"Metal borohydrides and derivatives – synthesis, structure and properties"

Paskevicius, Mark; Jepsen, Lars H.; Schouwink, Pascal; Cerny, Radovan; Ravnsbæk, Dorthe B.; Filinchuk, Yaroslav; Dornheim, Martin; Besenbacher, Flemming; Jensen, Torben R.

Abstract

A wide variety of metal borohydrides, MBH4, have been discovered and characterized during the past decade, revealing an extremely rich chemistry including fascinating structural flexibility and a wide range of compositions and physical properties. Metal borohydrides receive increasing interest within the energy storage field due to their extremely high hydrogen density and possible uses in batteries as solid state ion conductors. Recently, new types of physical properties have been explored in lanthanide-bearing borohydrides related to solid state phosphors and magnetic refrigeration. Two major classes of metal borohydride derivatives have also been discovered: anion-substituted compounds where the complex borohydride anion, BH4, is replaced by another anion, i.e. a halide or amide ion; and metal borohydrides modified with neutral molecules, such as NH3, NH3BH3, N2H4, etc. Here, we review new synthetic strategies along with structural, physical and chemical properties for metal boro...

Document type: Article de périodique (Journal article)

Référence bibliographique


DOI: 10.1039/c6cs00705h
Metal borohydrides and derivatives
- synthesis, structure and properties -

Mark Paskevicius, Lars H. Jepsen, Pascal Schouwink, Radovan Černý,
Dorthe B. Ravnsbæk, Yaroslav Filinchuk, Martin Dornheim,
Flemming Besenbacher, Torben R. Jensen

a Center for Materials Crystallography, Interdisciplinary Nanoscience Center (iNANO), and
Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark
b Laboratory of Crystallography, DQMP, University of Geneva, 1211 Geneva, Switzerland
c Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej
55, 5230 Odense M, Denmark
d Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Place L.
Pasteur 1, B-1348 Louvain-la-Neuve, Belgium
e Helmholtz-Zentrum Geesthacht, Department of Nanotechnology, Max-Planck-Straße 1, 21502
Geesthacht, Germany
f Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, DK-
8000 Aarhus C, Denmark

* Corresponding author: trj@chem.au.dk
Contents

Abstract

1. Introduction

2. Synthesis of metal borohydrides and derivatives
   2.1 Solvent-based synthesis of monometallic borohydrides
   2.2 Trends in the mechanochemical synthesis of metal borohydrides
   2.3 Trends in the mechanochemical synthesis of metal borohydride-halides
   2.4 Mechanochemical reactions, general considerations
   2.5 Mechanical synthesis in different gas atmosphere
   2.6 Single crystal growth of metal borohydrides
   2.7 Synthesis of metal borohydrides with neutral molecules

3. Trends in structural chemistry of metal borohydrides
   3.1 Monometallic borohydrides, the s-block – pronounced ionic bonding
   3.2 Monometallic borohydrides with the d- and f-block
   3.3 Strongly covalent molecular monometallic borohydrides
   3.4 Bimetallic s-block borohydrides
   3.5 Bimetallic d- and f-block borohydrides
   3.6 Bimetallic p-block borohydrides
   3.7 Tri-metallic borohydrides
   3.8 General trends in the structural chemistry of metal borohydrides
   3.9 Comparisons between metal borohydrides and metal oxides

4. Structure of anion substituted metal borohydrides
   4.1 Metal borohydride halides - fully ordered structures
   4.2 Metal borohydride halides - partly ordered structures
   4.3 Metal borohydride halides - fully disordered structures
   4.4 Metal borohydride halides forming solid solutions
   4.5 General trends for halide substitution in metal borohydrides
   4.6 Trends in series of bimetallic borohydride halides
   4.7 Metal borohydride closo-boranes
4.8 Metal borohydride amides

5. Derivatives of metal borohydrides with neutral molecules

5.1 Ammine metal borohydrides
5.2 Hydrazine metal borohydride complexes
5.3 Ammonia borane metal borohydride complexes
5.4 Metal borohydride crystallizing with organic solvents

6. Thermal properties of metal borohydrides

6.1 Thermodynamics of hydrogen release and uptake
6.2 Thermolysis of monometallic borohydrides
6.3 Thermolysis of bi- and trimetallic borohydrides
6.4 Eutectic melting of bi- and trimetallic borohydrides
6.5 Trends in thermal decomposition for metal borohydrides
6.6 The released gas from metal borohydrides, stability of diborane
6.7 Additives to improve reaction kinetics
6.8 Reactive Hydride Composites
6.9 Hydrolysis – decomposition by reaction with water
6.10 Nanoconfinement

7. New properties and future perspectives of metal borohydrides

7.1 Porous metal borohydrides for gas adsorption
7.2 Metal borohydrides as ion conductors
7.3 Metal borohydrides with optical properties
7.4 Metal borohydrides with magnetic properties
7.5 Perspectives for design of novel metal borohydrides
7.6 CO₂-recycling with metal borohydrides
7.7 A possible paradigm shift for solid state hydrogen storage

8. Conclusions

9. Acknowledgements

10. References
Metal borohydrides and derivatives – synthesis, structure and properties

Mark Paskevicius, Lars H. Jepsen, Pascal Schouwink, Radovan Černý, Dorthe B. Ravnsbæk, Yaroslav Filinchuk, Martin Dornheim, Flemming Besenbacher and Torben R. Jensen

A wide variety of metal borohydrides, MBH₄, have been discovered and characterized during the past decade, revealing an extremely rich chemistry including fascinating structural flexibility and a wide range of compositions and physical properties. Metal borohydrides receive increasing interest within the energy storage field due to their extremely high hydrogen density and possible uses in batteries as solid state ion conductors. Recently, new types of physical properties have been explored in lanthanide-bearing borohydrides related to solid state phosphors and magnetic refrigeration. Two major classes of metal borohydride derivatives have also been discovered: anion-substituted compounds where the complex borohydride anion, BH₄⁻, is replaced by another anion, i.e. a halide or amide ion; and metal borohydrides modified with neutral molecules, such as NH₃, NH₂BH₃, N₂H₄, etc. Here, we review new synthetic strategies along with structural, physical and chemical properties for metal borohydrides, revealing a number of new trends correlating composition, structure, bonding and thermal properties. These new trends provide general knowledge and may contribute to the design and discovery of new metal borohydrides with tailored properties towards the rational design of novel functional materials. This review also demonstrates that there is still room for discovering new combinations of light elements including boron and hydrogen, leading to complex hydrides with extreme flexibility in composition, structure and properties.

