A Series of Mixed-Metal Borohydrides**

Dorthe Ravnsbæk, Yaroslav Filinchuk,* Yngve Cerenius, Hans J. Jakobsen,
Flemming Besenbacher, Jørgen Skibsted, and Torben R. Jensen*

The transition towards a sustainable and reliable energy system capable of meeting the increasing energy demands is considered one of the greatest challenges in the 21st century. However, one of the major obstacles is that renewable energy sources are unevenly distributed both geographically and over time, and most countries need to integrate several different sources. Hydrogen is a potential, extremely interesting energy carrier system,[1] but a major challenge in a future "hydrogen economy" is the development of a safe, compact, robust, and efficient means of hydrogen storage, in particular for mobile applications.[2] No single material has yet been identified that fulfills all the criteria for hydrogen storage, despite considerable research and technological efforts.[3]

Borohydride-based materials have recently received great attention owing to their high gravimetric hydrogen contents, but the utilization of this class of materials in real, practical technological applications is often hampered by unfavorable thermodynamic and kinetic properties.[4,5] Much research has focused on improving the properties of known interesting hydrogen storage materials such as $LiBH_4$, which possesses an extremely high hydrogen content (18.4 wt%) but unfortunately has a high enthalpy of decomposition (-67 kJ mol^{-1}) and therefore a high decomposition temperature. Thus, researchers have tried to improve the thermodynamic properties by design of a reactive hydride composite $2 LiBH_4/MgH_2$, which reduces the enthalpy of decomposition from -67 to -42 kJ mol^{-1} and which is still capable of reversibly storing 11.5 wt% H_2.[6,7] Recently, cation substitution in $LiBH_4$ has also been realized by, for example, the synthesis of LiK-$(BH_4)_2$, which unfortunately possesses the same high thermodynamic stability as $LiBH_4$ and KBH_4.[8] The kinetic properties of alanates ($[AlH_4]^-$)[9] and magnesium-based systems have been successfully improved by the exploitation of a variety of catalytic additives, but these materials appear less efficient than borohydride-based systems owing to their high chemical reactivity.[10] Numerous other improvements of known materials have been explored, for example, incorporation of $LiBH_4$ into nanoporous scaffolds,[11] but there has been no major breakthrough that allows the synthesis of ideal hydrogen storage materials with high hydrogen content, low hydrogen decomposition temperature (i.e. appropriate thermodynamic properties), and fast "refueling" of the material (i.e. good kinetic properties). Therefore, there is a great need for new types of compounds, such as ternary borohydrides involving a combination of very different elements, such as alkali metals and transition metals.[12]

Herein, we report the synthesis and detailed structural, physical, and chemical characterization of a new series of borohydride-based materials, $LiZn_2(BH_4)_5$, $NaZn_2(BH_4)_5$, and $NaZn(BH_4)_3$. These materials have completely novel structures, very high hydrogen contents, and low decomposition temperatures (Table 1). Our findings are useful as

[*] Dr. Y. Filinchuk
Swiss–Norwegian Beam Lines at ESRF
BP-220, 38043 Grenoble (France)
Fax: (+33) 476-88-2694
E-mail: yaroslav.filinchuk@esrf.fr

D. Ravnsbæk, Prof. H. J. Jakobsen, Dr. J. Skibsted, Dr. T. R. Jensen
Interdisciplinary Nanoscience Center (iNANO) and
Department of Chemistry, University of Aarhus
8000 Aarhus C (Denmark)
Fax: (+45) 8619-6199
E-mail: trj@chem.au.dk

Dr. Y. Cerenius
MAX-lab, Lund University, 22100 Lund (Sweden)

Prof. F. Besenbacher
Interdisciplinary Nanoscience Center (iNANO) and
Department of Physics and Astronomy
University of Aarhus, 8000 Aarhus C (Denmark)

Table 1: Structural data, hydrogen content, and decomposition temperatures for the new alkali-metal zinc borohydrides.

