Supporting Information

Sodium Magnesium Amidoborane: The First Mixed-Metal Amidoborane

Hui Wu,^{1,2,*} Wei Zhou,^{1,2} Frederick E. Pinkerton,³ Martin S. Meyer,³ Qingrong Yao,⁴ Gadipelli Srinivas,^{1,5} Terrence J. Udovic,¹ Taner Yildirim,^{1,5} John J. Rush^{1,2}

¹NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6102; ²Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742-2115; ³Chemical Sciences and Materials Systems Laboratory, General Motors Research and Development Center, Warren, MI 48090-9055 ⁴Guilin Electronic University, Guilin, GuangXi, P.R.China, ⁵Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104-6272

Email: huiwu@nist.gov

Experimental Section

Six samples with NaH:MgH₂:AB ratio of 1:1:1; 1:1:2; 1:1:3; 1:0.5:2; 1:0.75:1.85; 1:0.5:1.75 were prepared in an identical fashion. Appropriate molar quantities of NaH, MgH₂ and AB (Aldrich)¹ were ball milled under 1 bar He using a Fritsch Pulverisette 7 planetary mill at 200 rpm for 80 min. After milling, the mixtures were stored in a He-filled glovebox for further structural and property characterizations.

Phase identification and equilibrium were monitored on samples sealed in 0.7 mm glass capillaries using a Rigaku X-ray diffractometer with a Cu K_{α} source. Data for structural studies were collected over 24 h at room temperature in the 20 range of 5-75° with a step size of 0.02° . Bragg peaks of the small amount of the unreacted MgH₂, NH₃BH₃, and NaNH₂BH₃ were observed across the composition range studied, together with a number of prominent additional peaks, which were indexed to a single extra phase with a tetragonal structure and lattice parameters of approximately a=9.415 Å and c=12.413 Å. Assessment of the extinction symbol associated with the space group of the new phase indicated the most probable to be $I4_1/a$. The structure of amidoborane was then partially solved using direct methods under this space group, which generated several candidate models with various NH₂BH₃⁻ orientations due to the uncertain H positions. Firstprinciples molecular dynamics simulated annealing were then performed to confirm the NH₂BH₃⁻ configuration with the lowest energy. Rietveld structural refinement on the optimal structural candidate was done using the GSAS package² on the XRD data of the sample with the optimal $Na_2Mg(NH_2BH_3)_4$ yield obtained for a precursor ratio of 1:1:2 NaH/MgH₂/NH₃BH₃. The NH₂BH₃⁻ group was kept as rigid body with common refined bond lengths and bond angles constrained as reasonable values due to the inadequate number of observations. One NH₂BH₃⁻ group together with lattice parameters were refined, yielding the agreement factors of $R_{wp}=0.0825$, $R_p=0.0704$ and $\chi^2=1.014$. The refined XRD pattern is shown in Figure S1. The atomic positions and bond lengths from refinement and calculations are listed in Table S1 and Table S2.

Neutron vibrational spectra (NVS) were measured at 5 K using the BT-4 Filter-Analyzer Neutron Spectrometer (FANS) with the Cu(220) monochromator under conditions that provided energy resolutions of 2-4.5% over the vibrational energy range probed.

Dehydrogenation of Na₂Mg(NH₂BH₃)₄ was characterized by temperature-programmeddesorption (TPD) performed on a Sieverts-type apparatus described previously.³ Samples were heated to 400°C at 2°C/min.

Weight loss measurements with simultaneous mass spectrometry (MS) were conducted in both a Cahn TG-2151 high pressure thermogravimetric analyzer (TGA) and a Hiden IGA-3 TGA. Based on species identified in an initial survey with the Hiden system that sampled all mass channels from 6 to 199 amu, the MS monitored the partial pressures for 2 amu (H₂), 16 amu (CH₄ and the MS crack of NH₃), 17 amu (NH₃ and the OH crack of H₂O), 18 amu (H₂O), 24 amu (B₂H₆), 27 amu (C₂H₄), 28 amu (N₂/CO), 32 amu (O₂), 44 amu (CO₂), and 80 amu [(BH)₃(NH)₃]. The molecular weight and cracking pattern of each species was taken into account in extracting semi-quantitative information. For the Cahn system, approximately 200 mg of sample were loaded into a stainless steel bucket and transferred into the TGA under a cover of liquid pentane to protect the sample from air exposure during transfer and purging. The pentane evaporated while the TGA was purged with flowing He gas. After evaporation the sample was heated at 2 °C/min to 450 °C in flowing He gas at 1.3 bar. The exhaust gas was sampled by an SRS CIS 100 MS operated in residual gas analysis (RGA) mode. For the Hiden system, approximately 100 mg of sample were placed in a stainless steel bucket and transferred into the TGA without air exposure via a sealed transfer container and utilizing a removable He gas interlock system. The sample was then heated at 1.7 °C/min to 400 °C. The results shown in Figure 4 were obtained with the Hiden system.

First-principles calculations based on density-functional theory (DFT) were performed by using the PWSCF package.⁴ 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 simulations⁵ 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,⁶ to rule out unstable candidates. A $2 \times 2 \times 1$ 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 mixed cation amidoborane compound.