1. Introduction

A wide variety of metal borohydrides have been discovered and characterized during the past few years, revealing an extremely rich chemistry, including fascinating structural flexibility and a wide variety of physical properties to be explored for possible future applications.¹⁻⁷ Hydrogen and boron form a variety of molecular compounds, boranes (BₙHₘ), which were intensively researched in the 1950’s as high energy rocket fuels. Since then, boranes have received significant academic interest, but metal borohydrides appear to have a larger potential for a variety of future applications due to their lower toxicity, lower volatility, and high hydrogen content. Thus, the focus of this review is on the compounds where boron and hydrogen form a negatively charged BH₄⁻ anion, counterbalanced by metal cations. The boron–hydrogen bond in the complex anion, e.g. BH₄⁻, is covalent, whereas the coordination to metals in the solid state is more diverse, ranging from ionic to more covalent with well-defined directionality.⁸ Two major classes of metal borohydride derivatives have recently been discovered. The first class includes mixed-anion compounds, where the complex anion BH₄⁻ is substituted by a halide anion or combined with a less similar anion such as an amide or borate.⁹⁻¹¹ The second class includes metal borohydrides coordinated to neutral H-rich molecules, such as NH₃, NH₂BH₃, N₂H₄, etc.⁶ This review focuses on new trends correlating composition, structure and properties of series of compounds, aiming to provide general knowledge, which contributes to the rational design and discovery of new metal borohydrides and derivatives with tailored properties.

The first homoletic metal borohydrides Al(BH₄)₃, Be(BH₄)₂, and LiBH₄ were discovered by Schlesinger, Brown and Burg and reported in 1940.¹²⁻¹⁴ Schlesinger and Brown discovered uranium borohydride, U(BH₄)₆, while working on the Manhattan project during World War II after being assigned with the task of finding volatile uranium compounds for use in the diffusion separation of uranium isotopes.¹⁵ U(BH₄)₆ was found to be one of the most...
volatile uranium compounds known, second only to uranium hexafluoride. Another compound of great importance, NaBH₄, was prepared for the first time by Brown and co-workers, during their research for the US Department of Defense, however, their work remained “classified” until 1953.¹⁶ The first application of a metal borohydride as a ‘hydrogen carrier’ dates back to World War II, when the hydrolysis of a NaBH₄ suspension was used for solid state storage of hydrogen for weather balloons. Later, in 1979, Herbert C. Brown was awarded the Nobel Prize in chemistry for his development of boron containing compounds as reducing reagents in organic synthesis, which today still remains the most important use of metal borohydrides. Over the decades many synthesis methods and new compounds have been reported, as borohydrides have constantly remained of interest in organic chemistry.¹⁷ Sodium borohydride was the first member to be structurally investigated in 1947, followed by K, Rb and Cs borohydrides in 1954.¹⁸,¹⁹ Titanium borohydride, Ti(BH₄)₃, the first genuine transition metal borohydride, was characterized in the gas phase by Dain et al. in 1991,²⁰ while the first full structural characterization of a transition metal borohydride in the solid state, Mn(BH₄)₂, was presented in 2009.²¹ During the past decade, metal borohydrides have received significant interest as hydrogen storage materials initiated by investigations of LiBH₄.²²–²⁶ Renewable energy sources have been highly sought after due to the ever increasing human energy consumption and made urgent by an increasing awareness of possible climatic changes and healthcare problems associated with the combustion of extreme amounts of fossil fuels.²⁷,²⁸ Unfortunately, renewable energy is unevenly distributed both over time and geographically, therefore it must be stored in an efficient way.²⁹ Renewable electricity may be stored directly in lithium based batteries or converted to hydrogen by electrolysis.³⁰,³¹ Hydrogen has the highest gravimetric energy content for any known compound, but is a gas at ambient conditions and is therefore

Mark Paskevicius is a Senior Lecturer in the Fuels and Energy Technology Institute at Curtin University in Australia. He began this position in 2017 after a 3 year research fellowship at Aarhus University in Denmark. His research is focussed on renewable energy storage. He is dedicated to developing new materials for solid-state hydrogen storage to store energy for automotive, stationary and concentrated solar thermal applications. He is also leading research into new solid-state ion conductors for battery applications, focussing on boron-rich materials.

Lars H. Jepsen obtained his PhD in chemistry and nanoscience from Aarhus University in 2015 under the supervision of Prof. Torben R. Jensen. Lars’ research was focused on synthesis and characterization of boron and nitrogen based complex metal hydrides, including crystal structure determination by combining powder X-ray diffraction, DFT calculations and solid-state NMR spectroscopy. Today Lars works as consultant at the Danish Technological Institute with the aim of supporting Danish and international companies with forefront knowledge and development within materials chemistry.

Pascal Schouwink obtained his PhD in 2014 at the Laboratory of Crystallography of the Department of Condensed Matter Physics of the University of Geneva, where he explored the functional aspects of complex hydrides using diffraction and different spectroscopies. Following a post doc centered around solid state ionic conductors he joined the École polytechnique fédérale de Lausanne (EPFL) in 2016, where he is responsible for the X-ray diffraction facility of ISIC. His interests concentrate on in situ studies of energy materials using both X-ray and neutron scattering, in particular on polycrystalline materials and thin films.

