

Tuning the Decomposition Temperature in Complex Hydrides: Synthesis of a Mixed Alkali Metal Borohydride**

E. Anne Nickels, Martin Owen Jones, William I. F. David,* Simon R. Johnson, Rebecca L. Lowton, Marco Sommariva, and Peter P. Edwards*

Metal borohydrides continue to attract considerable interest as potential hydrogen storage materials owing to their very large gravimetric hydrogen densities. In terms of the equally important performance parameter, the thermal decomposition temperature T_{dec} , it has emerged^[1–3] that the degree of charge transfer between the metal cation and the BH_4^- anion is a key component for any ultimate materials design. Although manipulation of T_{dec} in single-cation borohydrides is clearly limited by the intrinsic properties of the individual metal (its characteristic electronegativity, for example), double and multiple cation substitution allows more extensive and precise control of T_{dec} . Although this approach is supported by bulk thermochemical studies,^[4,5] there are few X-ray structural investigations of double cation substitutions in these important materials. Such structural information is key to assessing whether genuine new multinary compounds are formed, or whether microscopic segregation of constituent phases takes place. Herein we report the first synthesis and crystal structure determination of a mixed alkali metal borohydride, $\text{LiK}(\text{BH}_4)_2$. Importantly in this new material, the observed decomposition temperature lies between that of the constituent phases. This finding of a genuine, dual-cation single-phase material offers the real prospect of chemical control of T_{dec} by the manipulation of multication combinations.

X-ray diffraction data of thirteen samples with varying initial ratio $\text{LiBH}_4:\text{KBH}_4$ were collected. $\text{LiK}(\text{BH}_4)_2$ (see Figure 1) was identified from the data as having the space group $Pnma$ and approximate lattice parameters $a = 7.9134 \text{ \AA}$, $b = 4.4907 \text{ \AA}$, and $c = 13.8440 \text{ \AA}$. The b -axis lattice parameter is very similar to that of orthorhombic LiBH_4

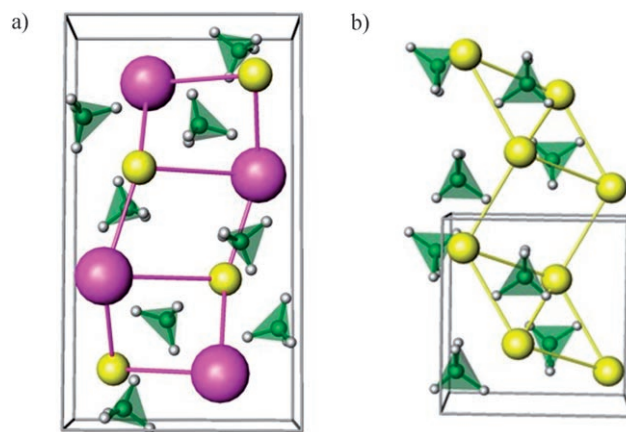


Figure 1. A schematic diagram of a) the proposed $\text{LiK}(\text{BH}_4)_2$ structure and b) that of orthorhombic LiBH_4 . K crimson, Li yellow, B green, H gray.

($4.43686(2) \text{ \AA}$ ^[6]), suggesting a degree of structural similarity between the phases.

The BH_4^- units in $\text{LiK}(\text{BH}_4)_2$ form an approximately tetrahedral coordination around the lithium ion, which is similar to that found in orthorhombic LiBH_4 . The Li–B bonds are greater in $\text{LiK}(\text{BH}_4)_2$ than in LiBH_4 but with a narrower range of angles (see Supporting Information). The larger Li···B separations observed in the new phase may originate from the presence of potassium cations in the structure, which are considerably larger than their lithium counterparts (Li^+ ionic radius $0.59 \text{ \AA}$, K^+ ionic radius $1.38 \text{ \AA}$ in tetrahedral coordination).^[7]

The arrangement of the BH_4^- units in $\text{LiK}(\text{BH}_4)_2$ and KBH_4 differs considerably. KBH_4 has an octahedral arrangement of BH_4^- units, whereas those in $\text{LiK}(\text{BH}_4)_2$ might be best described as monocapped trigonal prisms (see Supporting Information).

The K···B distances in KBH_4 are $3.364 \text{ \AA}$,^[8] whereas in $\text{LiK}(\text{BH}_4)_2$ the (seven) distances are $3.404(3)(18) \text{ \AA}$ (twice), $3.409(3) \text{ \AA}$ (twice), $3.431(3) \text{ \AA}$ (twice), and $3.475(3) \text{ \AA}$ (once). It is thought that these larger separations arise because of the greater number of BH_4^- units present around the potassium cation.

