

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Sulfurized Metal Borohydrides

M. Paskevicius,^a B. Richter,^a M. Polański,^b S. P. Thompson^c and T. R. Jensen^aReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The reactions between metal borohydrides and elemental sulfur are investigated in-situ during thermal treatment and are found to be highly exothermic (up to 700 J/g). These reactions are exceptionally rapid, occurring below 200 °C, also resulting in the sudden release of substantial quantities of hydrogen gas. For NaBH₄ this hydrogen release is pure, with no detectable levels of H₂S or B₂H₆. The reaction results in the formation of an array of metal-boron-sulfur compounds. These MBH₄-S compounds are interesting for possible uses in high energy applications (fuels or explosives), hydrogen generation, and metal-boron-sulfur precursors.

1. Introduction

Metal borohydrides are a versatile class of compounds with applications in energy storage, hydrogen generation and as reducing agents in organic synthesis. The first metal borohydrides were discovered in 1940 (Al(BH₄)₃, Be(BH₄)₂ & LiBH₄)¹⁻³ and in 1979 H.C. Brown received the Nobel Prize in Chemistry for his research into boron compounds as reducing agents in organic chemistry. Sodium borohydride, in particular, was identified as a promising material for hydrogen generation through hydrolysis in 1953.⁴ The hydrolysis reaction occurs more rapidly at elevated temperature and under acidic conditions as follows:



The hydrolysis of NaBH₄ is a promising technology for hydrogen generation and thus energy storage due to its excellent energy storage density (< 10.8 wt.% H). However, practical hydrogen storage capacities are much lower due to the excess water required to dissolve NaBH₄ and its product NaBO₂.⁵ Sodium borohydride is also the least expensive metal borohydride on a hydrogen-basis,⁶ leading to heavy research, even today, into a reversible energy generation/storage cycle through hydrolysis.⁵ Interestingly, exothermic reduction reactions of NaBH₄ have also been investigated for niche technical applications, such as for self-heating shaving cream.⁷

Metal borohydrides have also been investigated for their use in fuel cell applications, typically denoted direct borohydride fuel cells (DBFC).⁸ In contrast to typical hydrogen-oxygen fuel cells, DBFC's involve the redox reaction between the borohydride

anion (BH₄⁻) and an oxidant to generate electricity. There are advantages in utilising the borohydride anion, including high power densities, low operating temperatures, high open-circuit potentials, and the use of non-precious metals. An alkaline solution of NaBH₄ is typically used in the following electrochemical reactions:⁸



Here, hydrolysis is an unwanted side reaction as hydrogen gas is not desired. Despite the low cost of NaBH₄ it still results in a high price point for this technology but the development of DBFC's is still in its infancy.

Is there an alternative to oxygen-based reactions? Sulfur is chemically similar to oxygen, with the same valence electron configuration. As such, many O-compounds have S analogues, i.e. Na₂O/Na₂S, H₂O/H₂S, CO₂/CS₂, etc. However, sulfur (EN = 2.58) is less electronegative than oxygen (EN = 3.44) and it can also act as an oxidising or reducing agent. In fact, sulfur has a very diverse structural chemistry, with over 30 solid polymorphs in its pure form.⁹ There has been a wealth of research into using sulphur for battery applications in the form of Li-S and Na-S batteries.^{10, 11} The Li-S battery converts between S and Li₂S through a series of polysulfide intermediates (Li₂S_n, n = 2 - 8). Despite the complexity of this system, elemental sulfur is one of the most actively researched cathode materials in recent years.¹⁰ The reactions between sulfur-rich and hydrogen-rich materials have only been recently investigated for the purpose of energy storage, with NaAlH₄-Al₂S₃.¹² In this system the hydrogen-release reactions are complex, proceeding through 6 distinct unknown intermediate compounds, but the system shows promising hydrogen reversibility.

Some early research was directed towards the incorporation of sulfur into borohydrides. The synthesis of NaBH₂S₃ was reported in 1968¹³ by the solvent-mediated reaction between NaBH₄ and S in tetrahydrofuran (THF). NaBH₂S₃ is denoted Lalancette's Reagent and is used as a reducing agent in organic synthesis with an intermediate reducing potential between LiAlH₄ and NaBH₄.^{14, 15} This compound is expected to only exist

^a Interdisciplinary Nanoscience Center (iNANO) & Institut for Kemi, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark.

^b Department of Advanced Materials and Technologies, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland.

^c Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK.

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

for a few hours in solution containing H₂B-S-S chains¹⁶ and unfortunately the structure could not be determined by X-ray diffraction¹⁷. Be, Mg, Ca, Sr and Ba sulfurated borohydrides (i.e. Ba(BH₂S₃)₂) have also been prepared as potential reducing agents for aldehydes, ketones, carbonyl compounds, azides, nitro compounds and epoxides^{15, 18}.