Radovan Černý did his PhD in Solid State Physics at the Charles University, Prague. In 1989 he came to the University of Geneva for a postdoctoral research, and was appointed Lecturer in 1995 and Associated Prof. in 2012. He is interested in the development of powder diffraction methodology, especially ab initio structure solution (computer program Fox), studies of structural defects and structural chemistry of inorganic compounds especially of metal hydrides where his group solved more than 120 crystal structures. Recently he turned his interest in the applied research on complex hydrides from hydrogen storage to solid electrolytes.
 Difficult to store in an efficient and compact way. This is a fundamental problem associated with the utilization of hydrogen as an energy carrier, which may be solved by the design of novel light weight metal hydrides, such as metal borohydrides. Research over the past decade has revealed a range of new light metal borohydrides possessing extremely high hydrogen densities, which may be considered for possible energy storage applications. However, in general, these compounds suffer from poor thermodynamic and kinetic properties, i.e., they are often too thermally stable and the hydrogen release and uptake reactions are too slow for practical applications.

A new approach is to allow multiple hydrides, denoted as reactive hydride composites (RHC), to react during the release of hydrogen to form a different dehydrogenated state. These composites change the hydrogen release pathway and may improve the thermodynamic and kinetic properties, enabling hydrogen release and uptake under more favourable conditions. The concept aims to lower the overall reaction enthalpy by introducing extra (endothermic) chemical reaction(s), i.e., by utilizing the well-known Hess law from chemistry, also denoted as Medima principles.

Composites of two or more metal borohydrides often induce co-melting or eutectic melting. Low temperature melting may reduce the hydrogen release temperature, as observed for \( \text{xLiBH}_4-(1-\text{x})\text{Mg(BH}_4)_2 \), or for preparation of molten metal borohydrides systems for convenient nanoconfinement, e.g., in the \( 0.725\text{LiBH}_4-0.275\text{KBH}_4 \) with \( T_m = 105 \degree\text{C} \). Metal borohydrides with low melting points could allow for fast and convenient re-fuelling of vehicles with similar technology to that known today for liquid fossil fuels.

Metal borohydrides are a multifunctional class of materials that may also be used as fast ion conductors for new types of batteries or for gas adsorption. They may also have optical, electronic and magnetic properties and can be used as reducing agents in organic synthetic chemistry. For this reason, mono-, bi- and trimetallic borohydrides have been exposed to intense research efforts to develop new synthesis strategies, perform structural characterization, and investigate physical and chemical properties. In the following, we critically review the progress of metal borohydrides and their derivatives, which may form the basis of future technological applications. The focus of this review is to discover new trends in synthesis, structure and properties and provide perspectives for further research that may act as inspiration for the development of novel materials towards rational materials design.

2. Synthesis of metal borohydrides and derivatives

A number of different synthetic approaches have been developed to prepare new types of metal borohydrides, including anion substitution and the preparation of derivatives including neutral molecules, such as ammonia, hydrazine, etc. A range of different chemical reactions can be undertaken in different media; and of those, metathesis, i.e., double substitution reactions, and addition reactions are the most common. In some cases, more complex or competing reactions are observed. Halide- and solvent-free mono-metallic borohydrides can be obtained using solvent-based methods, mechanochemical methods successfully provide numerous bi- and tri-metallic borohydrides, whereas solid–gas reactions are important for the preparation of ammine metal borohydrides. Typically, air and moisture sensitive reagents are utilized, which need to be manipulated in a glove box or using standard vacuum and Schlenk techniques in dry and inert atmosphere. In general, metal borohydrides, anhydrous metal halides and many solvents are hygroscopic and readily absorb water. The hydrates of metal borohydrides containing metals with low electronegativity are often stable at RT but react with water at elevated temperatures and evolve hydrogen. Metal borohydrides of...
metals with higher electronegativity may adsorb water and react exothermically at RT, releasing hydrogen. Alkali metal borohydrides are stable in basic aqueous solution and closo-boranes are stable in neutral and acidic solutions. This section reveals general trends in chemical reactions for the synthesis of different metal borohydrides and their derivatives under different physical conditions. Hydrogen release and uptake reactions in metal borohydrides and synthesis of some of those from the elements are discussed in Section 6.

2.1 Solvent-based synthesis of monometallic borohydrides

The first successful solvent-based synthesis of a metal borohydride was accomplished by Wiberg and Bauer in 1950 by a reaction between diethylmagnesium, Mg(CH2CH3)2, and diborane, B2H6, in ether.55 Since diborane is challenging to handle, i.e. poisonous, self-igniting and explodes in contact with air or moisture, a borane complex such as triethylamine borane, (C2H5)3NBH3 or dimethylsulfide borane, (CH3)2SBH3, is safer and easier to handle. Solvent mediated addition reactions take place between a borane donor and a metal hydride or a metal alkyl compound. The obtained product is commonly a solvate that needs further treatment in order to produce a solvent-free product.56,57 This approach has provided the first open-structured alkyl compound. The obtained product is commonly a solvate and easier to handle. Solvent mediated addition reactions take place between a borane donor and a metal hydride or a metal alkyl compound. The obtained product is commonly a solvate that needs further treatment in order to produce a solvent-free product.56,57

Metal borohydrides are also often synthesized via a quantitative metathesis reaction, illustrated by the preparation of Al(BH4)_3 from aluminum trichloride and lithium borohydride in an organic solvent (e.g. toluene).60

\[ 3\text{LiBH}_4(s) + \text{AlCl}_3(s) \rightarrow \text{Al(BH}_4)_3(l) + 3\text{LiCl}(s) \]  

Metal borohydrides and halides often have different solubilities in solvents, allowing for salt-free products to be obtained in high yield. A weakly coordinating solvent that only dissolves the metal borohydride allows for the removal of the metal halide by solvent extraction. The reaction kinetics and yield can be improved by using finely ground reactants with large surface area.