	$LiZn_2(BH_4)_5$	$NaZn_2(BH_4)_5$	$NaZn(BH_4)_3$
space group	*Cmca*	*P2$_1$/c*	*P2$_1$/c*
a [Å]	8.6244(3)	9.397(2)	8.2714(16)
b [Å]	17.8970(8)	16.635(3)	4.5240(7)
c [Å]	15.4114(8)	9.1359(16)	18.757(3)
β [°]	90	112.658(19)	101.689(11)
Z	8	4	4
V [Å^3]	2378.76(19)	1318.0(5)	687.3(2)
M [g mol^{-1}]	211.93	227.98	132.91
ρ [g cm^{-3}]	1.18	1.15	1.28
$\rho_v(H_2)$ [kg H$_2$ m^{-3}]	112.6	101.6	116.9
$\rho_m(H_2)$ [wt%]	9.51	8.84	9.10
T_{dec} [°C]	127	95	103

general guidelines and inspiration for the design and synthesis of novel materials for hydrogen storage.

Mechanochemical methods, such as ball milling (BM), are among the most commonly used preparative methods for synthesis of borohydride hydrogen storage materials. Several chemical reactions may occur simultaneously during BM,

depending on the physical and chemical conditions, and usually a mixture of phases is obtained. We have synthesized lithium and sodium zinc borohydrides according to the reaction in Equation (1):

$$5 \, MBH_4 + 2 \, ZnCl_2 \rightarrow MZn_2(BH_4)_5 + 4 \, MCl \quad (M = Li \, or \, Na) \qquad (1)$$
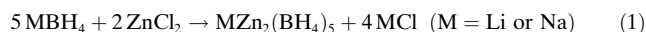
The ideal $LiBH_4$:$ZnCl_2$ ratio of 2.5:1 gives complete conversion to $LiZn_2(BH_4)_5$, which is the only new phase observed for other ratios as well. In the $NaBH_4$/$ZnCl_2$ system a competitive reaction [Eq. (2)] occurs, and mixtures of $NaZn_2(BH_4)_5$ and $NaZn(BH_4)_3$ are obtained for different $NaBH_4$:$ZnCl_2$ ratios. $ZnCl_2$-rich compositions also yield Na_2ZnCl_4 as one of the products.

$$3 \, NaBH_4 + ZnCl_2 \rightarrow NaZn(BH_4)_3 + 2 \, NaCl \qquad (2)$$
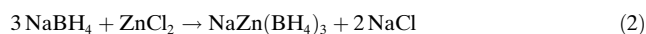
The new M-Zn-BH_4 phases reveal remarkable structural diversity, as shown by synchrotron radiation powder X-ray diffraction (SR-PXD). They represent two novel types of structures, $NaZn(BH_4)_3$ and $MZn_2(BH_4)_5$, which have no distinct analogues among other known inorganic compounds. The structure of $NaZn_2(BH_4)_5$ was identified as a monoclinically distorted derivative of the lithium-containing analogue. Two independent zinc atoms in $MZn_2(BH_4)_5$ (M = Li, Na) have nearly planar trigonal coordination (coordination number CN = 3) by three BH_4 groups, similar to the Be atoms in $Be(BH_4)_2$.[13] The Li and Na atoms in these two related structures have a saddle-like coordination (CN = 4), which has not been observed earlier for alkali-metal atoms in borohydrides.[5] All BH_4 groups in $MZn_2(BH_4)_5$ are linearly coordinated by two metal atoms (the angles in the two structures cover the range 164.5(16)–179.6(8)°), similar to the $Mg(BH_4)_2$ structures.[14–16] The BH_4 groups are coordinated through the two opposite tetrahedral edges, bridging either two Zn atoms or one Zn and one M atom.

It is remarkable that $MZn_2(BH_4)_5$ consists of two identical doubly interpenetrated three-dimensional (3D) frameworks, which implies that there are no covalent bonds between them (Figure 1 and Supporting Information, Table S1). This type of structural topology is common for coordination polymers involving organic ligands, also known as metal–organic frameworks (MOFs),[17] but here it is observed for the first time in metal hydrides. This similarity to MOFs suggests directionality and some covalent character of the metal–BH_4 interaction. Indeed, the Zn−H bonds in $LiZn_2(BH_4)_5$ are very short; the refined distances are all below 2 Å, reaching 1.652(15) Å at the lower limit. Zn−B contacts are also very short (2.108(10)–2.312(9) Å). The average Zn−B distance of 2.17 Å in $LiZn_2(BH_4)_5$ is longer than the corresponding 1.97 Å average in $Be(BH_4)_2$ for the trigonally coordinated Be atom,[13] but it is considerably shorter than in all other metal borohydrides.[5] It was recently found that the three-dimensional framework in $Mg(BH_4)_2$ contains empty voids large enough to accommodate small molecules like H_2O.[16] $MZn_2(BH_4)_5$ structures, although not porous, reveal another case of strong and directional metal–BH_4 bonding that defines the structural architecture.

