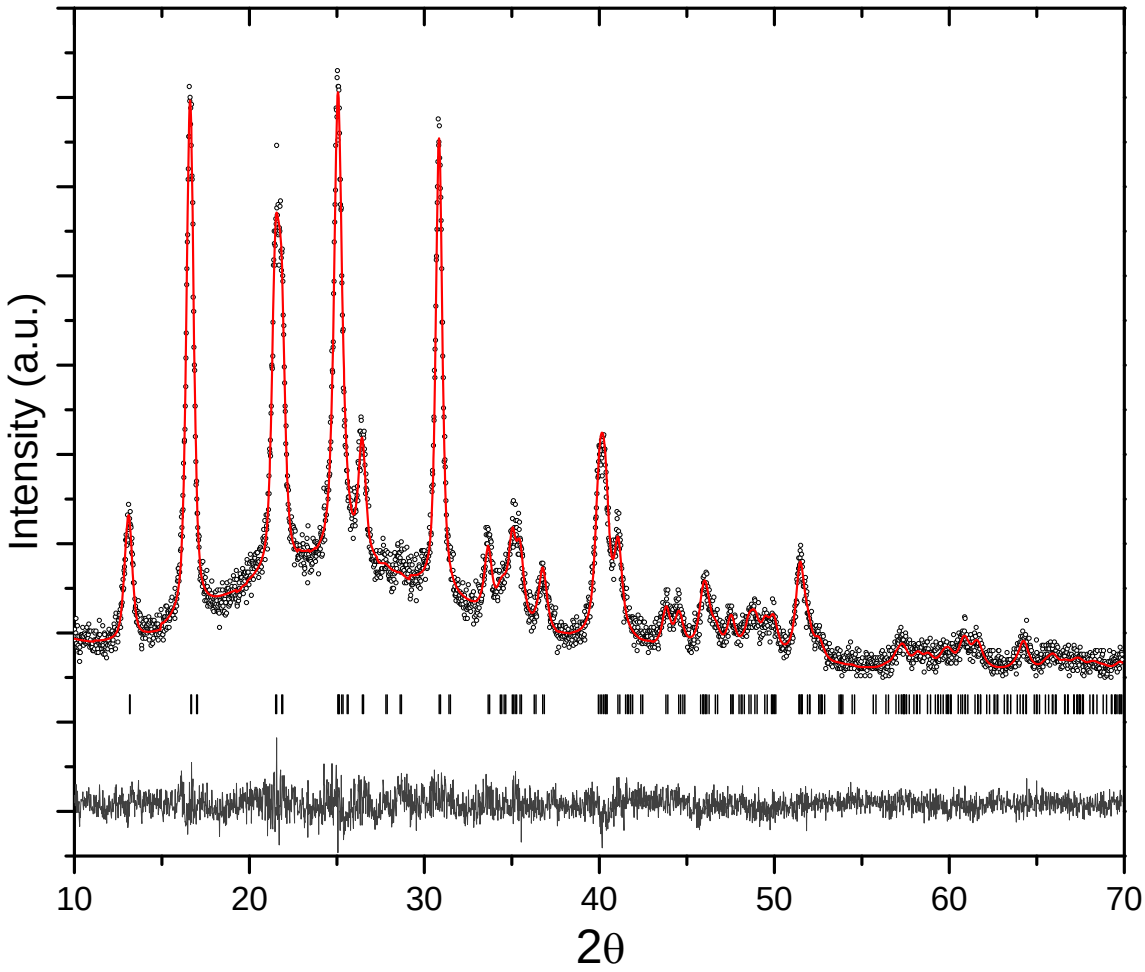

Figure S2. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) XRD profiles for $Ca(BH_4)_2(NH_3BH_3)_2$ at 298 K. Vertical bars indicate the calculated positions of Bragg peaks for $Ca(BH_4)_2(NH_3BH_3)_2$.