A limitation of solvent-based methods is that the thermodynamically most stable compound is obtained, which is often a monometallic borohydride, typically obtained as a polymorphic pure product. Therefore, reaction mixtures containing two or more metals tend to form mixtures of two or more monometallic borohydrides rather than the bi- or trimetallic borohydrides, which are obtainable through mechanochemical synthesis. Thus, very few bimetallic solvates have been discovered, e.g. in diethyl ether, Et2O, LiMn[BH4]3-1/2(Et2O) and NaMn[BH4]3-2/3(Et2O).61 Recently, a new method was developed for the production of bimetallic metal borohydrides using bulky organic cations and weakly coordinating anions.62-64 The metathesis reaction is carried out in organic solvents, CH2Cl2, CHCl3, or toluene, and utilizes precursors such as [Cat][Zn(BH4)3] or [Cat][Y(BH4)3], where [Cat] symbolizes bulky cations, e.g. [Ph4P] or [nBu4][N]. The method is also useful for producing less stable bimetallic borohydrides, i.e. LiY(BH4)3, NaY(BH4)3 or LiZn2(BH4)3.62-63

The use of dimethyl sulphide, S(CH3)2, as a co-solvent and extraction solvent has several advantages: (i) the reaction is allowed to proceed faster as the products are being dissolved in S(CH3)2 as they form, (ii) weak solvent coordination allows for solvent removal at moderate conditions, (iii) the product dissolved in the solvent can readily be separated from the byproducts (i.e. LiCl) by filtration. In this manner, the formation of ternary chlorides is avoided, e.g. Li- or NaMn-chlorides, or bimetallic borohydrides, previously reported to form mechanochemically from MnCl2 and LiBH4 or NaBH4.64-65

Recently, yttrium and gadolinium borohydrides were prepared using dimethyl sulfide as a solvent, providing new solvates as intermediates, M'[BH4]3-S(CH3)2 (M = Y, La, Ce or Gd), which transform to z-M[BH4]3 or Gd[BH4]3 at T ~ 140 °C.66,67 Other halide-free rare-earth metal borohydrides, Eu[BH4]3 and Sm[BH4]3, are prepared by a metathesis reaction of trivalent metal chlorides and LiBH4 in ether, combined with solvent extraction using dimethyl sulfide to remove the halide salts.68 Donor atoms in solvents typically have increasing strength of coordination in the series Si < N < O and are increasing difficult to remove from the metal borohydride products.

2.2 Trends in the mechanochemical synthesis of metal borohydrides

Mechanochemistry is an alternative synthesis approach to bring chemicals together on the atomic scale. Investigations indicate that the induced pressure and reactant composition are of major importance in determining the obtained reaction product.52 High-energy ball milling induces high pressure and mechanical stress between the reacting materials, which can facilitate chemical reactions, in contrast to traditional solid-state synthesis techniques, which are mainly ‘temperature-driven’, i.e. increasing cation diffusion in the solid state with increasing temperature.69 Previously, ball milling was mainly aimed at the preparation of alloys and solid solutions of metals, i.e. products with statistical distribution of atoms, but now also encompasses the synthesis of ionic, ionic/covalent materials and also organic materials, i.e. crystalline materials with ordered distribution of atoms. In some cases, materials can be obtained by mechanochemistry, which apparently cannot be obtained by other means.52

High energy mechanochemistry can be very fruitful in the preparation of metal borohydrides where the ball trajectories approach the center of the milling vial, which contrasts grinding mode where the balls follow the circumference of the vial. This treatment maximizes the ‘intrinsic pressure’ at grain boundaries and limits frictional heating of the sample. Sample heating may be further reduced using pauses during the mechanochemical treatment.70 Continuous prolonged ball milling may lead to decomposition of the sample, but may also produce new materials, e.g. anion-substituted Na[BH4]3-Cl or nano-sized vanadium boride.71-73 Mechanochemical synthesis can be performed under a variety of different conditions, e.g. at cryogenic conditions, in
a solvent, or in different gases at elevated pressures (the latter is often denoted reactive ball-milling when the gas takes part in the reaction).\textsuperscript{74–77} Hence, mechanochemistry is a versatile technique, which can be used for the preparation of a wide range of materials.\textsuperscript{82}

New bi- and trimetallic borohydrides can often be prepared by mechanochemical methods. In cases where pure monometallic borohydrides are available as precursors (e.g. prepared by solvent-based methods) addition reactions may be utilized as exemplified by the synthesis of Cs\textsubscript{2}LiY(BH\textsubscript{4})\textsubscript{6}.\textsuperscript{78} A major advantage is that a pure product may be obtained.

\[2\text{CsBH}_4(s) + \text{LiBH}_4(s) + \text{Y(BH}_4)_3(s) \rightarrow \text{Cs}_2\text{LiY(BH}_4)_6(s)\] (2.2)

Monometallic borohydrides may be prepared via metathesis reactions, \textit{i.e.} double substitution, usually between a metal halide and a metal borohydride. The reaction scheme (2.3) illustrates the synthesis of Mn(BH\textsubscript{4})\textsubscript{2} from LiBH\textsubscript{4} and MnCl\textsubscript{2}.\textsuperscript{21,79}

\[\text{MnCl}_2(s) + 2\text{LiBH}_4(s) \rightarrow \text{Mn(BH}_4)_2(s) + 2\text{LiCl(s)}\] (2.3)

The drawback is obviously the formation of a mixture of an unwanted metal halide along with the product. The system ZnCl\textsubscript{2}–KBH\textsubscript{4} (M = Li or Na) can be used to illustrate the complexity of reaction products from mechanochemical synthesis, which may proceed via more complex chemical reactions during ball milling.\textsuperscript{70}

\[2\text{ZnCl}_2(s) + 5\text{LiBH}_4(s) \rightarrow \text{LiZn}_2\text{(BH}_4)_3(s) + 4\text{LiCl(s)}\] (2.4)

\[2\text{ZnCl}_2(s) + 5\text{NaBH}_4(s) \rightarrow \text{NaZn}_2\text{(BH}_4)_3(s) + 4\text{NaCl(s)}\] (2.5)

\[\text{ZnCl}_2(s) + 3\text{NaBH}_4(s) \rightarrow \text{NaZn(BH}_4)_3(s) + 2\text{NaCl(s)}\] (2.6)

Reaction schemes (2.5) and (2.6) illustrate that small deviations in the composition of reactants, e.g. from (1 : 2.5) to (1 : 3), may lead to significantly different reaction products, both in terms of the stoichiometry and crystal structures, \textit{i.e.} the structures of NaZn(BH\textsubscript{4})\textsubscript{3} and NaZn\textsubscript{2}(BH\textsubscript{4})\textsubscript{3} are significantly different, which may suggest that the synthesis mechanism for these compounds is also different.