The goal in the present research is to determine if sulfurated borohydrides are found in the solid-state and to examine the reaction pathway between borohydrides and sulfur. A detailed understanding of the reaction pathways between sulfur and borohydrides could open new ways to release or store hydrogen in energy dense materials. Sulfur-based chemistry is complex and there are many sulfur-based reactions that have yet to be explored. Research into sulfur-hydrogen systems is very relevant, especially with the recent superconductivity breakthrough in the sulfur-hydrogen system, with a superconductivity transition temperature of 203 K (-70 °C) at high pressure.¹⁹

2. Experimental

2.1 Synthesis

All chemical handling was conducted either by inert Schlenk techniques or in an argon glovebox (MBRAUN, Germany) at less than 1 ppm H₂O and O₂. Mixtures of borohydrides and sulfur were prepared based on the stoichiometry of possible known intermediate compounds (LiBH₃SH, NaBH₂S₃ and KBH₂S₃): LiBH₄:S = 1:1, NaBH₄:S = 1:3 and KBH₄:S = 1:3.^{13, 16} Stoichiometric mixtures were ball milled at room temperature within WC vials for 1 h (in 5 minute cycles with 2 minutes rest) in a Fritsch P4 mill at 350 rpm.

A ball milled mixture of NaBH₄ + 3S (0.5 g) was also added to 10 mL of cold (0 °C) tetrahydrofuran and stirred for 1 h, resulting in gas evolution. Upon heating to room temperature (25 °C) a yellow, slightly cloudy solution remained. Evacuation at room temperature for 2 h resulted in a yellow powder.

2.2 Characterisation

Differential scanning calorimetry (DSC) was undertaken on 2 instruments to provide reliable unbiased results. The first instrument was a PerkinElmer STA 6000 coupled to a Hiden Analytical HPR-20 quadrupole mass spectrometer (MS) for evolved gas analysis. Here, 5 - 10 mg samples were placed in Al crucibles with vented lids and thermally ramped at 5 °C/min under a constant flow of argon (20 mL/min). Sample containment was difficult during the large exothermic gas release events, causing some levels of sample deposition on the walls of the DSC instrument, this was made even more problematic by the vaporisation of excess sulfur. Thermogravimetry (TG) showed significant mass losses during gas release events (Figure S1-S3) indicating sample loss from the crucible. The second instrument was a Setaram Sensys Evo 3D. Here, 5 - 10 mg samples were placed in Al₂O₃ crucibles and covered with Al₂O₃ powder to reduce sample loss, which was partially successful. Before transition of the sample from the glovebox to the DSC, the crucible was filled to its top with

pentane to prevent oxidation of the powder during transfer. The pentane was then evaporated under helium flow within the DSC before measurements began. DSC exotherms from both instruments were comparable and were integrated and averaged to provide a more reliable measure of energy output. Temperature programmed photographic analysis (TPPA) was performed by sealing samples within a glass vessel under argon, followed by heating within a custom Al block (5 °C/min) using a known method.²⁰

Fourier transform infra-red (FTIR) spectra were collected on a NICOLET 380 FT-IR (Thermo Scientific) coupled with a Smart Orbit stage for attenuated total reflectance (ATR) analysis with a diamond. Samples were briefly air-exposed (< 10 s) when transferred to the instrument.

In-situ Raman spectra were collected at Diamond (Beamline I11) using a 532 nm 250 mW laser (focussed on the sample within a sapphire capillary using a 65 mm working distance probe) coupled to an iHR550 spectrometer (Horiba) equipped with a 600 line grating. Heating was provided by a Cyberstar hot air blower located beneath the sample capillary.

In-situ powder X-ray diffraction (PXD) data were collected at Maxlab (MAX II, Beamline I711) at $\lambda = 0.9938 \text{ \AA}$ using a Titan CCD 165 mm detector. A custom sample cell was utilised,²¹ coupled with a hot air blower for thermal ramping at either 5 or 10 °C/min. Temperature was recorded by a K-type thermocouple calibrated using a NaCl PXD standard via its known thermal expansion coefficient.²¹ Samples were sealed within single crystal sapphire capillaries within an argon glovebox and heated under 1 bar of Ar.

3. Results and Discussion

The interactions between sulfur and the 3 lightest alkali metal borohydrides (LiBH₄, NaBH₄ and KBH₄) have been investigated. The NaBH₄-S system is first discussed as it is the most complex example with samples synthesised by either solid-state or wet chemical methods.

3.1 Sodium Borohydride – Sulfur System

Early studies into the reaction between NaBH₄ and sulfur were performed in the 1960's^{22, 23}, where this reaction was found to occur exothermically from 160 - 280 °C with complete dehydrogenation and the formation of NaBS₃. To investigate the reaction in more detail, *in-situ* PXD and mass spectrometry of evolved gases were performed (Figure 1). A mixture of NaBH₄ and S is observed at room temperature. Near 100 °C sulfur undergoes a polymorphic transition from the $\alpha \rightarrow \beta$ polymorph, followed by melting at 110 °C. After this point, there is a mixture of molten sulfur and crystalline NaBH₄ until 185 °C. Interestingly there is no immediate reaction between the reactants, even when sulfur becomes molten. However, at 185 °C there is an instant and dramatic change in the diffraction pattern, indicating the complete consumption of NaBH₄. This reaction is also reflected in the gas MS, with the strong evolution of hydrogen gas at this point (No H₂S or B₂H₆ is detected). An insight into why the reaction does not immediately occur when