Atom	Site	Х		У		Z	
		Exp	Cal.	Exp.	Cal.	Exp.	Cal.
В	16f	0.5360(7)	0.54704	0.5049(4)	0.50530	0.2351(3)	0.22544
Ν	16f	0.6204(7)	0.62798	0.3769(4)	0.37545	0.2821(3)	0.27531
H1	16f	0.4919	0.51417	0.5843	0.59308	0.3054	0.29385
H2	16f	0.4335	0.43732	0.4588	0.46164	0.1848	0.18294
Н3	16f	0.6098	0.61969	0.5777	0.56678	0.1755	0.15768
H4	16f	0.7066	0.72019	0.4121	0.40725	0.3245	0.31150
Н5	16f	0.6540	0.66140	0.3152	0.31094	0.2201	0.21433
Mg	4a	0.5	0.5	0.25	0.25	0.375	0.375
Na	8 <i>d</i>	0.5	0.5	0.0	0.0	0.0	0.0

Table S1. Experimental and calculated structural parameters of LiNH₂BH₃ (Space group $I4_1/a$ (*origin 2*), No. 88, *a*=9.4114(7) Å, *c*=12.712(1) Å)

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: $U_{Mg}=2.6(2)$, $U_{Mg}=3.4(1)$, $U_B=2.8(3)$, $U_N=1.8(2)$, and $U_H=6.6$ (x100 Å²). [NH₂BH₃⁻] ion (rigid body): Center of the body (center of B-N bond) (0.6204(7), 0.3769(4), 0.2821(3)). Orientation angle about *a*, *b*, *c*axis: 20.7(8)°, 9.3(4)°, -31.0(3)°. B-N distance: 1.571(4) Å, B-H distance (constrained with standard deviation< 0.005Å): 1.236 Å. N-H distance (constrained with standard deviation< 0.005Å): 1.028Å. Table S2. Experimental and Calculated atomic distances of $Na_2Mg(NH_2BH_3)_4$ and comparison with pure NH_3BH_3 , $LiNH_2BH_3$ and $Ca(NH_2BH_3)_2$.

Distances		Length (Å)			
	Na ₂ Mg(NH	2BH3)4	LiNH ₂ BH ₃	Ca(NH ₂ BH ₃) ₂	NH ₃ BH ₃
	Exp.	Cal.	Cal.	Cal.	Cal.
N-B	1.561(4)	1.579	1.547	1.546	1.592
N-H	1.028 ^a	1.029/1.028	1.025	1.025	1.028/1.033
B-H	1.236 ^a	1.235/1.238/1.242	1.243	1.241	1.228/1.221
H _N -H _B	-	2.107/2.211	2.249	2.328	2.027
Mg-N	2.027	2.104	2.063(Li-N)	2.466 (Ca-N)	
Mg-H	-	2.609/2.670			
Na-B	3.009/3.068 /3.550	2.900/3.007 /3.634			
Na-H	-	2.943/2.722 /2.426/2.419/2.383			

^a B-H and N-H bond were constrained.

Figure S1. (a) Experimental (circles), calculated (line), and difference (line below observed and calculated patterns) XRD profiles for $Na_2Mg(NH_2BH_3)_4$ at 298 K. The patterns also contain peaks from small amounts of unreacted MgH₂ and NaNH₃BH₃. Vertical bars indicate the calculated positions of Bragg peaks for $Na_2Mg(NH_2BH_3)_4$, MgH₂ and NH₃BH₃(from the top), respectively. Unreacted NaNH₃BH₃ was not included in the refinement (see from the difference profile).



Figure S2 Observed and first-principles calculated neutron vibrational spectra of $Na_2Mg(NH_2BH_3)_4$. Error bars represent plus and minus the combined standard uncertainty.



The observed phonon bands can be assigned to the rocking and librational modes of B-H (40 meV) and N-H (68-72 meV), B-H and N-H collective librational modes (75 meV)), NH₂-BH₃ bending and waggling modes (106-110 meV), B-N stretching modes (112-113 meV), NH₂BH₃⁻ deformation and torsion modes (135 meV), B-H and N-H bending modes (142-147 meV), and scissoring modes of B-H (150-160 meV) and N-H (197-202 meV). In particular, two vibrational modes are observed at 49 meV and 59 meV, which correspond to the Mg-N stretching modes and the deformation modes of the Mg[NH₂BH₃]₄ tetrahedra, indicating strong and directional Mg-N ionic bonding. In general, the calculated spectra agree well with the observed NV spectra, and thus further support the validity of the determined structure.





Figure S4. TPD results of hydrogen release from $Na_2Mg(NH_2BH_3)_4$ with 2°C/min heating rate to 300°C. The amount of H₂ gas released (top panel) has been normalized as n (H₂ gas)/ mol NH₃BH₃. The hydrogen release rates are shown in the lower panels.



Figure S5. XRD pattern of Na₂Mg(NH₂BH₃)₄ after desorption up to 400°C. Dehydrogenation product of Na₂Mg(NH₂BH₃)₄ is dominated by an amorphous residue and a minor NaBH₄ phase. Pattern also contains reflections of Mg. Mg is the desorption product of MgH₂ from the unreacted precursor.



References:

^{(&}lt;sup>1</sup>) 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.

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