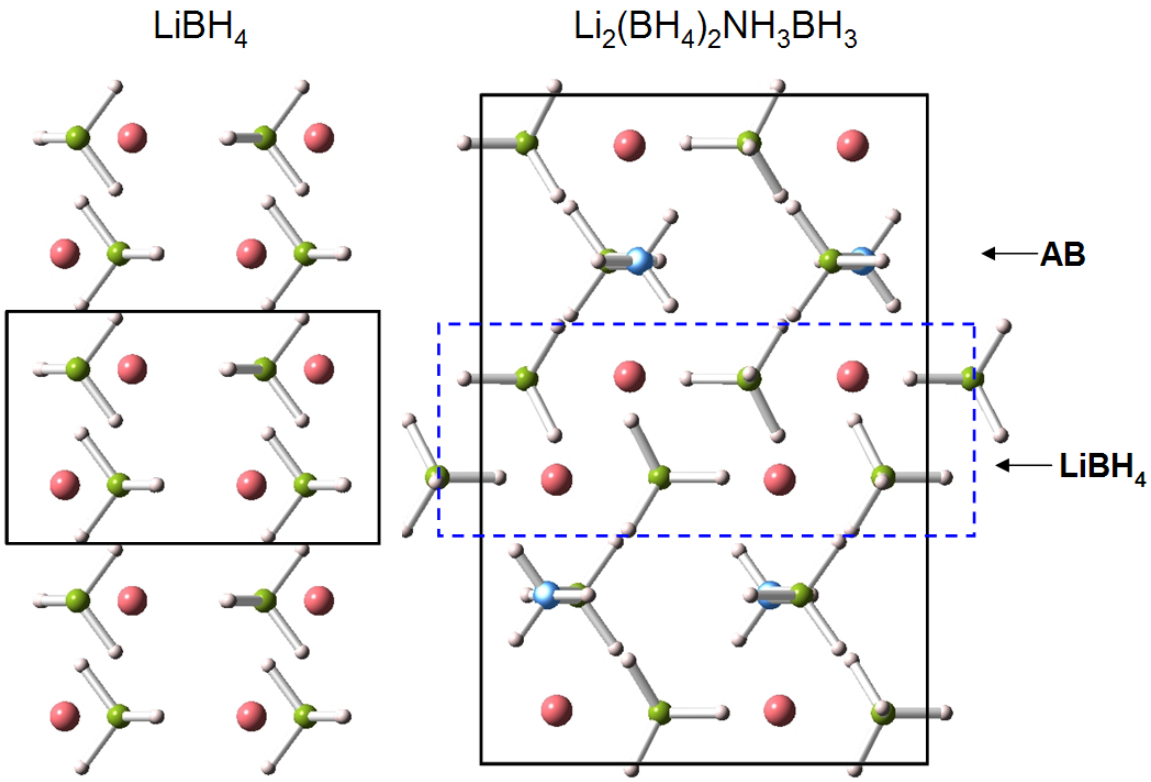

Figure S3 Comparison of the structures ([001] view) of $LiBH_4$ and $Li_2(BH_4)_2NH_3BH_3$. Note: $Li_2(BH_4)_2NH_3BH_3$ contains alternating layers of $LiBH_4$ and NH_3BH_3. The unit cells of $LiBH_4$ and $Li_2(BH_4)_2NH_3BH_3$ are plotted in grey line. The $LiBH_4$ block in $Li_2(BH_4)_2NH_3BH_3$ cell is highlighted in blue.