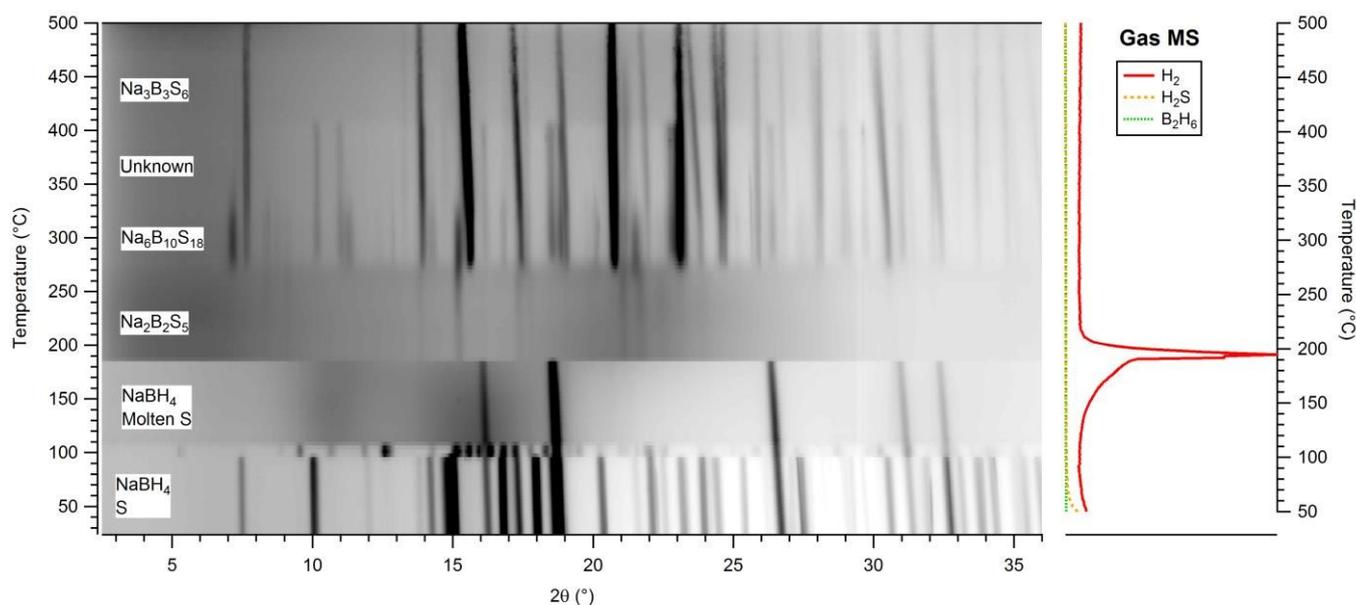


Figure 1: *In-situ* PXD data (Maxlab, $\lambda = 0.9938 \text{ \AA}$) of $\text{NaBH}_4 + 3\text{S}$ during thermal ramping at $5 \text{ }^\circ\text{C}/\text{min}$ with gas mass spectroscopy (MS) analysis.

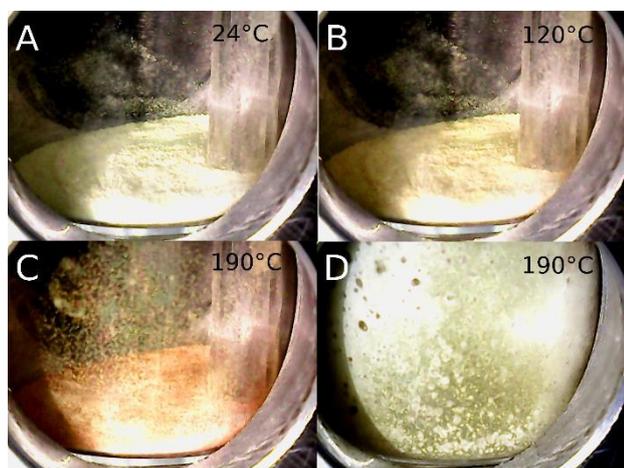


Figure 2: Temperature programmed photographic analysis (TPPA) of $\text{NaBH}_4 + 3\text{S}$ during thermal ramping at $5 \text{ }^\circ\text{C}/\text{min}$. The powder is A) yellow at $24 \text{ }^\circ\text{C}$, B) darker yellow at $120 \text{ }^\circ\text{C}$, C) orange at $190 \text{ }^\circ\text{C}$ with droplets on the glass, D) also at $190 \text{ }^\circ\text{C}$ an instant reaction occurs ($< 100 \text{ ms}$) resulting in a colour change back to yellow.

sulfur melts may be gained by understanding the molten sulfur system.²⁴ Just after melting, S_8 molecules dominate the melt and a minimum viscosity is reached at $157 \text{ }^\circ\text{C}$ when the S_8 molecules begin to rupture and polymerise into linear chains. At $187 \text{ }^\circ\text{C}$ a maximum S-S-...-S-S chain length is reached, followed by rapid chain shortening. It is at this temperature that sulfur rapidly reacts with NaBH_4 .