Further complications occur due to strong or weak coupling between the chemical reactions that occur during mechanochemical synthesis. Besides the main reaction that forms the product, competing side reactions may also take place, \textit{e.g.} producing bimetallic halides. Sodium chloride produced in reaction (2.5) or (2.6) may further react with the reactant, zinc chloride:

\[\text{ZnCl}_2(s) + 2\text{NaCl(s)} \rightarrow \text{Na}_2\text{ZnCl}_4(s)\] (2.7)

Thus, the synthesis of NaZn\textsubscript{2}(BH\textsubscript{4})\textsubscript{3} only partly proceeds (reaction scheme (2.5)), due to the formation of a stable ternary metal chloride, Na\textsubscript{2}ZnCl\textsubscript{4}, by a simultaneous and competing reaction (scheme (2.7)). The reaction schemes, (2.5) or (2.6) and (2.7), are weakly coupled by the fact that the reaction products contain varying amounts of NaCl, Na\textsubscript{2}ZnCl\textsubscript{4}, NaZn\textsubscript{2}(BH\textsubscript{4})\textsubscript{3}, and reactants. Thus, reaction schemes (2.5)–(2.7) cannot simply be added to provide a scheme for the total reaction.

Sodium scandium borohydride, NaSc(BH\textsubscript{4})\textsubscript{4}, can also be prepared mechanochemically and is assumed to follow the metathesis reaction (2.8).\textsuperscript{80}

\[\text{ScCl}_3(s) + 4\text{NaBH}_4(s) \rightarrow \text{NaSc(BH}_4)_4(s) + 3\text{NaCl(s)}\] (2.8)

However, reaction (2.8) is strongly coupled to the synthesis of a ternary sodium scandium chloride, Na\textsubscript{3}ScCl\textsubscript{6} via an addition reaction:

\[\text{ScCl}_3(s) + 3\text{NaCl(s)} \rightarrow \text{Na}_3\text{ScCl}_6(s)\] (2.9)

Reaction (2.9) is much faster than the formation of the borohydride, NaSc(BH\textsubscript{4})\textsubscript{4} (2.8) and these reactions, (2.8) and (2.9) are strongly coupled so they can be added to form an overall reaction (2.10). Therefore, the optimal ratio of reactants ScCl\textsubscript{3}–NaBH\textsubscript{4} to synthesize NaSc(BH\textsubscript{4})\textsubscript{4} turns out to be 1:2. This mechanochemical synthesis leads to a maximum NaSc(BH\textsubscript{4})\textsubscript{4} yield of 22 wt% for a sample with composition (1:2) as suggested by reaction (2.10) and not the ratio (1:4) suggested in reaction (2.8).

\[2\text{ScCl}_3(s) + 4\text{NaBH}_4(s) \rightarrow \text{NaSc(BH}_4)_4(s) + \text{Na}_3\text{ScCl}_6(s)\] (2.10)

The above considerations are also valid for synthesis of KSc(BH\textsubscript{4})\textsubscript{4}, but not for synthesis of LiSc(BH\textsubscript{4})\textsubscript{4} where no ternary halide is formed.\textsuperscript{70,81}

There is a tendency for more complex chemistry and other chemical reactions to occur when the heavier alkali metals and halides are used as reactants. Mechanochemical synthesis of M\textsubscript{x}ZnX\textsubscript{4}, M = Li or Na, X = Cl or Br from stoichiometric mixtures of MX and ZnX\textsubscript{4} reveals that reaction times and activation energy decrease as Li\textsubscript{3}ZnCl\textsubscript{4} > Na\textsubscript{2}ZnCl\textsubscript{4} > Na\textsubscript{2}ZnBr\textsubscript{4}.\textsuperscript{82}

The formation of ternary halides can be avoided in the synthesis of trimetallic borohydrides by varying the ratio between borohydrides and halides if at least two reactants are available as mono-metallic borohydrides. While reaction (2.11) produces the ternary salt, Li\textsubscript{4}MCl\textsubscript{4}, the alternative reaction (2.12) avoids this byproduct formation.\textsuperscript{83}

\[15\text{LiBH}_4 + 5\text{MCl}_3 + 5\text{ZnCl}_2 \rightarrow \text{Li}_4\text{MZn}_3\text{(BH}_4)_15 + 4\text{LiCl}\]
\[+ 4\text{Li}_4\text{MCl}_4\quad M = \text{Mg or Mn}\] (2.11)

\[13\text{LiBH}_4 + \text{M(BH}_4)_2 + 5\text{ZnCl}_2 \rightarrow \text{Li}_4\text{MZn}_3\text{(BH}_4)_15 + 10\text{LiCl}\] (2.12)

This observation also suggests that the formation of bimetallic halide salts can be considered a side reaction where the produced metal halide reacts with remaining reactants. In some cases, such side reactions can be suppressed partly or fully by using an excess of metal borohydride reactants, \textit{e.g.} LiBH\textsubscript{4}, which may shift the reaction equilibrium towards the bi- or trimetallic borohydrides and the monometallic halide, \textit{e.g.} LiCl.

### 2.3 Trends in the mechanochemical synthesis of metal borohydrides-halides

Metal borohydride halides can be prepared with either ordered or disordered crystal structures, where in the latter case solid solutions occur. The system ZnCl\textsubscript{2}–KBH\textsubscript{4} will be used to illustrate the complexity of the mechanochemical synthesis. Ball milling a...
mixture of ZnCl₂·KBH₄ (1:1) leads to an addition reaction and a single product, KZn[BH₄]Cl₂.⁵⁴

\[ \text{ZnCl}_2(s) + \text{KBH}_4(s) \rightarrow \text{KZn(BH}_4\text{)Cl}_2(s) \]  
(2.13)