The BH_4^- units in $\text{LiK}(\text{BH}_4)_2$ appear to be distorted in a similar manner to those reported in the orthorhombic structure of LiBH_4 by Soulie et al.^[6] (see Supporting Information). Specifically, while KBH_4 has all equivalent B–H bonds,^[8] those in orthorhombic LiBH_4 ^[6] and $\text{LiK}(\text{BH}_4)_2$ are separated into two equivalent pairs. $\text{LiK}(\text{BH}_4)_2$ was found to have a narrower range of B–H bond lengths than LiBH_4

[*] Prof. W. I. F. David, Dr. M. Sommariva
ISIS Facility
Rutherford Appleton Laboratory
Chilton, Didcot, Oxon, OX11 0QX (UK)
Fax: (+44) 1235-445-720
E-mail: bill.david@rl.ac.uk

E. A. Nickels, Dr. M. O. Jones, Dr. S. R. Johnson, R. L. Lowton,
Prof. P. P. Edwards
Inorganic Chemistry Laboratory
University of Oxford
South Parks Road, Oxford, OX1 3QR (UK)
Fax: (+44) 1865-272-656
E-mail: peter.edwards@chem.ox.ac.uk

[**] We wish to thank Prof. Andy Fitch and Dr. Michela Brunelli for assistance at the ESRF, Grenoble. E.A.N., R.L.L., P.P.E., M.O.J., and S.R.J. acknowledge RAL and the EPSRC for funding.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

(0.1354 Å compared with 0.2512 Å in LiBH_4). This intermediate level of distortion is consistent with the “mean electronegativity” asserted by the mixed lithium and potassium ions compared to that exerted by a single cation as suggested by Du et al.^[9] Recent work by Hartman et al. suggests that this distortion may be as a result of increased librational and dynamical distortion as the high temperature phase transition is approached.^[10]

The new phase, $\text{LiK}(\text{BH}_4)_2$, is present across the full range of the reaction series, and lattice constants for $\text{LiK}(\text{BH}_4)_2$ remain constant to one decimal place for all precursor ratios, with the optimal $\text{LiK}(\text{BH}_4)_2$ yield obtained for a precursor ratio of 2:1 $\text{LiBH}_4/\text{KBH}_4$. This result appears anomalous, as it would be expected that a 1:1 ratio of precursors would produce single phase $\text{LiK}(\text{BH}_4)_2$. Further studies to explain this observation, elucidate the mechanism of $\text{LiK}(\text{BH}_4)_2$ formation, and obtain pure-phase $\text{LiK}(\text{BH}_4)_2$ are currently underway.

Preliminary gravimetric analysis (Figure 2) of the decomposition of $\text{LiK}(\text{BH}_4)_2$ from a sample with LiBH_4 and KBH_4 impurities (77.5wt % $\text{LiK}(\text{BH}_4)_2$, 11.2wt % LiBH_4 and

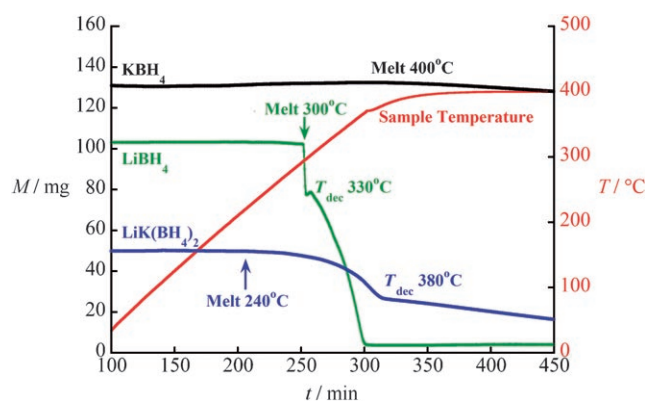


Figure 2. Thermogravimetric data (y axis on left) and sample temperature T (y axis on right, relating to red curve) plotted as a function of time for LiBH_4 (green), KBH_4 (black), and majority $\text{LiK}(\text{BH}_4)_2$ (blue).