The Zn atoms in $NaZn(BH_4)_3$ have a distorted tetrahedral coordination with CN = 4, while the saddle-like coordination of the Na atom by BH_4 groups is similar to that in $MZn_2(BH_4)_5$. Metal atoms and BH_4 groups in $NaZn(BH_4)_3$ form a 3D framework. The change in coordination number from three to four for Zn leads to much longer Zn−B separations, varying from 2.43(6) to 3.16(6) Å. The average Zn−B separation of 2.74 Å in $NaZn(BH_4)_3$ is much longer than the 2.42 Å average of the Mg−B separation in hexagonal $Mg(BH_4)_2$, in which the metal atoms are also tetrahedrally coordinated by the BH_4 groups.[16] Interestingly, while one of
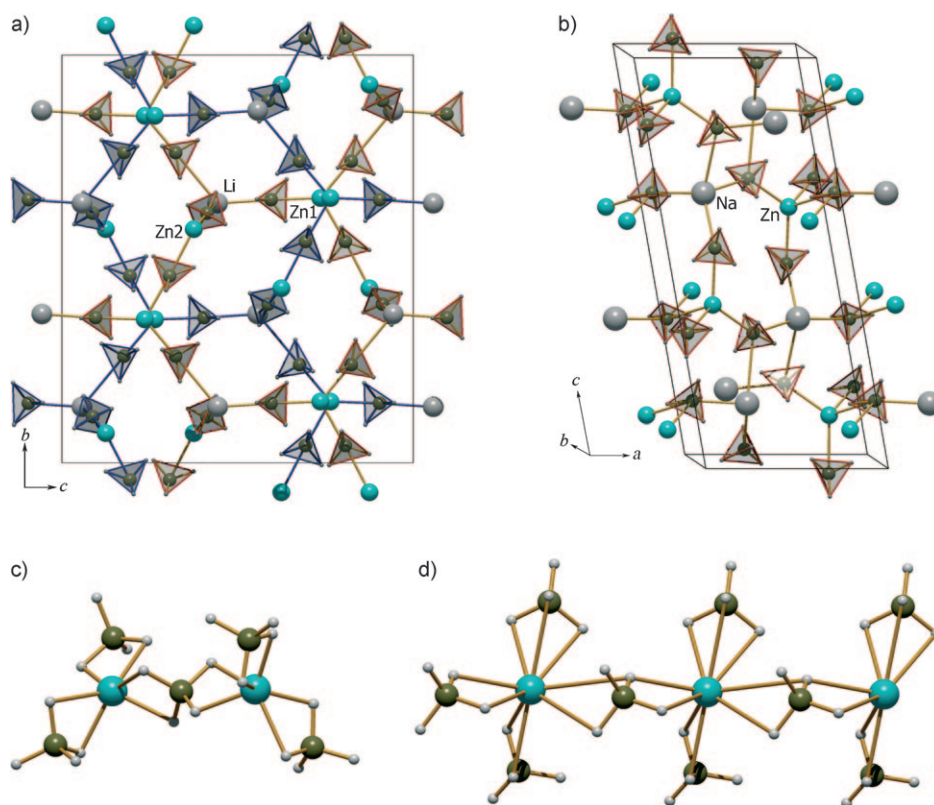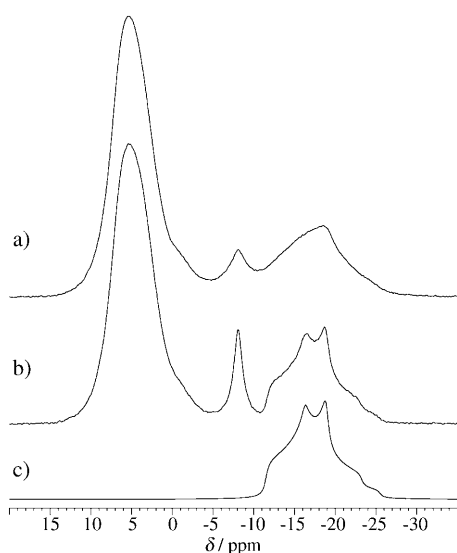

