

Structures and Crystal Chemistry of Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$

Hui Wu,^{*,†,‡,§} Wei Zhou,^{†,‡} Terrence J. Udovic,[†]
John J. Rush,^{†,‡} and Taner Yildirim^{†,§}

NIST Center for Neutron Research, Gaithersburg, Maryland
20899, Department of Materials Science and Engineering,
University of Maryland, College Park Maryland 20742,
Department of Materials Science and Engineering,
University of Pennsylvania, Philadelphia,
Pennsylvania 19104

Received November 21, 2007

Revised Manuscript Received January 8, 2008

Intensive investigations have been undertaken to search for new light metal hydrides and complex hydrides that possess high hydrogen-storage capacities. Among these, a series of studies in $(1-x)\text{LiBH}_4 - x\text{LiNH}_2$ systems have attracted great interest.^{1–3} At least four quaternary complex hydride phases with distinct crystalline diffraction peaks have been observed.² Many efforts, both experimentally^{3–6} and theoretically^{7,8} have been made to determine the crystal structure of the most stable phase, $\text{Li}_4\text{BN}_3\text{H}_{10}$, which was observed in a range of $x = 0.66–0.75$. The previously reported structures determined using X-ray and neutron diffraction on hydride samples possess identical space groups and similar lattice parameters. However, the atomic coordinate differences result in bond length discrepancies as large as 0.2 Å. Such unusual bond lengths and the resulting deformed anion groups, if they were true, would cause extra electron transfer and consequently lead to significant changes in the electronic structures, bondings, coordination environments, structure–stability, and properties of this ionic compound. Another composition, Li_2BNH_6 ($x = 0.5$), was also reported to be stable as a single or major phase in the XRD pattern. However, the exact crystal structure has not been correctly determined. Therefore, to understand the composition-dependent structure variations and reveal the potentially interesting chemistry, it is critical to obtain accurate structure information, especially for the hydrogen atoms, which requires high-resolution neutron diffraction data on isotopically labeled (i.e., ^7Li , ^{11}B , and D) samples.

Herein, we present the crystal structures and the neutron vibrational spectra of the quaternary hydrides Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$. Combined high-resolution neutron powder diffraction (NPD), neutron vibrational spectroscopy (NVS) and first-principles calculations allow us to gain more insight into both the structure and dynamics of these novel hydride phases. The NPD samples were isotopically labeled with compositions of $^7\text{Li}_2^{11}\text{BND}_6$ and $^7\text{Li}_3^{11}\text{BN}_2\text{D}_8$. Such labeling avoids the large neutron absorption from natural Li and B and the high incoherent scattering background from H. The compounds were synthesized by mixing stoichiometric ratios (1:1 and 1:2) of isotopically labeled borohydride and amide precursors and afterward annealing at 338 and 413 K, respectively. See the Supporting Information for details.

The crystal structures of Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$ were solved and refined from NPD data. For both isotopically labeled samples, all independent atomic positions, thermal displacements, and lattice parameters were refined without any constraints. The final Rietveld fit of NPD patterns showed excellent goodness of fit and thus gave us explicit and accurate information on the crystal structure, local atomic coordinations, and bond lengths. Details about the structure solution and refinement are in the Supporting Information. For simplicity, we use general symbols Li, B, and H instead of the isotopes ^7Li , ^{11}B , and D in the discussion below. We also emphasize that the refined structures on the isotopically labeled samples essentially do not differ from those with natural elements.