The reaction between NaBH_4 and sulfur is also extremely rapid when visually observed (Figure 2). After reaching the melting point of sulfur the powder begins to darken in colour, but is not an obvious melt. At $190 \text{ }^\circ\text{C}$ the powder is orange in colour before the rapid decomposition reaction occurs. There are also condensation drops on the surface of the glass, likely due to the high vapour pressure of sulfur at this temperature (2.5 mbar).²⁵ Almost instantaneously, the powder is displaced throughout the container in conjunction with rapid gas release and a sharp sound. The reaction also results in a stark colour change of the

powder back to yellow. The rapid timescale of the reaction is also evidenced by DSC data (Figure S1). Two minor endotherms are observed near $100 \text{ }^\circ\text{C}$, from the polymorphic transition of S and its melting. At $185 \text{ }^\circ\text{C}$ a large, sharp exotherm is observed due to the reaction between NaBH_4 and S. The exothermic event during hydrogen release is exceptionally high at 545 J/g . For comparison, 2,4,6-trinitrotoluene (TNT) exhibits an exothermic event of 4203 J/g .²⁶

After the reaction between NaBH_4 and S the PXD data indicate that a large component of the products is amorphous (broad diffraction halos at $d = 3.6$ and 5.4 \AA). However, there is some crystalline $\text{Na}_2\text{B}_2\text{S}_5$, which increases with temperature. At $275 \text{ }^\circ\text{C}$ three new compounds are formed ($\text{Na}_6\text{B}_{10}\text{S}_{18}$, $\text{Na}_3\text{B}_3\text{S}_6$, and an unknown), commensurate with the disappearance of the amorphous diffraction halos. The $\text{Na}_6\text{B}_{10}\text{S}_{18}$ is only short lived and disappears by $350 \text{ }^\circ\text{C}$, whereas the unknown compound sharply disappears at $410 \text{ }^\circ\text{C}$, leaving only crystalline $\text{Na}_3\text{B}_3\text{S}_6$. The remaining sample stoichiometry ($\text{Na}:\text{B}:\text{S} = 1:1:2$) is not the same as the starting reagents ($1:1:3$), suggesting that a large quantity of sulfur has also vaporised.

The reaction between NaBH_4 and S can also be initiated by wet chemistry. The reaction is known to proceed in THF or diglyme to form NaBH_2S_3 .¹³ This compound is not observed during thermal studies (without the use of a solvent) and thus a solvent-mediated formation mechanism for NaBH_2S_3 is expected. Sulfur is slightly soluble in THF (11 g/kg at $22 \text{ }^\circ\text{C}$), which could assist the reaction.²⁷ Reactions can also be undertaken using Se or Te instead of S, with faster, more explosive reactions.²⁸ Yellow crystals can be precipitated from a THF solution of NaBH_4 and S, but they are not stable over time. FTIR data for a sample directly after synthesis are shown in Figure 3. The compound presents both B-H and C-H stretching bands, indicative of a solvate complex. Interestingly the B-H bands are shifted to higher wavenumber in regards to pure NaBH_4 , indicating a different B-H bonding environment, likely due to the incorporation of S into the complex. Unfortunately,

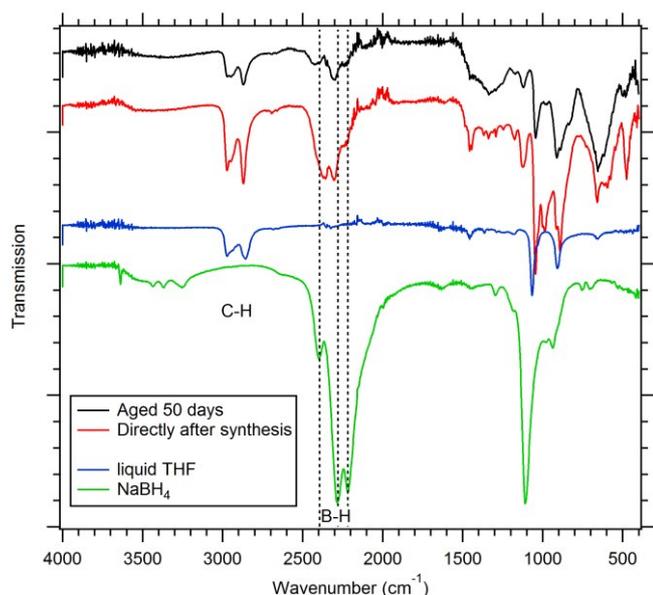


Figure 3: FTIR spectra from the reaction products of $\text{NaBH}_4 + 3\text{S}$ in THF.

the complex does not appear to be stable, with significant changes in the B-H stretching bands over time (50 days).

