Supporting material
Structural Prediction, Analysis and Decomposition Mechanism of Solid $M(NH_2BH_3)_n$ (M=Mg, Ca and Al)

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S1: MC packing algorithm

Polymorph's Monte Carlo packing algorithm follows a simulated annealing procedure intended to search for the lowest minima of the energy function *E* of molecular crystals. The simulated annealing method works around minima value of *E* by treating the search for the global minimum of *E* as a thermodynamic problem. At some non-zero temperature, *T*, the crystal changes its structure randomly, and its energy fluctuates accordingly. To prevent the simulation from becoming trapped in a local minimum, cooling begins at a relatively high temperature; every crystal structure (within the constraints of the space group and asymmetric unit contents) can then theoretically be reached, and ergodicity therefore ensured [1].

The simulation consists of two phases, heating and cooling. First, each trial crystal is heated. During heating, one starts from a set minimum temperature (300 K in our case). Each new trial temperature T_{new} is obtained using Eq. 1, where T_{old} is the temperature used in a previous step and T_h is a heating factor (1 in our case). Heating continues until either a pre-set maximum temperature is reached (3×10^5 K in our case) or a specified number of consecutive trial moves have been accepted.

$$T_{new} = T_{old} \times (1.0 + T_h) \quad (1)$$

The cooling phase simulates the annealing of a heated structure. At high temperatures the algorithm is able to globally sample the phase space of possible packing arrangements. At low temperatures the algorithm samples areas of energetically favourable packing arrangements more locally. If a trial is accepted during cooling, the temperature to be used in the next trial step, T_{new}, is obtained using Eq. 2, where T_{old} is the temperature used in a previous step and T_c is a user-definable cooling factor (0.0005 in our case).

$$T_{new} = T_{old} \times (1.0 + T_c) \quad (2)$$

The simulation ends when T is so low that the crystal is frozen (300 K in our case). Then one can optimize at 300 K all the found structures during the annealing procedure and determine the structure of the lowest energy.

The determination of space group is based on the principle pointed by Belsky[2] and determined syngony and cell parameters from XRD experiments [3,4].

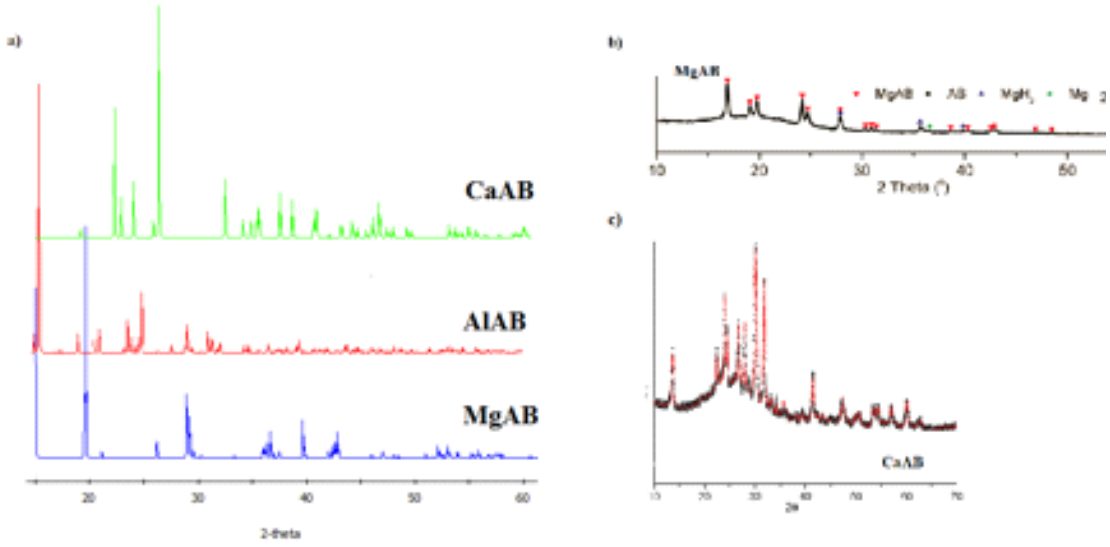

Figure S1. a) The computationally predicted XRD for MgAB, CaAB and AlAB, (b) experimental powder XRD for MgAB ref. [3], (c) experimental single crystal XRD for CaAB ref. [4].