In both Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$, the geometry of the BH_4^- tetrahedra and NH_2^- resulting from the present refinements have nearly ideal configurations. For Li_2BNH_6 , the mean B–H bond length is 1.208 Å and N–H bond lengths are 0.990(7) and 1.034(7) Å. For $\text{Li}_4\text{BN}_3\text{H}_{10}$, the mean B–H bond length is 1.195 Å and N–H bond lengths are 0.996(6) and 1.002(4) Å. All these differ markedly from those in the previous XRD and neutron studies, where the N–H bond lengths were found to be anomalously short, 0.83 Å to 0.86 Å, or the NH_2^- groups were abnormally deformed with an H–N–H bond angle of 126° and a significant difference of N–H lengths as large as 0.1 Å, and the BH_4^- tetrahedra were deformed with one B–H significantly shorter than the other three: The dimensions and configurations of BH_4^- and NH_2^- in the present study are found to be close to those in $^7\text{Li}^{11}\text{BD}_4$ (nearly ideal tetrahedra with a mean B–H distance of 1.214 Å),⁹ and to those in LiND_2 ¹⁰ (0.99 and 1.00 Å), respectively. These bond lengths in $\text{Li}_4\text{BN}_3\text{H}_{10}$ also compare favorably with those from our own and others first-principles calculations. Interestingly, our refined B–H bond lengths indicated that the size of BH_4^- slightly decreases with its concentration in the structure, i.e., from LiBH_4 to Li_2BNH_6 to $\text{Li}_4\text{BN}_3\text{H}_{10}$, the mean B–H length changes from 1.214 to 1.208 Å and to 1.195 Å. After our study on the isotopically labeled samples, we have noticed

* To whom correspondence should be addressed. E-mail: huiwu@nist.gov.

† NIST Center for Neutron Research.

‡ University of Maryland.

§ University of Pennsylvania.

- (1) Pinkerton, F. E.; Meisner, G. P.; Meyer, M. S.; Balogh, M. P.; Kundrat, M. D. *J Phys. Chem. B* **2005**, *109*, 6.
- (2) Meisner, G. P.; Scullin, M. L.; Balogh, M. P.; Pinkerton, F. E.; Meyer, M. S. *J Phys. Chem. B* **2006**, *110*, 4186.
- (3) Noritake, T.; Aohi, M.; Towata, S.; Ninomiya, A.; Nakamori, Y.; Orimo, S. *Appl Phys. A: Mater. Sci. Process.* **2006**, *83*, 277.
- (4) Filinchuk, Y. E.; Yvon, K.; Meisner, G. P.; Pinkerton, F. E.; Balogh, M. P. *Inorg. Chem.* **2006**, *45*, 1433.
- (5) Chater, P. A.; David, W. I. F.; Johnson, S. R.; Edwards, P. P.; Anderson, P. A. *Chem. Commun.* **2006**, *23*, 2439.
- (6) Yang, J. B.; Wang, X. J.; Cai, Q.; Yelon, W. B.; James, W. J. *J. Appl. Phys.* **2007**, *102*, 033507.
- (7) Herbst, J. F.; Hector, L. G., Jr. *Appl. Phys. Lett.* **2006**, *88*, 231904.
- (8) Siegel, D. J.; Wolverson, C.; Ozolins, V. *Phys. Rev. B* **2007**, *75*, 014101.

(9) Hartman, M. R.; Rush, J. J.; Udovic, T. J.; Bowman, R. C., Jr.; Hwang, S. J. *J. Solid State Chem.* **2007**, *180*, 1298.

(10) Nagib, M.; Jacob, H. Z. *Anorg. Allg. Chem.* **1972**, *391*, 271.

a very recent structural study on Li_2BNH_6 from a sample without isotope enrichment.¹¹ The NH_2^- in this structure was found abnormally deformed and the hydrogen positions were declared unreliable due to the poor quality of the neutron data. The apparent discrepancies and the largely deformed BH_4^- and NH_2^- in these studies are due to the light H and Li atoms, complicating artifacts of X-ray interactions with strong N–H bond polarization, the high neutron absorption cross sections associated with naturally occurring Li and B, and the large incoherent neutron scattering cross section of H. Therefore, the B–H and N–H bond lengths from the present NPD study using isotopically labeled samples are more reliable. In addition, we also note that recent NPD structure refinements on samples without ^{11}B enrichment provide incorrect B–H bond lengths and an anomalously short Li–B distance (1.73 Å). Our determined Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$ structures provided a good structural starting point for the theoretical calculations on the electronic structures, phonon density of states, and reaction energetics.