Thermal treatment of the $\text{NaBH}_4\text{-S-THF}$ complex proceeds differently to the unsolvated mixture of NaBH_4 and S (Figure 4). The THF complex is observed as a new crystalline compound, with some trace of NaBH_4 , but not S. The complex desolvates and decomposes from 50 – 200 °C, with THF, H_2 and H_2S detected by the MS. This results in an amorphisation of the sample, followed by the crystallisation of a mixture of compounds at 220 °C. Here, the major phase is $\text{Na}_2\text{B}_2\text{S}_5$ followed by a slow conversion to $\text{Na}_3\text{B}_3\text{S}_6$ in contrast to the more complex reaction pathway of unsolvated NaBH_4 and S. Indeed, the gas release is also dramatically different for the solvated sample, with a less violent release of H_2 all the way up to 400 °C with traces of H_2S . Pyrolysis of NaBH_2S_3 has previously been reported to generate 1:3 $\text{H}_2\text{:H}_2\text{S}$ after heating to 300 – 400 °C¹³, but this

does not seem to be the case here. H_2S release could possibly be due to reactions between sulfur and moisture (H_2O) in this early study. Another dramatic difference is that no exothermic events are observed in the DSC data from the $\text{NaBH}_4\text{-S-THF}$ complex, clearly demonstrating a different reaction pathway to the unsolvated compound.

3.2 Lithium Borohydride – Sulfur System

The reaction between LiBH_4 and sulfur occurs at a lower temperature than for NaBH_4 (Figure 5). The reaction pathway is different in this case where the primary reaction results in boron-free Li_2S and boron-rich $\text{Li}_2\text{B}_{12}\text{H}_{12}$. This is in contrast to the $\text{NaBH}_4\text{-S}$ system, where all known reaction products are ternary Na-B-S compounds, with no sign of Na-S or Na-B-H products. The formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at 150 °C is unexpected as it normally forms above 330 °C in the decomposition of pure LiBH_4 .²⁹ However, reactions between borohydrides and diborane (B_2H_6) can result in $\text{MB}_{12}\text{H}_{12}$ compounds at lower temperatures.^{30–32} The conversion from LiBH_4 to $\text{Li}_2\text{B}_{12}\text{H}_{12}$ at 150 °C in the presence of S is also confirmed by in-situ Raman spectroscopy (Figure 6). Here, B-H bands from BH_4^- groups are present in the $\text{LiBH}_4\text{-S}$ sample at 50 °C near 2300 cm^{-1} . A clear transition of the B-H bands is seen at 150 °C to 2450 cm^{-1} , indicating the presence of a higher borane such as $\text{Li}_2\text{B}_{12}\text{H}_{12}$.²⁹ The B-H bands at 2450 cm^{-1} persist until 250 °C, in conjunction with the crystalline $\text{Li}_2\text{B}_{12}\text{H}_{12}$ polymorph seen in PXD data, which disappears above 250 °C. In fact, a very broad band at 2450 cm^{-1} is also present as early as 100 °C in the Raman data, suggesting that $\text{Li}_2\text{B}_{12}\text{H}_{12}$ may begin to form at very low temperatures.

The gas released from the $\text{LiBH}_4\text{-S}$ system is not pure hydrogen, as is seen for $\text{NaBH}_4\text{-S}$. Instead, a mixture of H_2 , B_2H_6 and H_2S is released from 90 to 300 °C. The presence of diborane may explain the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ due to the possibility of a solid-gas reaction between B_2H_6 and LiBH_4 . There are 4 distinct gas release events, also evidenced by mass losses in TGA data (Figure S2). The first event occurs at 105 °C with primarily