Figure 1. Crystal structures of a) $LiZn_2(BH_4)_5$ and b) $NaZn(BH_4)_3$. The doubly interpenetrated three-dimensional framework is highlighted in blue and light brown. c) Zn^{2+} and $[BH_4]^-$ units are strongly associated into isolated $[Zn_2(BH_4)_5]^-$ ions of trigonal-planar Zn centers in the Zn-rich $MZn_2(BH_4)_5$ compounds. d) The more alkali-metal-rich $NaZn(BH_4)_3$ contains 1D anionic $[\{Zn(BH_4)_3\}_n]^{n-}$ chains with tetrahedrally coordinated Zn atoms. Zn blue, B brown, M dark gray (M = Li, Na), H light gray.

the BH$_4$ groups in NaZn(BH$_4$)$_3$ exhibits a nearly linear coordination by two metal atoms, the other two show trigonal-planar coordination. The latter is quite unusual, as it has been observed only in β-Ca(BH$_4$)$_2$.[18,19]
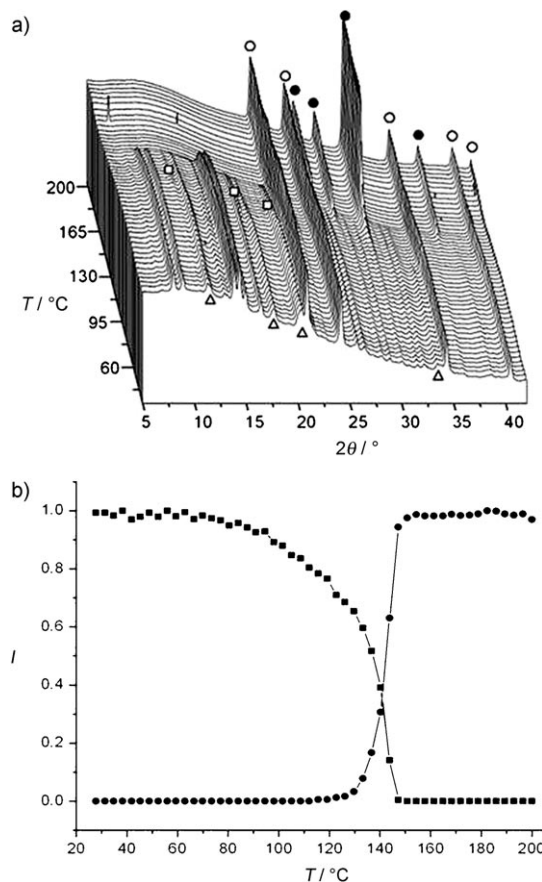
The M/Zn/BH$_4$ phases were also characterized using ^{7}Li, ^{11}B, and ^{23}Na magic-angle spinning (MAS) NMR spectroscopy. Generally, the ^{11}B resonances from these borohydride units exhibit a small, characteristic shift towards lower frequency ($\delta(^{11}$B$) \approx -42$ to -46 ppm) compared to the corresponding resonances from LiBH$_4$ ($\delta(^{11}$B$) = -41.2$ ppm) and NaBH$_4$ ($\delta(^{11}$B$) = -42.0$ ppm), which may reflect the coordination to the Zn^{2+} ions. An ^{11}B MQMAS NMR spectrum[20] of the NaZn(BH$_4$)$_3$ sample resolves two resonances in a 1:2 ratio, which indicates that two of the three distinct ^{11}B sites are quite similar. The complexity of the reaction products is apparent from the ^{23}Na MAS NMR spectrum of the NaZn(BH$_4$)$_3$ sample (Figure 2b), which shows overlapping resonances for the two ^{23}Na sites in Na$_2$ZnCl$_4$ and the single site from NaCl in the range -2 to 10 ppm, a resonance from NaBH$_4$ at $\delta(^{23}$Na$) = -8.4$ ppm, and a peak with second-order quadrupolar lineshape for a single ^{23}Na site in NaZn(BH$_4$)$_3$ at lower frequency. This distinct lineshape, as demonstrated by the simulation (Figure 2c), shows that NaZn(BH$_4$)$_3$ is present in the sample as a highly crystalline phase, while the observation of a unique ^{23}Na site is in agreement with the crystal structure derived from SR-PXD (Figure 1). The additional line broadening for NaZn(BH$_4$)$_3$ in the spectrum recorded without ^{1}H decoupling (Figure 2a) and the low-frequency shift of the resonance demonstrate that the Na$^+$ ion is coordinated to the [BH$_4$]$^-$ units.

