Electronic Supplementary Information (ESI)

A simple and efficient approach to synthesize amidoborane ammoniates: Case study for $Mg(NH_2BH_3)_2(NH_3)_3$ with unusual coordination structure

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Details on the Structural Determination of $Mg(NH_2BH_3)_2(NH_3)_3$:

The XRD reflections of the $Mg(NH_2BH_3)_2(NH_3)_3$ sample can be indexed to a tetragonal structure with lattice parameters of approximately a=9.875Å and c=20.006 Å. Assessment of the extinction symbol associated with the space group of the new phase indicated the most probable to be *P4/ncc*. The structure of this new compound was solved by direct-space methods using simulate annealing under this space group. One unit cell contains two Mg in the special positions, one NH_2BH_3 group in the general position, two NH_3 groups in the special positions and one NH_3 in the general position. Due to the limit number of the laboratory X-ray observations and the uncertain H positions, First-principles molecular dynamics simulated annealing calculations were performed to find the most likely orientations of the NH_2BH_4 and NH_3 groups (see below). Rietveld structural refinement on the optimal structural model was done using the GSAS package[1]. The $NH_2BH_3^-$ and NH_3 groups were kept as rigid bodies with common refined bond lengths and bond angles constrained as reasonable values due to the inadequate number of observations. B-N, B-H and N-H distances in NH_2BH_3 were defined as 1.57 Å, 1.24 Å and 1.018 Å. The N-H distances in NH_3 were constrained as 1.03 Å. The refinement based on laboratory X-ray data cannot provide highly accurate atomic coordinates, especially for H, hence only positions and not the orientations of NH_3 units and the rotational orientations along B-N in the NH_2BH_3 units were refined. Isotropic displacement parameters were constrained for the same type of atoms or rigid bodies. The cell parameters for the *P4/ncc* structure: *a*=9.8908(5) Å and *c*= 20.061(1) Å. The

agreement factors are: R_{wp}=0.0594, R_p=0.0475 and χ^2=2.191. The atomic positions from refinement are listed in Table 1.

First-principles calculations based on density-functional theory (DFT) were performed by using the PWSCF package.[2] We used a Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 544 eV and a 2×2×1 *k*-point mesh (generated using the Monkhorst-Pack scheme) were found to be sufficient for the total energy to converge to within 0.1 meV/atom. Car-Parrinello molecular dynamics simulations[3] were used to help in searching for the most likely orientations of the NH_2BH_3 and NH_3 groups. The conventional unit cell was 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. This information was used in combination with XRD pattern matching to derive the best crystal structure solution of $Mg(NH_2BH_3)_2(NH_3)_3$.

Table S1. Experimental and calculated structural parameters of $Mg(NH_2BH_3)_2(NH_3)_3$ (Space group *P4/ncc* (setting 2), No. 130, a=9.8908(5) Å, c= 20.061(1) Å, and V=1962.5(3)Å^3)

| Atom	Site	x	y	z
Mg1	*4a*	0.25	0.75	0.25
B1	*16g*	0.1284(4)	0.5719(3)	0.1455(2)
N1	*16g*	0.2725(4)	0.5663(3)	0.1799(2)
H1	*16g*	0.2949	0.4749	0.2006
H2	*16g*	0.3502	0.5865	0.1481
H3	*16g*	0.1402	0.5816	0.0841
H4	*16g*	0.0630	0.4715	0.1581
H5	*16g*	0.0642	0.6724	0.1647
Mg2	*4c*	0.25	0.25	0.4613(2)
N2	*16g*	0.2784(5)	0.4779(3)	0.4659(2)
H6	*16g*	0.3617	0.4905	0.4359
H7	*16g*	0.3039	0.5231	0.5105
H8	*16g*	0.2033	0.5360	0.4444
N3	*4c*	0.25	0.25	0.5702(4)
H9	*16g*	0.2894	0.1648	0.5923
H10	*16g*	0.1573	0.2643	0.5923
H11	*16g*	0.3085	0.3293	0.5868
N4	*4c*	0.25	0.25	0.3566(4)
H12	*16g*	0.2118	0.3398	0.3388
H13	*16g*	0.3452	0.2392	0.3369
H14	*16g*	0.1905	0.1751	0.3367