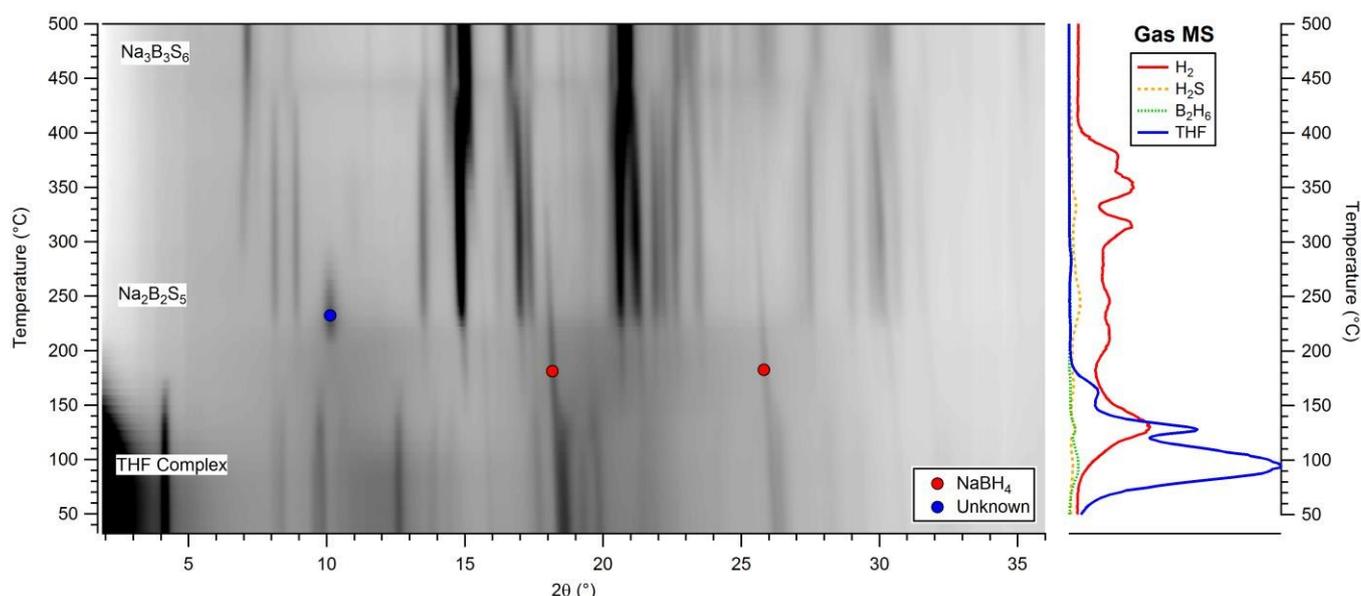


Figure 4: *In-situ* PXD data (Maxlab, $\lambda = 0.9938 \text{ \AA}$) of THF complex during thermal ramping at 5 °C/min with gas mass spectroscopy (MS) analysis.

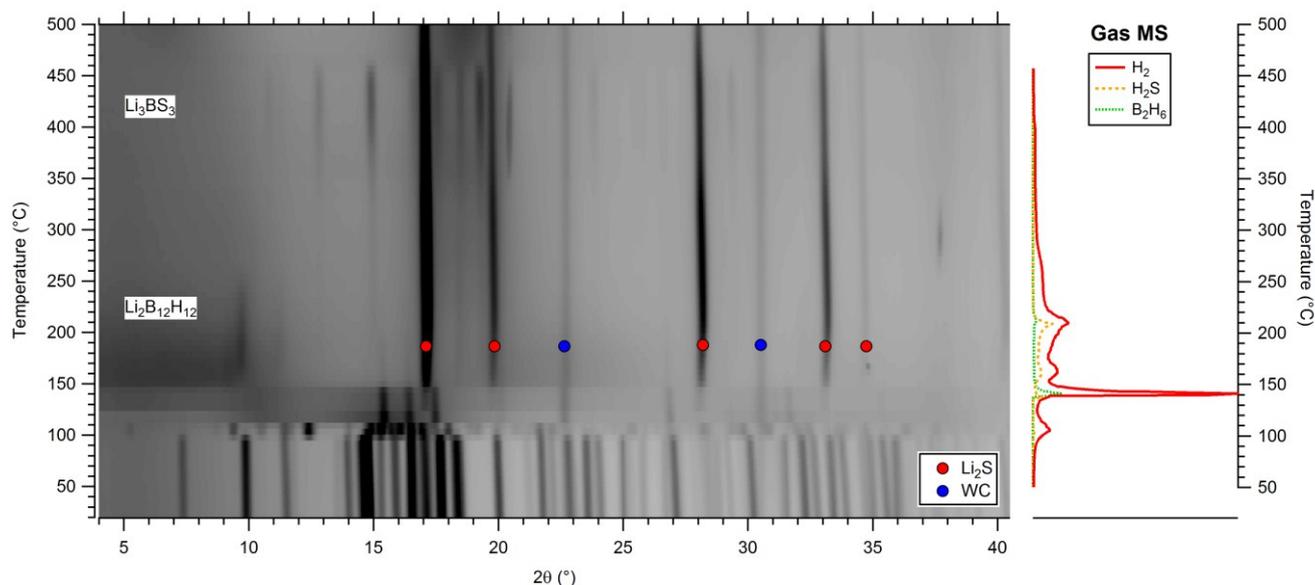


Figure 5: *In-situ* PXD data (Maxlab, $\lambda = 0.9938 \text{ \AA}$) of $\text{LiBH}_4 + \text{S}$ during thermal ramping at $10 \text{ }^\circ\text{C}/\text{min}$ with gas mass spectroscopy (MS) analysis.

hydrogen evolution and minor H_2S . This event corresponds with the melting point of sulfur and indicates an immediate, but partial, reaction between molten sulfur and LiBH_4 . A rapid gas release event occurs at $140 \text{ }^\circ\text{C}$ (H_2 , B_2H_6 , H_2S) coupled with a strong exothermic event (Figure S2) of 700 J/g . Most LiBH_4 is consumed at this point with the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and traces of Li_3BS_3 . A final gas release (H_2 and H_2S) occurs from 200 to $300 \text{ }^\circ\text{C}$ when $\text{Li}_2\text{B}_{12}\text{H}_{12}$ decomposes/reacts, followed by the steady formation of more Li_3BS_3 . Before this point, most boron is 'locked up' within $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and does not appear to react with sulfur to form crystalline Li_3BS_3 . At $450 \text{ }^\circ\text{C}$ the crystalline diffraction peaks from Li_3BS_3 disappear, replaced by a broad diffraction halo at $d = 3.1 \text{ \AA}$, possibly due to melting or amorphisation.