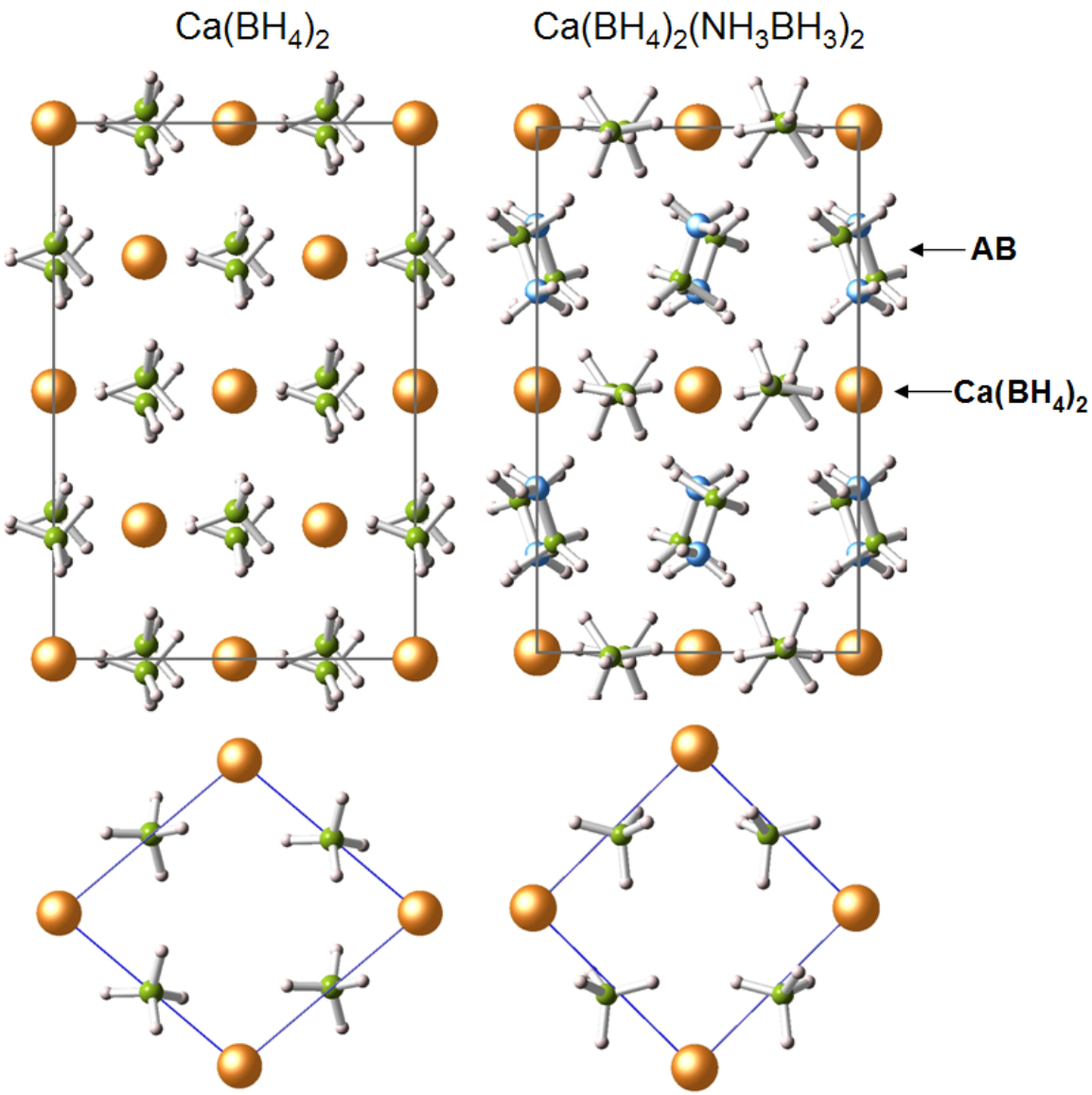

Figure S4 Top: Comparison of the structures ([001] view) of $Ca(BH_4)_2$ and $Ca(BH_4)_2(NH_3BH_3)_2$. Note: $Ca(BH_4)_2(NH_3BH_3)_2$ contains alternating layers of $Ca(BH_4)_2$ and NH_3BH_3. Bottom: comparison of lattice arrangement of $Ca(BH_4)_2$ and the $Ca(BH_4)_2$ layer of $Ca(BH_4)_2(NH_3BH_3)_2$.