A: Table S1~S3 Structural information for MABs (M=Ca, Mg, Al) obtained in this study (The values in the brackets are the experimental results)

Table S1 Structural information for MgAB obtained after geometry optimization with CASTEP

MgAB			
Syngony		monoclinic	
space group		C2	
a	8.417	α	90.00
b	6.038	β	126.08
c	7.293	γ	90.00
Fractional coordinates in Å (x y z)			
B1	0.772	0.289	0.169
N2	0.975	0.284	0.208
H3	0.760	0.450	0.269
H4	0.137	0.799	0.962
H5	0.247	0.622	0.244
H6	0.083	0.251	0.377
H7	0.010	0.439	0.181
Mg8	0.000	0.063	0.000

Table S2 Structural information for CaAB obtained after geometry optimization with CASTEP

CaAB			
Syngony		monoclinic	
space group		C2	
a	9.256(9.100)	α	90.00
b	4.415(4.371)	β	92.92(93.19)
c	6.613(6.441)	γ	90.00
Fractional coordinates in Å (x y z)			
H1	0.922	0.914	0.713
H2	0.137	0.341	0.250
H3	0.857	0.051	-0.017
H4	0.643	0.123	0.601
H5	0.343	0.786	0.299
N6	0.674	0.012	0.733
B7	0.834	0.078	0.796
Ca8	0.000	0.604	0.000

Table S3 Structural information for AlAB obtained after geometry optimization with CASTEP

AlAB			
Syngony		orthorhombic	
space group		PBCA	
a		17.151	
b		7.562	
c		12.387	
Fractional coordinates in Å (x y z)			
Al1	0.329	0.802	0.040
N2	0.341	0.548	0.024
H3	0.400	0.525	0.045
H4	0.340	0.528	-0.059
N5	0.336	0.880	-0.110
H6	0.392	0.928	-0.123
H7	0.301	0.988	-0.125
N8	0.423	0.896	0.098
H9	0.419	0.909	0.181
H10	0.434	1.023	0.068
H11	0.226	0.478	0.111
H12	0.280	0.274	0.031
H13	0.320	0.363	0.169
H14	0.362	0.611	-0.190
H15	0.249	0.677	-0.172
H16	0.312	0.790	-0.288
H17	0.490	0.630	0.113
H18	0.498	0.754	-0.031
H19	0.557	0.843	0.099
B20	0.497	0.774	0.068
B21	0.291	0.411	0.087
B22	0.314	0.730	-0.194

Table S4. Comparison of CaAB and MgAB structural parameters determined in this work with the ones determined in other experimental and computational studies.

	This work Calc	Ref 4 Exp ESI	Ref 4 Calc Table 1/ESI	Ref 5 Calc Table 2/ CASTEP	Ref 5 Calc Table 2/ VASP	Ref 6 Calc Table2
CaAB						
Ca-N	**2.480**	**2.452**	**2.466**	**2.446**	**2.435**	**2.476**
N-B	1.547	1.547	1.546	1.538	1.541	1.546
N-H	1.031/1.031	1.022/1.022	1.025/1.025	1.027/1.031	1.020/1.022	1.022/1.022
B-H	1.231/1.243/ 1.249	1.243/1.245/ 1.251	1.230/1.243/ 1.250	1.226/1.240/ 1.252	1.228/1.247/ 1.260	1.229/1.242/ 1.249
MgAB						
Mg-N	**2.123**	**-**	**-**	**-**	**-**	**2.111**
N-B	1.556	-	-	-	-	1.556
N-H	1.033/1.034	-	-	-	-	1.023/1.024/ 1.025
B-H	1.218/1.245/ 1.256	-	-	-	-	1.237/1.245/ 1.254/

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