3.3 Potassium Borohydride – Sulfur System

The reaction between KBH_4 and S appears to occur steadily according to PXD data (Figure 7), with a slow decrease in KBH_4 peak intensity. However, MS and DSC data (Figure S3) suggest

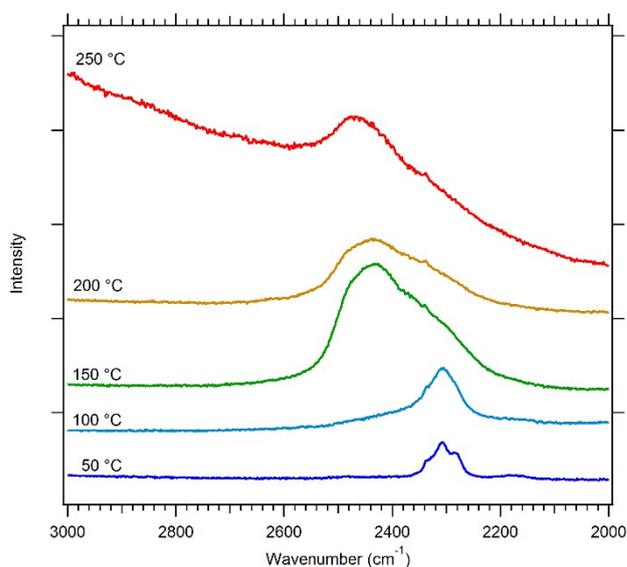


Figure 6: *In-situ* Raman spectra of $\text{LiBH}_4 + \text{S}$ collected at elevated temperature.

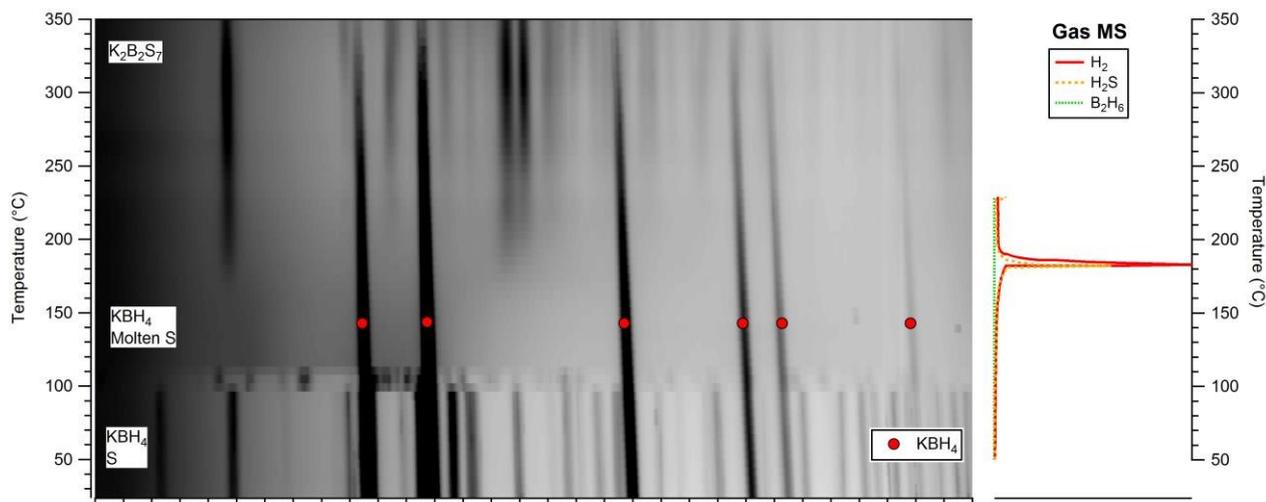


Figure 7: *In-situ* PXD data (Maxlab, $\lambda = 0.9938 \text{ \AA}$) of $\text{KBH}_4 + 3\text{S}$ during thermal ramping at $10 \text{ }^\circ\text{C}/\text{min}$ with gas mass spectroscopy (MS) analysis.

that a rapid reaction occurs at 180 °C with H₂/H₂S evolution and an exothermic event (159 J/g). This reaction is less complex than for Li or Na, where a direct formation of a single metal-B-S compound, K₂B₂S₇, occurs. There is also no sign of K₂B₁₂H₁₂ or any other intermediate compounds in the PXD data.

Conclusions

The reactions between metal borohydrides and elemental sulfur are highly exothermic and thus not viable for reversible hydrogen storage applications. However, these systems are interesting and relevant for a number of reasons. There are extremely rapid hydrogen release events at modest temperatures, and for NaBH₄-S the hydrogen release is pure. This system allows for high volumes of hydrogen gas to be quickly generated, by simply heating an energy dense composite. The exothermic nature of the reactions between borohydrides and sulfur may also allow for their incorporation as high-energy fuels or possibly explosives. On the other hand, their ability to form a range of metal-boron-sulfur compounds may also be harnessed to avoid the typical high temperature synthesis of these compounds from elemental mixtures.