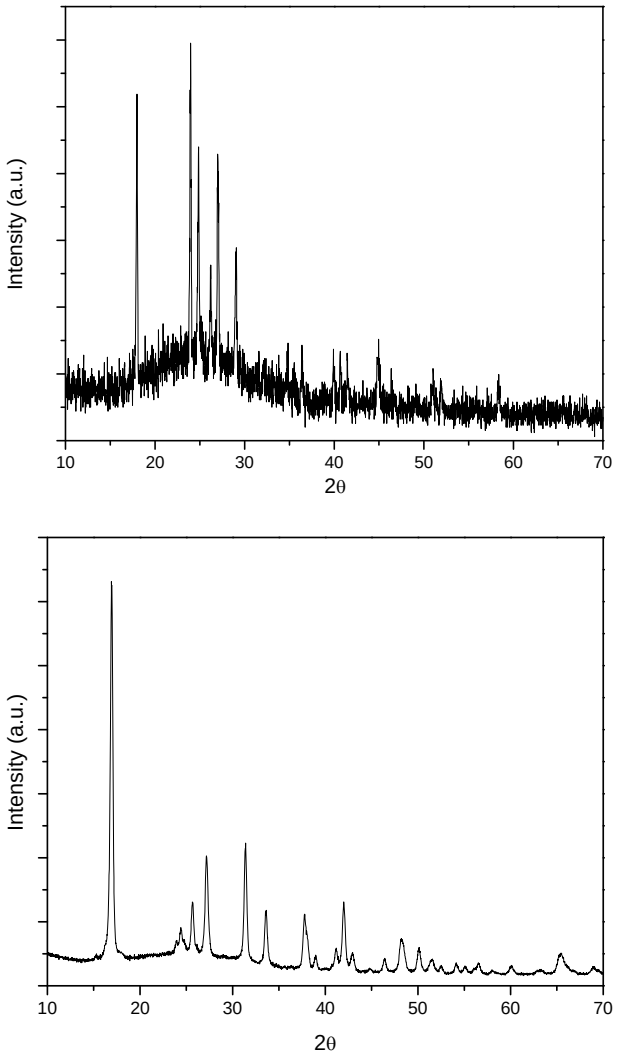

Figure S5 Top: XRD pattern of $Li_2(BH_4)_2NH_3BH_3$ after the 1st step desorption, indicating the product is $LiBH_4$. Bottom: XRD pattern of $Ca(BH_4)_2(NH_3BH_3)_2$ after the 1st step desorption, the main product is $Ca(BH_4)_2$.

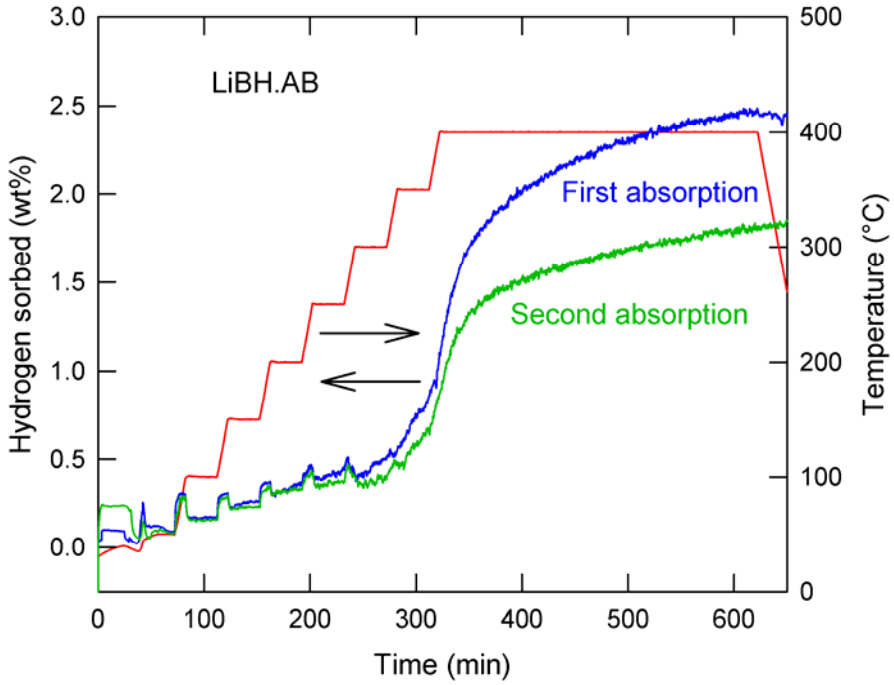

Figure S6(a) First and second rehydrogenation for LiBH·AB up to 400ºC.