In this case, there are significant differences between the structures of the reactants and the product. The latter contains a heteroleptic complex ion containing BH₄⁻ as a ligand, i.e. \([\text{Zn(BH}_4\text{)Cl}_2]^-\) where Zn coordinates to two chloride ions and two hydrogen atoms in \(\eta^2\text{-BH}_4\).⁶⁴ This clearly demonstrates that ball milling may initiate complex chemical reactions involving bond breaking and bond formation.⁵³ In contrast, three novel potassium zinc borohydrides/chlorides are observed in ball-milled KBH₄·ZnCl₂ mixtures with molar ratios in the range 1.5:1 to 3:1, KZn[BH₄]Cl₂, K₂Zn[BH₄]Cl₃·x and KZn[BH₄]Cl₅·x.⁸⁵

Mechanochemical treatment may also facilitate one solid to dissolve into another, i.e. an addition reaction, which leads to formation of a solid solution, e.g. formation of a hexagonal solid solution h-Li[BH₄]ClBr where the two anions, BH₄⁻ and Br⁻, are statistically distributed on the same crystallographic position, formed by mechanochemical treatment of LiBH₄-LiBr.⁸⁶

In some cases, the crystallinity of the sample and also the overall sample composition may be modified by thermal treatment of the sample. For example, the composition of Na₂[BH₄]Cl₂ changed to NaY[BH₄]Cl₂ at \(T = 230^\circ\text{C}\).⁸⁷ The rare-earth metals are yet another example: LiCe[BH₄]Cl and LiLa[BH₄]Cl were prepared by ball milling,⁴ whereas LiGd[BH₄]Cl only crystallized after heat treatment at \(T = 195^\circ\text{C}\).⁸⁸ A similar trend is observed for the synthesis of metal borohydride amides e.g. Li₂[BH₄](NH₃), Li₂[BH₄](NH₃)₃, Na₂[BH₄](NH₃) and Mg[BH₄](NH₃),⁸⁹-⁹¹ which are all metal cation conductors. These compounds are formed through ball milling (and annealing) of M[BH₄]ₙ·MNH₂. In this case, NH₃ does not substitute for BH₄⁻ to form solid solutions as for Cl⁻, instead, new structures are formed with distinct sites for BH₄⁻ and NH₃⁻. A detailed analysis of the unit cell volumes of LiBH₄, KBH₄ and LiK[BH₄]₂ indicates that the formation of the bimetallic borohydride is facilitated by a more dense packing as compared to the reactants.⁹⁷ Thus, formation of LiK[BH₄]₂ is pressure-induced and takes place during ball milling, but not by annealing. This is in agreement with DFT calculations suggesting that LiK[BH₄]₂ should decompose to the reactants at ambient conditions.⁹³ In contrast, the unit cell volumes of the solid solution Na₁₋ₓKBH₄ is larger than the sum of reactant volumes, \((1 - x)\text{NaBH}_4 + x\text{KBH}_4\).⁹³ Hence, the formation of Na₁₋ₓKBH₄ is temperature-induced and occurs upon annealing, i.e. thermal expansion, but not during ball milling.

### 2.4 Mechanocatalytic reactions, general considerations

Table 1 highlights the range of different chemical reactions that are typically observed during the synthesis of metal borohydrides by mechanochemistry. The literature suggests that monometallic borohydrides are more likely to form when LiBH₄ is used as the precursor, possibly driven by the formation of the stable halide, LiCl. Furthermore, an excess of LiBH₄ may improve the crystallinity of reaction products. The heavier alkali metal borohydrides have a significantly greater tendency to form bimetallic halide salts, MₓM'Xₙ via addition reactions (the nomenclature is explained in Table 1). Such reactions may occur when LiCl is present together with a heavier metal halide, M'Xₙ or LiCl may be incorporated into the product producing ordered bimetallic borohydrides chlorides, LiCe[BH₄]Cl₂ (except in the case of Li₂CdCl₄ and Li₂MCl₄, M = Mg, Mn). A range of rarer reactions can also be observed, which are considered analogous to the general reactions, (1)–(4) or combinations of those. For example, mono- or bimetallic borohydride chlorides with crystallographically disordered structures i.e. NaY[BH₄]Cl₂ can be formed either by substitution (eqn (4)) or complex (eqn (2)) reactions.⁸⁷

Generally, di- and tripositive metal halides, MBH₄·M'Clₑₙ, have very different reactivities and stabilities depending on their metal electronegativity and d-electron configuration. Therefore, different milling times are required to successfully obtain the desired product. For example, synthesis of MSc[BH₄]Cl₄ (M = Li, Na or K) occurs by ball-milling MBH₄·ScCl₃ (2:1) for 120–180 min, while the cadmium borohydrides, xCd[BH₄]Cl₂, β-Cd[BH₄]₂, KCd[BH₄]₄ and K₂Cd[BH₄] are formed from MBH₄·CdCl₂ (M = Li, Na or K) after only 20–30 min mechanochemical treatment. Only the transition metals with d⁰, d⁵ or d¹⁰ electron configurations have sufficient stability to allow for mechanochemical preparation.⁸ However, transition metal borohydrides, M'[BH₄]ₓ, M' = Cr²⁺ (d⁶), Fe²⁺ (d⁶) and Co⁴⁺ (d⁵), were recently prepared in solution at \(T < -30^\circ\text{C}\), and stabilised by ammonia–metal coordination, i.e. formation of M'[NH₃]ₓ[BH₄]₁ₓ compounds.⁴⁴

#### 2.5 Mechanical synthesis in different gas atmosphere

Solvent-free synthesis of monometallic borohydrides, e.g. lithium borohydride, LiBH₄, formed in an addition reaction between lithium hydride, LiH, and diborane, B₂H₆ gas at \(T = 120^\circ\text{C}\) has recently been demonstrated.⁹⁵ The formation of LiBD₄ from LiD and B₂D₆ was followed using in situ powder neutron diffraction, which reveals that the nucleation of LiBD₄ begins at \(T \sim 102^\circ\text{C}\, i.e. with the formation of the hexagonal polymorph, h-LiBD₄. However, the reaction is incomplete and the yield is only \(\sim 50\%\) even at elevated temperatures (187°C)

**Table 1** Generalization of chemical reactions observed during mechanochemical synthesis of metal borohydrides from MBH₄–M'Xₙ reactant mixtures along with selected examples. Nomenclature: X = halide anion, M = alkali metal cation and M' = di- or tri-positive metal