11.3wt % KBH_4), using a Hidden Isochema Intelligent Gravimetric Analyser, appears to show $\text{LiK}(\text{BH}_4)_2$ with a reduced melting point (240°C) and intermediate decomposition temperature compared to LiBH_4 (melts 300°C and decomposes 330°C) and KBH_4 (melts 400°C) if measured under identical heating rates (2°C min^{-1} to 400°C) and environment (dynamic vacuum at 10^{-6} mbar).

Figure 3 shows a comparison of thermal decomposition temperature with Pauling electronegativity for $\text{LiK}(\text{BH}_4)_2$ (average electronegativity of Li and K) and a number of other common borohydride materials. It can be seen that the data for $\text{LiK}(\text{BH}_4)_2$ fit well with the correlation identified by Nakamori et al.,^[2] and lie between those for lithium and for potassium. It should be noted that $\text{LiK}(\text{BH}_4)_2$, which is almost of identical formula weight to twice that of NaBH_4 , has a lower decomposition temperature than NaBH_4 .

In summary, the first mixed alkali metal borohydride, $\text{LiK}(\text{BH}_4)_2$, has been synthesized and has a structure closely related to that of orthorhombic LiBH_4 . The decomposition

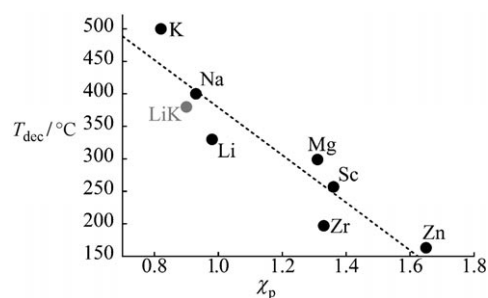


Figure 3. A plot of thermal decomposition temperature T_{dec} in Celsius vs. Pauling electronegativity for a number of borohydrides $\text{M}(\text{BH}_4)_n$, with $\text{LiK}(\text{BH}_4)_2$ denoted as LiK. The dotted line is included as a guide for the eye. The data for Li and LiK represents dynamic vacuum conditions (Figure 2).

temperature lies between those of the congener compounds. This approach illustrates a viable general route to the chemical control of the desorption temperatures of complex hydrides.

Experimental Section

Thirteen samples of general composition $n\text{LiBH}_4:(12-n)\text{KBH}_4$ ($n = 0, 1, 2, \dots, 12$) were prepared in an identical fashion. Appropriate molar quantities of LiBH_4 and KBH_4 (Sigma-Aldrich) were ground together under an inert argon atmosphere, packed into an alumina crucible, and placed in a quartz tube. The tube was fitted with a Young's tap and evacuated to 10^{-6} mbar. After sealing, all the samples were heated to 125°C for 12 h.

High-resolution X-ray diffraction data of the samples were collected on the ID31 diffractometer (ESRF, Grenoble) at a wavelength and step size of 0.79953 Å and 0.003° , respectively. All X-ray data consisted of sharp Bragg peaks, which indicates a high degree of crystallinity.

Detailed structural modeling of these diffraction data was performed using the profile refinement program TOPAS.^[11] The presence of LiBH_4 and KBH_4 Bragg peaks was observed across the full composition range, together with a number of prominent additional peaks, which were indexed to a single extra phase with an orthorhombic structure and lattice parameters of approximately $a = 7.9134$ Å, $b = 4.4907$ Å, and $c = 13.8440$ Å. Assessment of the extinction symbol associated with the space group of the new phase using DASH^[12] indicated the most probable to be $Pn\bar{a}$, which corresponds to space groups $Pn2_1a$ and $Pnma$. This further strengthened the likelihood of structural similarity between the new phase and LiBH_4 , which adopts the space group $Pnma$. A probable composition of the new phase was surmised from a comparison of the lattice volumes of the precursors, LiBH_4 and KBH_4 , which have volumes per formula unit of 54.2 Å³ and 76.1 Å³, respectively. The new phase has a volume per formula unit of 123.0 Å³, (assuming four formula units per unit cell, which is consistent with the extinction symbol $Pn\bar{a}$), and is approximately the sum of the values for LiBH_4 and KBH_4 (130.3 Å³), suggesting that the new phase may possess a $\text{LiK}(\text{BH}_4)_2$ stoichiometry.