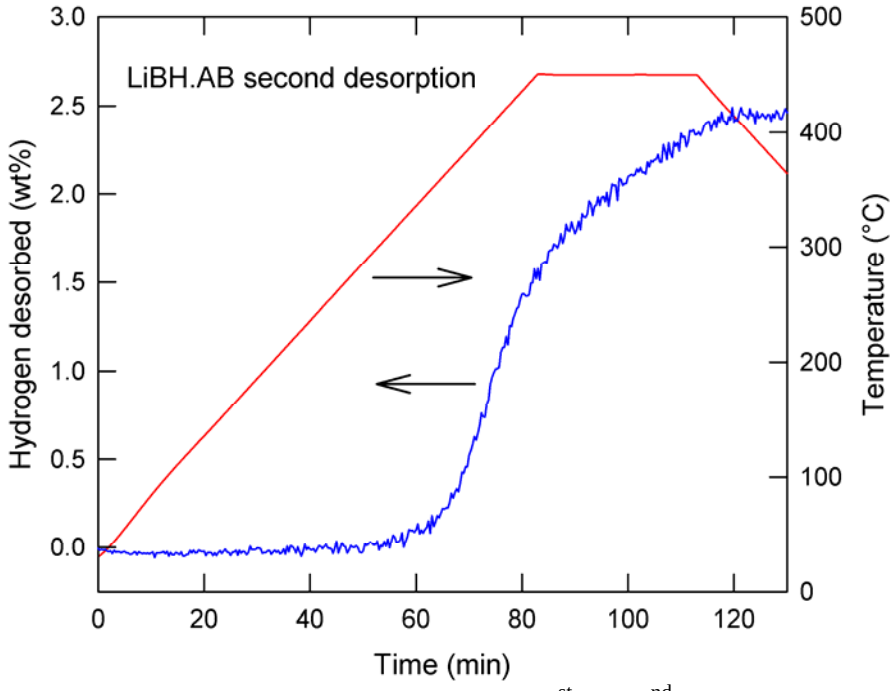

Figure S6(b) Second desorption (between 1st and 2nd hydrogenation) for LiBH·AB. RGA indicates that the second desorption is comprised only of H_2.

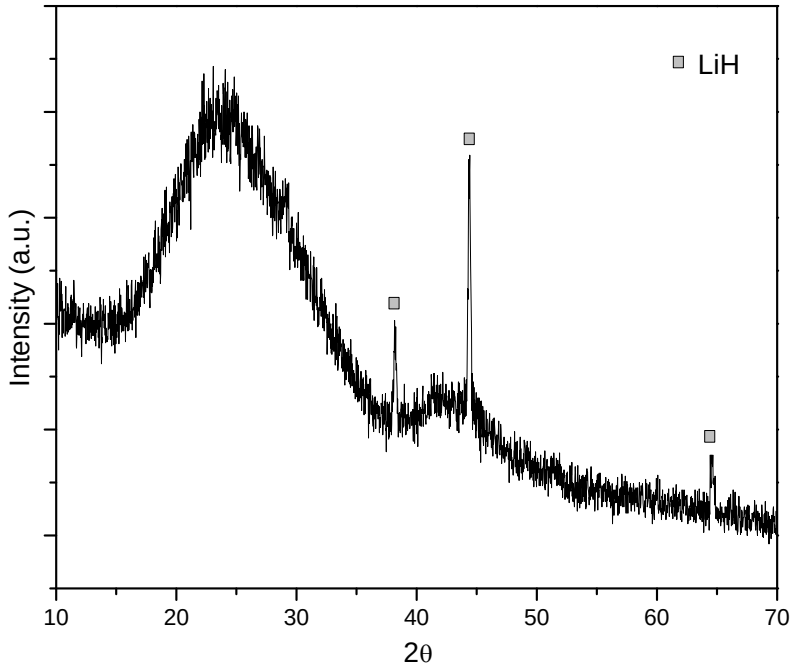

Figure S7 XRD pattern of LiBH·AB after rehydrogenation

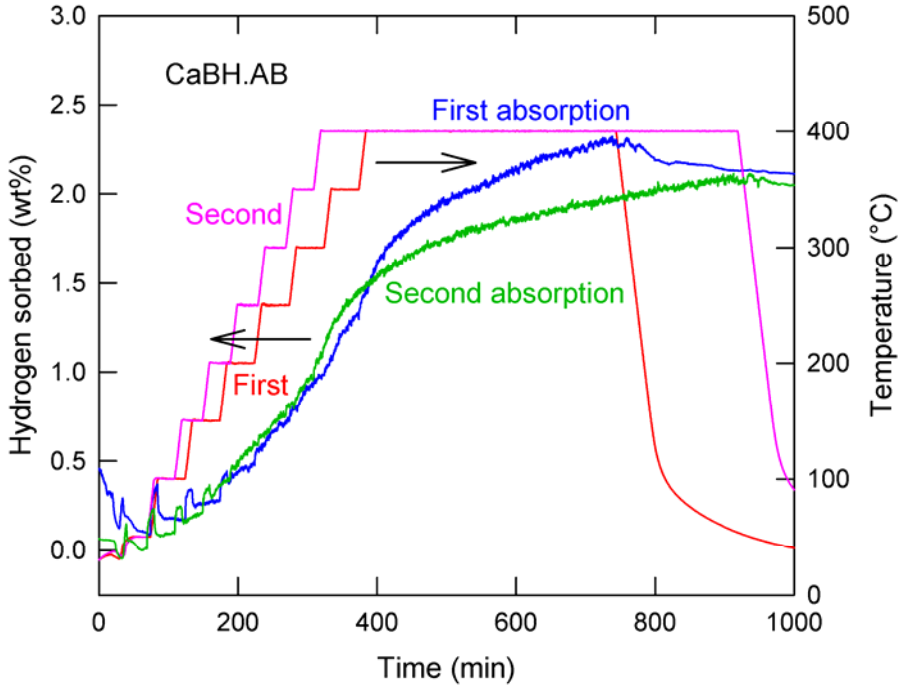

Figure S8(a) First and second rehydrogenation for CaBH·AB up to 400ºC.