Acknowledgements

MP acknowledges financial support from The Danish Council for Independent Research for DFF Mobility 1325-00072. Beamlines I711 at MAX II synchrotron, Lund, Sweden and I11 at Diamond, Didcot, England (award EE10224) are thanked for the allocated beamtime. DSC/TG/MS measurements were supported by the Polish Ministry of Science (Iuventus Plus IP 2012007272 project and Key Project POIG.01.03.01-14-016/08).

Notes and references

- H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, 1940, 62, 3429-3435.
- H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *J. Am. Chem. Soc.*, 1939, 61, 536-536.
- H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *J. Am. Chem. Soc.*, 1940, 62, 3421-3425.
- H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, 1953, 75, 215-219.
- S. S. Muir and X. Yao, *Int. J. Hydrogen Energy*, 2011, 36, 5983-5997.
- J. Yamamoto, *Sodium Borohydride Digest*, http://www.dow.com/assets/attachments/industry/pharma_medical/chemical_reagents/reducing_agents/sodium_borohydride_digest.pdf, 2003.
- M. Cordon, A. Dillarstone; Colgate-Palmolive, *US 4,439,416*, 1984.
- J. Ma, N. A. Choudhury and Y. Sahai, *Renew. Sus. Energy Reviews*, 2010, 14, 183-199.
- R. Steudel and B. Eckert, 'Solid Sulfur Allotropes Sulfur Allotropes' in *Elemental Sulfur and Sulfur-Rich Compounds I*, ed. R. Steudel, Springer Berlin Heidelberg, 2003.
- L. F. Nazar, M. Cuisinier and Q. Pang, *MRS Bull.*, 2014, 39, 436-442.
- B. L. Ellis and L. F. Nazar, *Curr. Op. Solid State Mater. Sci.*, 2012, 16, 168-177.
- D. A. Sheppard, L. H. Jepsen, T. R. Jensen, M. Paskevicius and C. E. Buckley, *J. Mater. Chem. A*, 2013, 1, 12775-12781.
- J. M. Lalancette, A. Frêche and R. Monteux, *Can. J. Chem.*, 1968, 46, 2754-2757.
- J. M. Lalancette and A. Frêche, *Can. J. Chem.*, 1969, 47, 739-742.
- H. Firouzabadi and M. Ghadami, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 2000, 166, 83-98.
- H. Binder and W. Diamantikos, *Z. Nat. B*, 1983, 38, 203-207.
- H. Binder and M. Hein, *Coord. Chem. Rev.*, 1997, 158, 171-232.
- H. Firouzabadi, B. Tamami and A. R. Kiasat, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 2000, 159, 99-108.
- A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov and S. I. Shylin, *Nature*, 2015, advance online publication.
- M. Paskevicius, M. B. Ley, D. A. Sheppard, T. R. Jensen and C. E. Buckley, *Phys. Chem. Chem. Phys.*, 2013, 15, 19774-19789.
- B. R. S. Hansen, K. T. Moller, M. Paskevicius, A.-C. Dippel, P. Walter, C. J. Webb, C. Pistidda, N. Bergemann, M. Dornheim, T. Klassen, J.-E. Jorgensen and T. R. Jensen, *J. Appl. Cryst.*, 2015, 48, 1234-1241.
- V. H. Nöth and G. Mikulaschek, *Z. Anorg. Allge. Chem.*, 1961, 311, 241-248.
- F. Chopin and P. Hagenmuller, *Bull. Soc. Chim. France*, 1965, 3031-3033.
- R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.*, 1943, 65, 639-648.
- W. A. West and A. W. C. Menzies, *J. Phys. Chem.*, 1928, 33, 1880-1892.
- M. Yao, L. Chen and J. Peng, *Propellants, Explosives, Pyrotechnics*, 2014, 40, 197-202.
- D. K. Padma, *Talanta*, 1986, 33, 550-552.
- J. M. Lalancette and M. Arnac, *Can. J. Chem.*, 1969, 47, 3695-3697.
- M. P. Pitt, M. Paskevicius, D. H. Brown, D. A. Sheppard and C. E. Buckley, *J. Am. Chem. Soc.*, 2013, 135, 6930-6941.
- L. H. Rude, U. Filso, V. D'Anna, A. Spyratou, B. Richter, S. Hino, O. Zavorotynska, M. Baricco, M. H. Sorby, B. C. Hauback, H. Hagemann, F. Besenbacher, J. Skibsted and T. R. Jensen, *Phys. Chem. Chem. Phys.*, 2013, 15, 18185-18194.
- A. Remhof, Y. Yan, D. Rentsch, A. Borgschulte, C. M. Jensen and A. Züttel, *J. Mater. Chem. A*, 2014, 2, 7244-7249.
- O. Friedrichs, A. Remhof, S. J. Hwang and A. Züttel, *Chem. Mater.*, 2010, 22, 3265-3268.