The decomposition of all synthesized new materials was investigated by in situ SR-PXD (Figure 3a). The diffracted intensities from selected phases were integrated and normalized (Figure 3b) to reveal changes in the relative amounts of the individual phases. In general, diffraction lines of MZn$_2$-

Figure 3. a) In situ SR-PXD data measured for LiZn$_2$(BH$_4$)$_5$ heated from room temperature to 200°C, $\Delta T/\Delta t = 4$°C min^{-1}, and $\lambda = 1.06476$ Å. The integrated normalized intensities for selected reflections of LiZn$_2$(BH$_4$)$_5$ and Zn are shown in (b) to visualize the decomposition reactions. Symbols: ○ LiCl, ● Zn, □ Li$_2$ZnCl$_4$, △ ZnCl$_2$. Unmarked peaks in (a) and ■ in (b) refer to LiZn$_2$(BH$_4$)$_5$.

(BH$_4$)$_5$, MCl, and occasionally small amounts of ZnCl$_2$ (and Na$_2$ZnCl$_4$ for M = Na) are visible in the powder patterns. Formation of M$_2$ZnCl$_4$ from MCl and ZnCl$_2$ is also observed. The main phase MZn$_2$(BH$_4$)$_5$ decomposes to metallic zinc and MBH$_4$ (see Table 1 for decomposition temperatures). Simultaneously, the produced MBH$_4$ reacts with M$_2$ZnCl$_4$ to form Zn and MCl. Diffraction from NaBH$_4$ is observed in a short temperature interval during the decomposition of NaZn$_2$-(BH$_4$)$_5$. As indicated, the decomposition of MZn$_2$(BH$_4$)$_5$ occurs through several coupled reactions, which overall can be described by the reaction in Equation (3):

$$2\,MZn_2(BH_4)_5 + M_2ZnCl_4 \rightarrow 5\,Zn + 4\,MCl + 5\,B_2H_6 + 5\,H_2 \qquad (3)$$
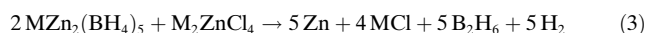
for M = Li and Na. The formation of diborane is verified by thermogravimetric analysis (TGA), which gave calculated and observed mass losses of 16.5 and 14.6%, respectively.

Figure 2. ^{23}Na MAS NMR spectra (7.05 T) of the sample including NaZn(BH$_4$)$_3$ obtained a) without and b) with high-power ^{1}H decoupling ($\gamma B_2/2\pi \approx 100$ kHz) using a spinning speed of 10.0 kHz. c) Optimized simulation of the central transition for the unique ^{23}Na site in NaZn-(BH$_4$)$_3$, corresponding to the isotropic chemical shift $\delta_{iso} = -11.2(2)$ ppm (relative to 1.0 M NaCl(aq)), and the quadrupole coupling parameters $C_Q = 1.16(5)$ MHz, $\eta_Q = 0.63(2)$.

Communications

Furthermore, $LiZn_2(BH_4)_5$ was found to decompose slowly at room temperature when stored in argon atmosphere. In argon atmosphere $LiZn_2(BH_4)_5$ turns gray owing to the formation of metallic zinc after approximately one week at room temperature or several months at $-35\,°C$. The other new material, $NaZn_2(BH_4)_5$, was found to slowly decompose to $NaZn(BH_4)_3$ both at room temperature and at $-32\,°C$. At elevated temperatures the thermal decomposition of $NaZn_2(BH_4)_5$ and $NaZn(BH_4)_3$ occurs in a similar manner to that described above for $LiZn_2(BH_4)_5$, that is, first $NaBH_4$ is formed, which then reacts with Na_2ZnCl_4 (at ca. $110\,°C$), and the final products are Zn and $NaCl$. In a previous study of a ball-milled $2\,NaBH_4/ZnCl_2$ sample, assigned to $Zn(BH_4)_2$, the mass spectroscopic measurements revealed evolution of diborane at $T > 85\,°C$.[21] Our studies indicate that the sample investigated in that work mainly consisted of $NaZn_2$-$(BH_4)_5$ and that $Zn(BH_4)_2$ has not yet been isolated.