Li_2BNH_6 contains two symmetry-independent Li^+ ions, each coordinated with four anion units (Figure 1). Li1 is surrounded by 3 BH_4^- and 1 NH_2^- . Li2 is coordinated by 3 NH_2^- and 1 BH_4^- . $\text{Li}_4\text{BN}_3\text{H}_{10}$ has three symmetry-independent Li^+ ions, each also tetrahedrally coordinated. Li1 is surrounded by 2 BH_4^- and 2 NH_2^- , Li2 by 3 NH_2^- and 1 BH_4^- , and Li3 by 4 NH_2^- . Interestingly, Li^+ in LiBH_4 and LiNH_2 are all tetrahedrally coordinated by either 4 BH_4^- or 4 NH_2^- . The Li–B and Li–N distances in these compounds are summarized in Table S7 in the Supporting Information. In all these compounds, each anion unit is also surrounded by 4 Li^+ . From Figure 1 (top two rows, right), $\text{Li}_4\text{BN}_3\text{H}_{10}$ can be generated from LiNH_2 through the partial substitution of NH_2^- by BH_4^- (0, $\frac{1}{4}$, and $\frac{1}{2}$ of NH_2^- in one $\text{Li}[\text{NH}_2^-]_4$ -tetrahedron). The local coordination environments of Li^+ in LiNH_2 (there are 8 Li^+ in a unit cell) were changed with BH_4^- substitution, resulting in tetrahedra in one unit cell that are $\frac{3}{8} \text{Li}[\text{NH}_2^-]_4$, $\frac{2}{8} \text{Li}[\text{NH}_2^-]_3[\text{BH}_4^-]_1$, and $\frac{3}{8} \text{Li}[\text{NH}_2^-]_2[\text{BH}_4^-]_2$. Thus, the consequential arrangement with “Li-tetrahedra ordering” can actually be described by a “ $\text{Li}_{32}[\text{BH}_4]_8[\text{NH}_4]_{24}$ ” cubic supercell, four times the original LiNH_2 tetragonal unit cell ($a_c \approx 2a_t \approx c_t$). The larger lattice parameter of $\text{Li}_4\text{BN}_3\text{H}_{10}$ is apparently due to the larger size of BH_4^- . With more BH_4^- substitution, the direct replacement of NH_2^- by BH_4^- would result in a too short distance between neighboring BH_4^- ions. Therefore, the lattice has to make a concerted rearrangement to accommodate the larger BH_4^- anion unit in the structure and maintain an appropriate BH_4^- distance. Figure 2 compares the structure of Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$. The similarities in the structures imply that Li_2BNH_6 can be viewed as an approximate derivative of $\text{Li}_4\text{BN}_3\text{H}_{10}$ by the transformation $a_h \approx \sqrt{2}a_c, c_h \approx \sqrt{3}/2a_c$. Given the BH_4^- and NH_2^- ratio of 18:18 in the hexagonal unit cell, and the volumes of LiBH_4 (52.4 Å³, 5 K) and LiNH_2 (31.9 Å³, 5 K) formula units, the calculated volume of Li_2BNH_6 should be 1516.5 Å³, 107.8 Å³ smaller than the observed value, leaving large voids in the structure. Compared to the relatively densely packed Li-