<table>
<thead>
<tr>
<th>Reaction type/no.</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metathesis/1</td>
<td>nMBH₄ + M'Xₙ → M'[BH₄]ₓ + nMX</td>
</tr>
<tr>
<td>Example 1</td>
<td>2LiBH₄ + MnCl₂ → Mn[BH₄]₂ + 2LiCl</td>
</tr>
<tr>
<td>Addition/2</td>
<td>yMBH₄ + xMX → M[BH₄]ₓXₙ</td>
</tr>
<tr>
<td>Example 0.75NaBH₄ + 0.25NaCl → Na[BH₄]₀.₇⁵Cl₀.₂₅</td>
<td></td>
</tr>
<tr>
<td>Metathesis-addition/3</td>
<td>(x + ny)[MBH₄ + yM'Xₙ] → MₓM'y[BH₄]ₓ+y + (ny)MX</td>
</tr>
<tr>
<td>Example 4LiBH₄ + ScCl₃ → LiSc[BH₄]₃ + 3LiCl</td>
<td></td>
</tr>
<tr>
<td>Metathesis-addition/4</td>
<td>M'Xₙ + nMBH₄ → M'[BH₄]ₓX + (n - 1)MX</td>
</tr>
<tr>
<td>Example CcCl₃ + 3LiBH₄ → LiCe[BH₄]Cl + 2LiCl</td>
<td></td>
</tr>
</tbody>
</table>
with the product containing small amounts of Li₂B₁₂H₁₂. A passivation layer of LiBH₄ is suggested to form on the surface of the LiH grains retarding the process. Mechanochemical treatment allows for the continuous removal of as-formed borohydride from the surface layer of particles, facilitating a more complete reaction. Diborane gas is produced by heating a ball milled 2.5LiBH₄–ZnCl₂ sample, i.e. decomposition of LiZn₃(BH₄)₃, which is considered a convenient and relatively safe source of diborane compared to pressurized gas bottles. This new gas-solid mechanochemical synthesis method has also successfully provided other metal borohydrides, such as Mg(BH₄)₂, Ca(BH₄)₂ and Y(BH₄)₃, by ball milling YH₃ in a B₂H₆ atmosphere. Direct synthesis of z-Y(BH₄)₃ by ball milling YH₃ in a B₂H₆ atmosphere gave yields above 75%, 98,99 and ball milling Y(BH₄)₃ in B₂H₆ has also led to the discovery of Y(B₂H₆)₃ and Yₓ(B₁₂H₁₂)ₓ, suggesting that higher boranes might also be formed during the decomposition of Y(BH₄)₃. These solid–gas reactions can be considered as addition reactions analogous to the solvent-based reactions described above (see Section 2.1). Thus, this analogy suggests that the solvent-free solid–gas reactions are only useful when Lewis base type ionic or polar covalent hydrides, such as LiH, providing an electron-pair donating H⁻ ion, or BH₄⁻, can be utilised as reactants to form a borohydride or higher borane. The solid–gas reactions are promising for extending the series of solvent-free metal boranes.

### 2.6 Single crystal growth of metal borohydrides

Despite significant efforts, single crystal investigations of metal borohydrides are very scarce. This is mainly due to the complications arising when attempting to grow metal borohydrides by classical solution chemistry. Solvents need to be carefully selected in order to avoid the formation of solvates. Unfortunately, non-coordinating apolar solvents often have low solubility limits. Notably, single crystal studies have been reported on mono-metallic compounds such as LiBH₄, NaBH₄, KB₄, Be(BH₄)₂, Mg(BH₄)₂, and Al(BH₄)₃, where crystals can be grown from a solution, by annealing the powder, or by recrystallizing from a melt. Techniques involving melting are useful for mono-metallic borohydrides but limited to bi- and trimetallic borohydrides that are sufficiently thermally stable (recall that a high number of these compounds are prepared mechanochemically, stabilized by high pressure rather than elevated temperature). Powder samples of framework-type metal borohydrides produced mechanochemically may, in some cases, be partly dissolved in a suitable solvent and then recrystallized to larger crystals. Single crystals of KCa(BH₄)₂ were recently prepared from flux, which can be an eutectically melting mixture of more stable alkali and/or earth alkali metal borohydrides with sufficiently large thermal stability.

Chemical vapour deposition (CVD) was reported as an approach for the crystal growth of Zr(BH₄)₄, which is formed by a metathesis reaction of ZrCl₄ and LiBH₄ during ball milling.

\[
\text{ZrCl}_4(s) + 4\text{LiBH}_4(s) \rightarrow \text{Zr(BH}_4)_4(s) + 4\text{LiCl(s)} \quad (2.14)
\]

The ball milled sample was stored in a vial at −30 °C for 2–4 weeks when transparent single-crystals with a rectangular shape were noticed under the lid, explained by the low sublimation temperature of Zr(BH₄)₄ (29 °C) because of its molecular structure. CVD is an elegant method for single crystal growth of metal borohydrides, which may be limited to volatile molecular compounds with low vapour pressures and sublimation temperatures.

The importance of producing single crystal samples stems not only from the fact that physical properties such as ionic conductivity can be highly anisotropic and powder averaging can present problems to such characterizations, but also from the necessity of providing accurate input for theoretical evaluations of hydrogen storage systems.

### 2.7 Synthesis of metal borohydrides with neutral molecules

Metal borohydrides form complexes with hydrogen-rich nitrogen-based neutral molecules, which can be in the solid state (e.g. ammonia borane, NH₃BH₃) or liquid state (e.g. hydrazine, NH₂NH₂) or gas state (e.g. ammonia, NH₃). These compounds are capable of generating large amounts of hydrogen by combining the hydrogen atoms present in the two counterparts. Borohydride complexes with water have similar properties but usually have a lower stability, where the hydrates of sodium, lithium, and calcium are characterized.