The significant structural diversity and low decomposition temperatures for the novel series of alkali-metal zinc borohydrides may be attributed to the ability to form more covalent bonds between Zn and BH_4 units than $M-BH_4$ bonds in alkali-metal borohydrides. The Pauling electronegativity of zinc is higher than those of the alkali metals, and this difference may contribute to the lower stability of Zn-based borohydrides. An apparent linear correlation between Pauling electronegativities and decomposition temperatures for borohydrides has been found,[22] which suggests that metals with a lower electronegativity should be used in borohydride materials. In the Zn-rich $MZn_2(BH_4)_5$, Zn and BH_4 units are strongly associated in isolated $[Zn_2(BH_4)_5]^-$ anions (Figure 1c) with M^+ countercations, similar to the isolated $[Sc(BH_4)_4]^-$ units in $LiSc(BH_4)_4$.[23,24] This arrangement stabilizes the phase, thereby enabling its synthesis at room temperature. The more alkali-metal-rich $NaZn(BH_4)_3$ is even more stable, although it contains 1D anionic $[\{Zn(BH_4)_3\}_n]^{n-}$ chains based on longer $Zn\cdots B$ distances. Variation in the ratio between the alkali metal and the transition metal, as well as the use of different metals, enables tuning of the hydrogen storage properties in alkali-metal/transition-metal/BH_4 systems. Therefore, a variety of novel mixed-cation transition-metal-based borohydrides may be discovered in the near future.

Experimental Section

The materials were prepared from MBH_4 (M = Li or Na) and $ZnCl_2$ mixed in the molar ratios 2:1, 3:1, and 4:1 and ball milled for 120 min in argon atmosphere. All handling and manipulation of the chemicals were performed in argon-filled gloveboxes.

Solid-state ^{11}B and ^{23}Na MAS and MQMAS NMR spectra were obtained on Varian INOVA-300 (7.05 T) and 400 (9.39 T) spectrometers using home-built CP/MAS NMR probes for 5 mm outer diameter (o.d.) rotors. The NMR experiments were performed at ambient temperatures using air-tight end-capped zirconia rotors, which were packed with the sample in the Ar-filled glovebox. Simulations of the MAS NMR spectra were performed using the STARS software package.[25]

Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed, and the decomposition temperatures were measured as the onset temperatures observed by DSC (heating rate $2\,°C\,min^{-1}$, RT to $450\,°C$, helium atmosphere, corundum crucibles).

The samples were initially investigated by powder X-ray diffraction ($Cu_{K\alpha_1}$ radiation) and subsequently by synchrotron radiation powder X-ray diffraction (SR-PXD). Data were collected at beamline BM01A at the European Synchrotron Radiation Facility, Grenoble, France. An MAR345 detector was used, and the selected X-ray wavelengths were 0.769748 and 0.699846 Å. All 2D SR-PXD data were integrated into 1D patterns. Structures of $LiZn_2(BH_4)_5$ and $NaZn(BH_4)_3$ were solved ab initio from PXD data. The structures were solved by direct-space methods using simulated annealing in the program FOX[26] and refined by the Rietveld method. The structure of $NaZn_2(BH_4)_5$ was identified as a monoclinically distorted derivative of the Li-containing analogue and refined by the Rietveld method. The agreement factors are: R_{wp} (not corrected for background) = 1.09%, R_p (corrected for background) = 5.30%, R_B = 3.56% for $LiZn_2(BH_4)_5$; R_{wp} = 3.22%, R_p = 9.39%, R_B = 7.51% for $NaZn_2(BH_4)_5$; R_{wp} = 3.23%, R_p = 12.1%, R_B = 7.27% for $NaZn$-$(BH_4)_3$. Cell parameters and space-group symmetry for the three new phases are listed in Table 1.

In situ time-resolved SR-PXD data were collected at I711 at the synchrotron MAX II, Lund, Sweden in the research laboratory MAX-Lab (1.09 mm o.d. sapphire tubes, $\lambda = 1.0648$ Å, RT to $200\,°C$, heating rate $4\,°C\,min^{-1}$).