Note: The uncertainties of the atomic coordinates for hydrogen atoms are not reported here because they were not freely refined. The isotropic thermal parameters (U_{iso}) were constrained to be identical for the same atom type or same rigid bodies: U_{Mg}=1.4(1), U_{NH3}=2.0(1), U_{NH2BH3}=2.2(2) (x100 Å^2). All atomic and rigid body positions are fully occupied. H atoms around N3 and N4 are disorderly distributed with occupancies of 0.25 at each *16g* general positions.
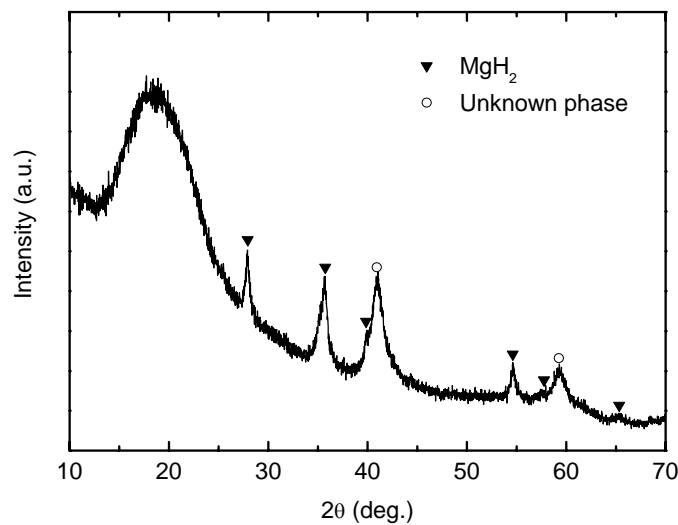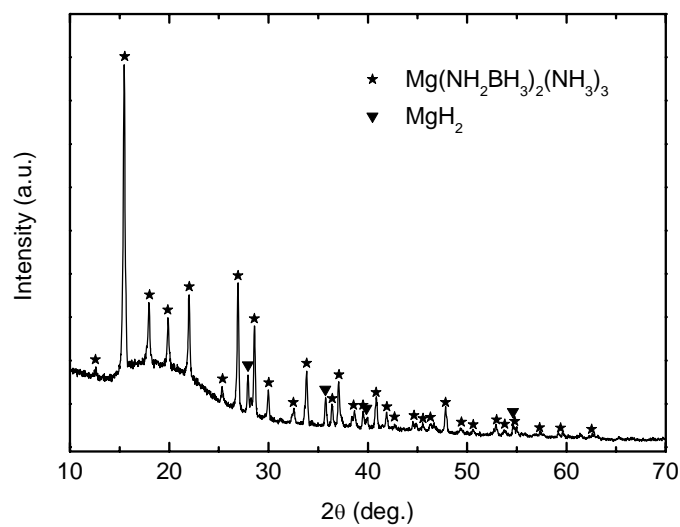
**Fig. S1** XRD pattern of the post-milled MgH_2 under NH_3 atmosphere for 2 h.
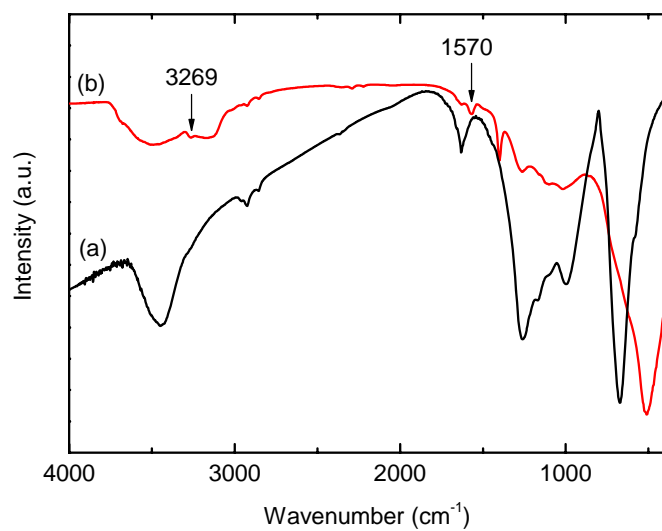
Fig. S2 FTIR spectra of (a) pristine MgH_2 and (b) the post-milled MgH_2 under NH_3 atmosphere for 2 h. The bands at 3269 and 1570 cm^{-1} should be assigned to the N-H bonds of $Mg(NH_2)_2$.