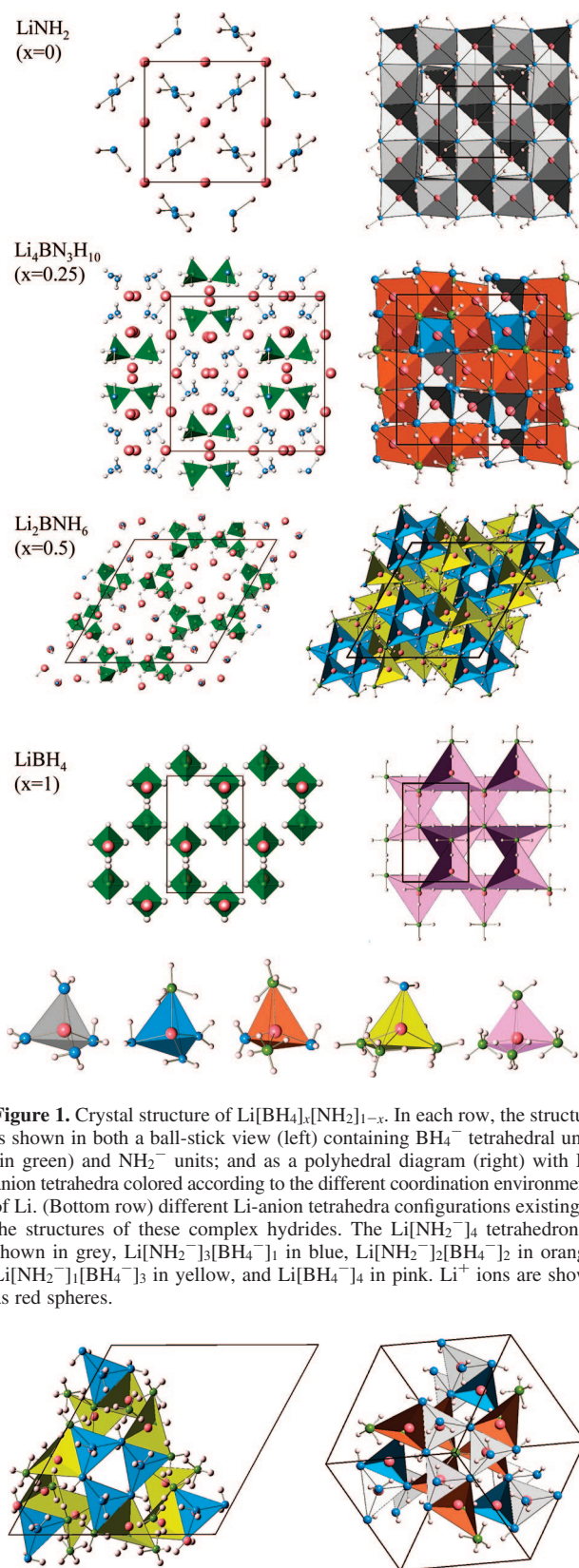


Figure 1. Crystal structure of $\text{Li}[\text{BH}_4]_x[\text{NH}_2]_{1-x}$. In each row, the structure is shown in both a ball-stick view (left) containing BH_4^- tetrahedral units (in green) and NH_2^- units; and as a polyhedral diagram (right) with Li-anion tetrahedra colored according to the different coordination environments of Li. (Bottom row) different Li-anion tetrahedra configurations existing in the structures of these complex hydrides. The $\text{Li}[\text{NH}_2^-]_4$ tetrahedron is shown in grey, $\text{Li}[\text{NH}_2^-]_3[\text{BH}_4^-]_1$ in blue, $\text{Li}[\text{NH}_2^-]_2[\text{BH}_4^-]_2$ in orange, $\text{Li}[\text{NH}_2^-]_1[\text{BH}_4^-]_3$ in yellow, and $\text{Li}[\text{BH}_4^-]_4$ in pink. Li^+ ions are shown as red spheres.

Figure 2. Comparison of structures of (left) Li_2BNH_6 (only half-shown for clarity) and (right) $\text{Li}_4\text{BN}_3\text{H}_{10}$ (viewed in the [111] direction), showing the structural progression upon the replacement of NH_2^- by BH_4^- and the resulting changes in the $\text{Li}[\text{NH}_2^-]_{4-n}[\text{BH}_4^-]_n$ tetrahedra, $n = 0, 1, 2, 3$. The Li tetrahedra with differently combined anions were colored as in Figure 1.

anion tetrahedra arrays in $\text{Li}_4\text{BN}_3\text{H}_{10}$, such large voids in Li_2BNH_6 suggested a less stable structure. Annealing

(11) Chater, P. A.; David, W. I. F.; Anderson, P. A. *Chem. Commun.* **2007**, 4770.