[1] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353–358.
[2] M. Felderhoff, C. Weidenthaler, R. von Helmolt, U. Eberle, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2643–2653.
[3] W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283–1315.
[4] S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.* **2007**, *107*, 4111–4132.
[5] Y. Filinchuk, D. Chernyshov, V. Dmitriev, *Z. Kristallogr.* **2008**, *223*, 649–659.
[6] J. J. Vajo, S. L. Skeith, F. Mertens, *J. Phys. Chem. B* **2005**, *109*, 3719–3722.
[7] U. Bösenberg, S. Doppiu, L. Mosegaard, G. Barkhordarian, N. Eigen, A. Borgschulte, T. R. Jensen, Y. Cerenius, O. Gutfleisch, T. Klassen, M. Dornheim, R. Bormann, *Acta Mater.* **2007**, *55*, 3951–3958.
[8] E. A. Nickels, M. O. Jones, W. I. F. David, S. R. Johnson, R. L. Lowton, M. Sommariva, P. P. Edwards, Angew. Chem. 2008, 120, 2859–2861; Angew. Chem. Int. Ed. 2008, 47, 2817–2819.
[9] B. C. Hauback, *Z. Kristallogr.* **2008**, *223*, 636–648.
[10] L. Mosegaard, B. Moller, J. E. Jørgensen, Y. Filinchuk, Y. Cerenius, J. C. Hanson, E. Dimasi, F. Besenbacher, T. R. Jensen, *J. Phys. Chem. C* **2008**, *112*, 1299–1303.
[11] A. F. Gross, J. J. Vajo, S. L. Van Atta, G. L. Olson, *J. Phys. Chem. C* **2008**, *112*, 5651–5657.
[12] H.-W. Li, S. Orimo, Y. Nakamori, K. Miwa, N. Ohba, S. Towata, A. Zuttel, *J. Alloys Compd.* **2007**, *446–447*, 315–318.
[13] D. S. Marynick, W. N. Lipscomb, *Inorg. Chem.* **1972**, *11*, 820–823.
[14] R. Černý, Y. Filinchuk, H. Hagemann, K. Yvon, *Angew. Chem.* **2007**, *119*, 5867–5869; *Angew. Chem. Int. Ed.* **2007**, *46*, 5765–5767.
[15] J. H. Her, P. W. Stephens, Y. Gao, G. L. Soloveichik, J. Riissenbeek, M. Andrus, J. C. Zhao, *Crystallogr. Sect. B* **2007**, *63*, 561–568.
[16] Y. Filinchuk, R. Černý, H. Hagemann, *Chem. Mater.* **2009**, *21*, 925–933.

[17] T. K. Maji, R. Matsuda, S. A. Kitagawa, *Nat. Mater.* **2007**, *6*, 142 – 148.

[18] F. Buchter, Z. Lodziana, A. Remhof, O. Friedrichs, A. Borgschulte, P. Mauron, A. Züttel, D. Sheptyakov, G. Barkhordarian, R. Bormann, K. Chlopek, M. Fichtner, M. Sørby, M. Riktor, B. Hauback, S. Orimo, *J. Phys. Chem. B*, **2008**, *112*, 8042 – 8048.

[19] Y. Filinchuk, E. Rönnebro, D. Chandra, *Acta Mater.* **2009**, *57*, 732 – 738.

[20] L. Frydman, J. S. Harwood, *J. Am. Chem. Soc.* **1995**, *117*, 5367 – 5368.

[21] E. Jeon, Y. W. Cho, *J. Alloys Compd.* **2006**, *422*, 273 – 275.

[22] Y. Nakamori, K. Miwa, A. Ninomiay, H. Li, N. Ohba, S. Towata, A. Zuttel, S. Orimo, *Phys. Rev. B* **2006**, *74*, 045126.

[23] H. Hagemann, M. Longhini, J. W. Kaminski, T. A. Wesolowski, R. Černý, N. Penin, M. H. Sørby, B. C. Hauback, G. Severa, C. M. Jensen, *J. Phys. Chem. A* **2008**, *112*, 7551 – 7555.

[24] S. J. Hwang, R. C. Bowman, J. W. Reiter, J. Rijssenbeek, G. L. Soloveichik, J. C. Zhao, H. Kabbour, C. C. Ahn, *J. Phys. Chem. C* **2008**, *112*, 3164 – 3169.

[25] J. Skibsted, N. C. Nielsen, H. Bildsøe, H. J. Jakobsen, *J. Magn. Reson.* **1991**, *95*, 88 – 117.

[26] V. Favre-Nicolin, R. Černý, *J. Appl. Cryst.* **2002**, *35*, 734 – 743.