S4
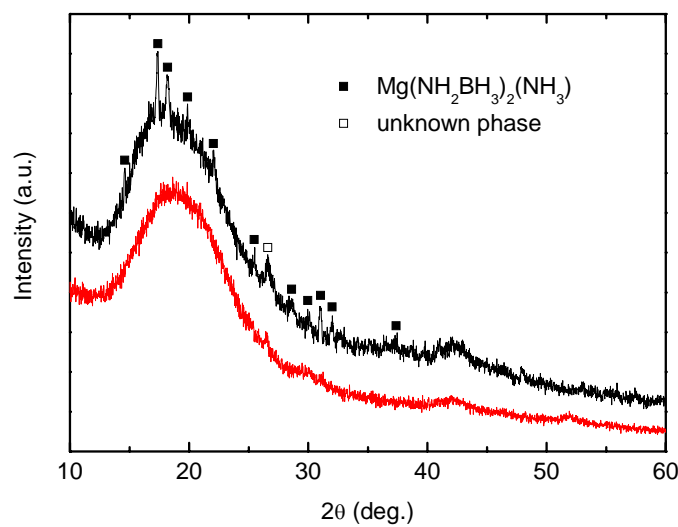
Fig. S3 XRD patterns of the starting MgAB·NH$_3$ sample (black line) and the post-milled MgAB·NH$_3$ under ammonia atmosphere for 10 min (red line). MgAB·NH$_3$ was prepared as described in Ref. 23. The ball mill conditions of MgAB·NH$_3$ under ammonia atmosphere are identical to that for the preparation of MgAB·3NH$_3$. We found that, after ball milling of 10 min, the diffraction peaks of MgAB·NH$_3$ disappeared, but the expected peaks of the MgAB·3NH$_3$ did not appear. The diffraction intensity of MgAB·3NH$_3$ was found to decrease a little when it was milled under ammonia atmospheres even for 10 h. Therefore, we deduced that the interaction of MgAB·NH$_3$ and ammonia gas during ball milling process may lead to an amorphorization of the MgAB·NH$_3$ or the production of other amorphous phase, but did not form MgAB·3NH$_3$.

Fig. S4 XRD pattern of the post-milled MgH_2 together with the liquid $AB(NH_3)_n$ complexes for 10 min.
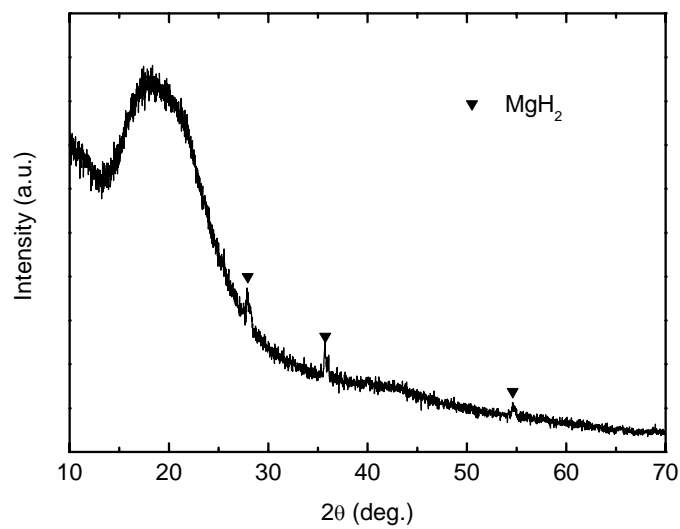
Fig. S5 XRD pattern of the post-heated $MgAB \cdot 3NH_3$ up to 300 °C.
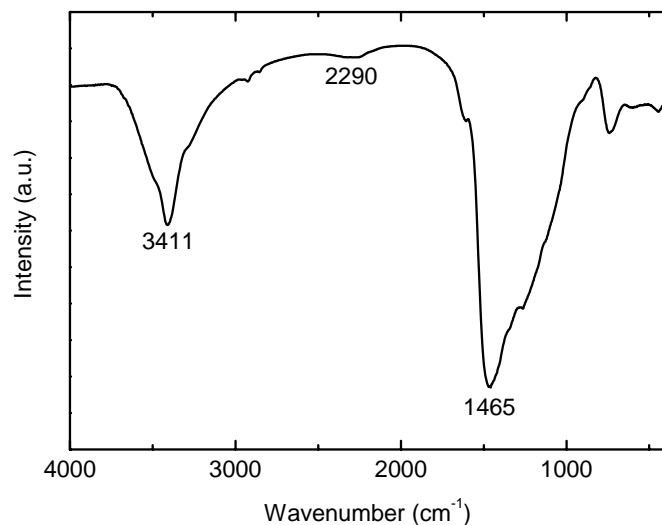
Fig. S6 FTIR spectrum of the post-heated MgAB·3NH$_3$ up to 300 °C.

Reference:

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