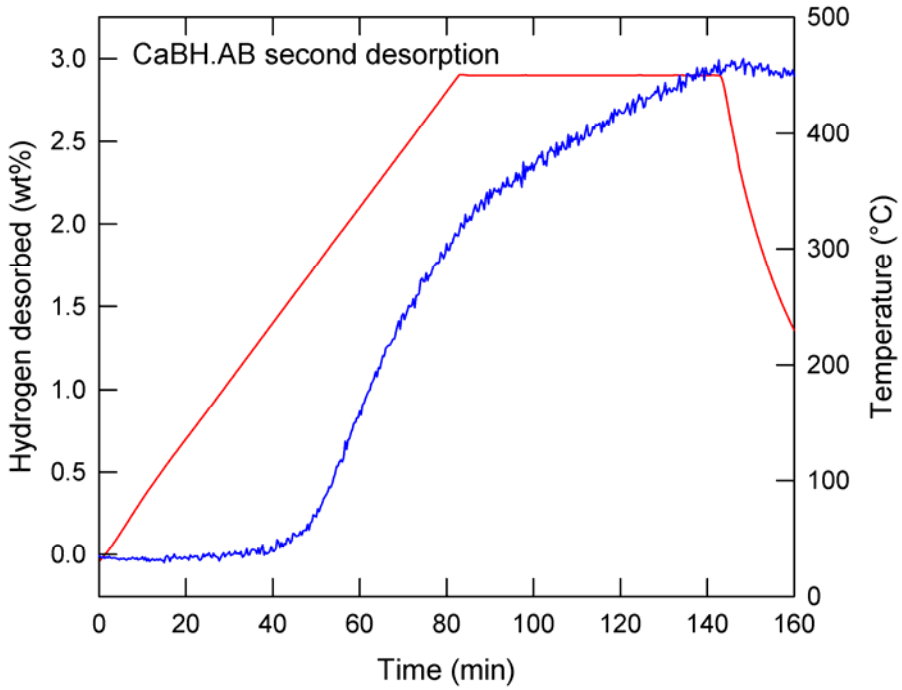

Figure S8(b) Second desorption (between 1st and 2nd hydrogenation) for CaBH·AB. RGA indicates that the second desorption is comprised only of H_2.

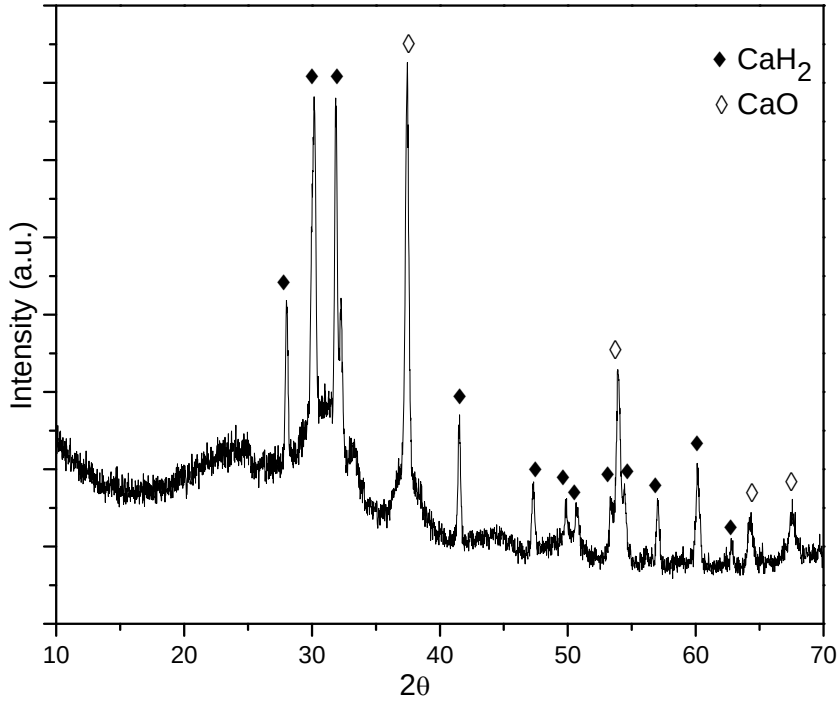

Figure S9 XRD pattern of CaBH·AB after rehydrogenation