Although it is probable that the space group of this new phase is $Pnma$, given the precedent of LiBH_4 , it was found to be more straightforward to work initially within the $Pn2_1a$ space group, which has no special positions. Simulated annealing studies whereby one potassium and two boron atoms (which dominate the scattering) were allowed to move within the asymmetric unit of $Pn2_1a$ were performed. All three atoms were minimized to positions consistent with the special position of $(x, 1/4, z)$ in $Pnma$. Subsequent optimization of the structure fit was thus performed in this centrosymmetric space group,

with these three atoms and the lithium atom restricted to the $(x, \frac{1}{4}, z)$ plane. Although lithium is a relatively weak scatterer, multiple simulated annealing analyses consistently returned the same lithium coordinates, with the observed Li...B distances consistent to those in LiBH_4 (see Supporting Information). Finally, two rigid-body constrained BH_4^- groups were allowed to rotate around the independent boron positions. Two hydrogen atoms were found to lie on the $(x, \frac{1}{4}, z)$ plane with the two other hydrogen atoms related to one another by the mirror plane along $(x, \frac{1}{4}, z)$ for both BH_4^- tetrahedra. This arrangement of hydrogen atoms is identical to the orientation of the BH_4^- groups in orthorhombic LiBH_4 .

In the final refinement, the quality of the data was sufficient to allow the coordinates of all hydrogen atoms to be refined unconstrained.

The refinement details and structural coordinates are listed in Table 1, with a graphical representation of a typical final fit to data

Table 1: Refined crystallographic data for $\text{LiK}(\text{BH}_4)_2$.

Atom	x/a	y/b	z/c	$B_{\text{iso}} [\text{\AA}^2]$
K	0.33814(12)	1/4	0.86851(7)	3.42(2)
Li	0.1885(9)	1/4	0.1349(6)	3.42(2)
B1	0.2508(7)	1/4	0.5460(4)	2.38(6)
H11	0.324(2)	0.456(4)	0.5288(13)	2.38(6)
H12	0.206(4)	1/4	0.614(2)	2.38(6)
H13	0.140(4)	1/4	0.498(2)	2.38(6)
B2	0.9292(7)	1/4	0.2397(4)	2.38(6)
H21	0.976(2)	0.452(4)	0.2057(15)	2.38(6)
H22	0.789(4)	1/4	0.218(2)	2.38(6)
H23	0.960(4)	1/4	0.316(2)	2.38(6)

For a starting composition of 2:1 $\text{LiBH}_4/\text{KBH}_4$ $a = 7.91337(5) \text{ \AA}$, $b = 4.49067(3) \text{ \AA}$, $c = 13.84396(11) \text{ \AA}$, $V = 491.964(10) \text{ \AA}^3$, $M = 75.7225 \text{ g mol}^{-1}$, $Pnma$ (No. 62), $Z = 4$, $R_{\text{wp}} = 10.344\%$, $R_{\text{exp}} = 6.467\%$, $c^2 = 1.600$.

shown in the Supporting Information. A schematic diagram representing the crystal structure of the new phase, together with that for orthorhombic LiBH_4 , is shown in Figure 1.

Received: October 25, 2007

Published online: February 28, 2008

Keywords: alkali metals · borohydrides · hydrogen storage · solid-state reactions · X-ray diffraction

- [1] W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283.
- [2] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, S. Orimo, *Phys. Rev. B* **2006**, *74*, 045126.
- [3] S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.* **2007**, *107*, 4111.
- [4] H. Li, S. Orimo, Y. Nakamori, K. Miwa, N. Ohba, S. Towata, A. Züttel, *J. Alloys Compd.* **2007**, *446–447*, 315.
- [5] Y. Nakamori, H. Li, K. Miwa, S. Towata, S. Orimo, *Mater. Trans.* **2006**, *47*, 1898.
- [6] J.-P. Soulie, G. Renaudin, R. Cerny, K. Yvon, *J. Alloys Compd.* **2002**, *346*, 200.
- [7] D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, **2003–2004**.
- [8] R. L. Luck, E. J. Schelter, *Acta Crystallogr. Sect. C* **1999**, *55*, IUC9900151 (cif access).
- [9] A. J. Du, S. C. Smith, G. Q. Lu, *Phys. Rev. B* **2006**, *74*, 193405.
- [10] M. R. Hartman, J. J. Rush, T. J. Udovic, R. C. Bowman Jr., S.-J. Hwang, *J. Solid State Chem.* **2007**, *180*, 1298.
- [11] A. A. Coelho, TOPAS, General Profile and Structure Analysis Software for Powder Diffraction Data, version 4.0; Bruker AXS: Karlsruhe, Germany, **2004**.
- [12] W. I. F. David, K. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell, J. C. Cole, *J. Appl. Crystallogr.* **2006**, *39*, 910.