Li_2BNH_6 at 363 K resulted in decomposition into $\text{Li}_4\text{BN}_3\text{H}_{10}$ and LiBH_4 . In addition, a previous phase diagram study indicated that Li_2BNH_6 has a more rigid stoichiometry than the $\text{Li}_4\text{BN}_3\text{H}_{10}$ phase, which was found to exist over a wide solid solution range.

In seeking an explanation for the rigid stoichiometry of Li_2BNH_6 , it is useful to consider the local bonding configurations in all possible types of $\{\text{Li}[\text{BH}_4^-]_n[\text{NH}_2^-]_{4-n}\}$ tetrahedra, $n = 0-4$. Among them, $\text{Li}[\text{BH}_4^-]_2[\text{NH}_2^-]_2$ shows the largest distortion due to the largest difference between BH_4 and NH_2 components (i.e., the largest difference between $\text{Li}-\text{B}$ and $\text{Li}-\text{N}$ distances). Such incompatibility can be accommodated in the $\text{Li}_4\text{BN}_3\text{H}_{10}$ structure through a small displacement of the neighboring ions. For Li_2BNH_6 , as mentioned above, $\text{Li}[\text{BH}_4^-]_1[\text{NH}_2^-]_3$ and $\text{Li}[\text{BH}_4^-]_3[\text{NH}_2^-]_1$ tetrahedra are present. Replacement of NH_2^- by BH_4^- in the former configuration would yield $\text{Li}[\text{BH}_4^-]_2[\text{NH}_2^-]_2$, which would severely compromise the local stability and could not be significantly improved by the displacement of its neighbors because its neighboring tetrahedra have also been converted into this same configuration. Replacement of NH_2^- by BH_4^- in $\text{Li}[\text{BH}_4^-]_3[\text{NH}_2^-]_1$ would not only induce the formation of $\text{Li}[\text{BH}_4^-]_2[\text{NH}_2^-]_2$ but also $\text{Li}[\text{BH}_4^-]_4$. In the latter case, the Li^+ has to move toward the original three BH_4^- to accommodate the new large anion unit, thus further reducing the overall energetic stability. As a result, $\text{Li}[\text{BH}_4^-]_2[\text{NH}_2^-]_2$ tetrahedra are completely avoided in the actual structure of Li_2BNH_6 . In general, any BH_4^- -rich quaternary compositions in the LiBH_4 - LiNH_2 system are expected to be unstable and indeed have not been observed. Complete substitution of NH_2^- by BH_4^- results in the formation of LiBH_4 with the presence of $\text{Li}[\text{BH}_4]_4$ tetrahedra exclusively.

Considering the structure variation from LiNH_2 to Li_2BNH_6 , these novel quaternary $\text{Li}-\text{B}-\text{N}-\text{H}$ phases can actually be viewed as solid solutions with the general formula $\text{Li}[\text{BH}_4]_x[\text{NH}_2]_{1-x}$ via a gradual substitution of BH_4^- for NH_2^- in the binary end member LiNH_2 (see Figure 1). Such a trend is also evident by the increased size of BH_4^- ions with increasing x . The structures of all these phases can thus be generalized as three-dimensional frameworks consisting of corner- and face-shared metal-anion tetrahedra, $\{\text{Li}[\text{BH}_4^-]_n[\text{NH}_2^-]_{4-n}\}$, $n = 0-4$, with Li in the center and various combinations of BH_4^- and NH_2^- units at the vertices. A prior phase diagram study showed there are at least four quaternary phases in LiBH_4 - LiNH_2 . However, the structure investigation of these phases are complicated by their instabilities and uncertainties of stoichiometry. From the present study, we believe the general view of the 3D structural construction with $\{\text{Li}[\text{BH}_4^-]_n[\text{NH}_2^-]_{4-n}\}$ tetrahedra as building units actually provides us new clues to determine the structure and the stoichiometry of the remaining unknown phases.

The neutron vibrational spectra of $\text{Li}_4\text{BN}_3\text{H}_{10}$ and Li_2BNH_6 are shown in Figure 3. The similarities in the spectra indicate some similarities in their structure. According to our first-

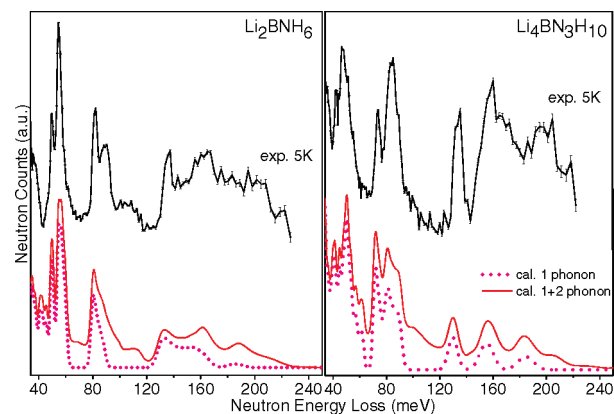


Figure 3. Neutron vibrational spectra and calculated phonon modes of Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$.

principles phonon calculations, the observed bands can be assigned to $\text{N}-\text{H}$ (80–90 meV, 180–190 meV) and $\text{B}-\text{H}$ (130–165 meV) bending and deformation modes, NH_2^- and BH_4^- collective and independent librational modes (53–65 meV), and low-frequency lattice modes. Some vibrations of BH_4^- and NH_2^- in the energy range below 60 meV are also found to be coupled with the motions of Li^+ . The calculated phonon modes agree reasonably well with the observed NV spectra for both compounds and thus are consistent with our determined structures. From the calculations, the $\text{B}-\text{H}$ stretching modes in these quaternary hydrides are within the same $\text{B}-\text{H}$ stretching region of LiBH_4 and $\text{Mg}(\text{BH}_4)_2$,¹² suggesting similar $\text{B}-\text{H}$ bond lengths in these borohydrides, in agreement with the refined $\text{B}-\text{H}$ distances.

In summary, the crystal structures of Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$ were correctly determined and refined using high-resolution neutron powder diffraction data on $^7\text{Li}_2^{11}\text{BND}_6$ and $^7\text{Li}_4^{11}\text{BN}_3\text{D}_{10}$. The present structures explicitly show the nearly ideal configurations for both BH_4^- and NH_2^- , clarifying the large discrepancies in the prior reports on artificial anion distortions and inaccurate bond distances. These novel quaternary $\text{Li}-\text{B}-\text{N}-\text{H}$ phases can be viewed as 3D frameworks with a general solid-solution formula $\text{Li}[\text{BH}_4]_x[\text{NH}_2]_{1-x}$, built up by corner- and face-shared $\{\text{Li}[\text{BH}_4^-]_n[\text{NH}_2^-]_{4-n}\}$ tetrahedra and formed via a gradual substitution of BH_4^- for NH_2^- from LiNH_2 to LiBH_4 .

Acknowledgment. We thank Prof. Michael Hartman (University of Michigan) for generously providing $^7\text{Li}^{11}\text{BD}_4$. This work was partially supported by the DOE through EERE Grant DE-AI-01-05EE11104 (T.J.U.) and BES Grant DE-FG02-98ER45701 (T.Y.)

Supporting Information Available: Details on materials synthesis, neutron experiments, structure data, and first-principles calculations; summary of all the reported $\text{Li}_4\text{BN}_3\text{H}_{10}$ structures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM703315E