#### Ammonia borane metal borohydride complexes.

Ammonia borane metal borohydride complexes are formed by addition reactions between NH₃BH₃ and LiBH₄, Mg(BH₄)₂, Ca(BH₄)₂ and Al(BH₄)₃. For the solids LiBH₄, Mg(BH₄)₂, Ca(BH₄)₂ the complexes are prepared by ball-milling. Interestingly, the mixture z-Mg(BH₄)₂–NH₃BH₃ (1:2) converts completely into Mg(BH₂)₂(NH₂BH₂) upon ball milling, while Mg(BH₄)₂(NH₂BH₂) is not formed when starting from amorphous Mg(BH₄)₂ and NH₂BH₂. This is counter-intuitive, since amorphous matter usually has higher reactivity, suggesting that there is a structural relationship allowing the borohydride to coordinate with neutral ligands. Optimal contact between reactants is offered by liquid Al(BH₄)₃ at ambient conditions to form single-crystals of Al[BH₄]₃:NH₂BH₃.

#### Hydrazine metal borohydrides.

Complexes with hydrazine are reported for LiBH₄, NaBH₄ and Mg(BH₄)₂, e.g. LiBH₄-NH₂NH₂. These compounds were synthesized by placing the precursor metal borohydride and hydrazine in different chambers of a sealed system at room temperature. Due to the vapour pressure, hydrazine typically absorbs into the borohydride over the course of hours. Alternatively, the complexes are formed by ball milling solid–liquid mixtures of M[BH₄]₃–NH₂NH₂.

#### Ammine metal borohydrides.

Metal borohydrides readily react with ammonia gas in solid–gas reactions forming ammine metal borohydrides, M[BH₄]₃–NH₃, except for the heavier alkali metal borohydrides: NaBH₄, KB₄, RbBH₄ and CsBH₄. However, the first ammine metal borohydrides, e.g. Zn[BH₄]₃–4NH₃, were synthesized in the 1950’s by solvent-based methods.

Recent literature reveals that the NH₃/BH₄ ratio (n/m) of ammine metal borohydrides, M[BH₄]₃–nNH₃, can be efficiently tailored by combining solvent based methods, solid–gas reactions and mechanochemistry. Initially, a metal borohydride is prepared by a solvent-based method or by solvent extraction.
of a mechanochemically prepared metal borohydride metal halide mixture, e.g. using a weakly coordinating solvent such as dimethyl sulﬁde, S(CH3)2. Ammine metal borohydrides may be prepared by passing dry NH3 gas through the solution of M(BH4)4 in S(CH3)2 or by a reaction between dry NH3 gas and solid M(BH4)3. Ammonia always coordinates to the metal by a strongly exothermic reaction and cooling is usually needed in order to obtain the metal borohydride containing the highest possible number of ammonia molecules for further synthesis, e.g. M(BH4)4,7NH3. M = Y, Gd or Dy prepared at T ∼ −5 °C.13 Synthesis of ammine metal borohydrides in more strongly coordinating solvents, such as THF, is also possible, however, the samples are contaminated by the formation of ammonia borane.126

Mechanochemical treatment of the ammine metal borohydride having the highest possible number of ammonia molecules and the corresponding metal borohydride in various ratios is a convenient way to get new ammine metal borohydrides with varying NH3/BH4 ratio. This approach is demonstrated for ammine manganic borohydride, Mn(BH4)2 · nNH3 for n = 1, 2, 3 and 6.24

\[ n\text{Mn}(\text{BH}_4)_2 \cdot 6\text{NH}_3(s) + (6 - n)\text{Mn}(\text{BH}_4)_2(s) \rightarrow 6\text{Mn}(\text{BH}_4)_2 \cdot n\text{NH}_3(s) \]  

(2.15)

3. Trends in structural chemistry of metal borohydrides

The past decade has experienced a major increase in the number of experimental structural studies of novel metal borohydrides, in particular using powder X-ray or neutron diffraction.124,125 Various equipment has been designed to enable this type of PXD characterization under high gas pressure and temperature.124,126 The interest in crystal chemistry of metal borohydrides was initiated in the late 1940’s by investigations into the most ionic and stable monometallic borohydrides, namely MBH4, M = Na, K, Rb and Cs.18,19 Later studies focused on the more challenging molecular, volatile and covalent compounds, e.g. Al(BH4)3, Zr(BH4)4 and Hf(BH4)4.126,127,128 In between these two extremes we ﬁnd numerous metal borohydrides with framework structures, pronounced bonding directionality and clearly some degree of covalency, e.g. Mg(BH4)2 and Mn(BH4)2.126,128,129

The successful structural analysis of LiBH4 in 2002 was the initiation of this renewed interest in metal borohydrides.24

The ﬁrst bimetallic borohydride, LiK(BH4)2, was discovered and characterized in 2008.130 Since then, a rapidly increasing number of bimetallic and also trimetallic borohydrides have been described, often containing complex anions. Some compounds fall within more than one of these categories, for instance, Li2Zn3(BH4)5 contains [Zn2(BH4)5]3− complex anions but can also be considered as being built from interpenetrated frameworks.70

Clearly, metal borohydrides exhibit a fascinating and surprisingly versatile crystal chemistry, which the following section will review, highlighting general trends and relationships. Initially, mono-metallic borohydrides will be discussed (Table 2), starting from the simple cubic ionic structures, moving towards more covalent and complex bi- and trimetallic borohydrides (Tables 3 and 4), including framework structures and anionic complexes.

3.1 Monometallic borohydrides, the s-block – pronounced ionic bonding

The alkali metal borohydrides, MBH4, M = Li, Na, K, Rb and Cs, primarily exhibit ionic bonding and theoretical studies show that there is almost no charge density (<5%) between the M+ and BH4− ions in their structures.173–176 An experimental charge density investigation of o-LiBH4 reveals transfer of 0.86 ± 0.09 e− (at 10 and 90 K) from Li to BH4 in accordance with the ionic structure description.175

Lithium borohydride. Four polymorphs of lithium borohydride, LiBH4, have been described and the orthorhombic o-LiBH4 (Pnna) structure at ambient conditions is unique.24 Single crystal XRD investigations of o-LiBH4 at 225 K unambiguously reveal nearly ideal tetrahedral geometry of the BH4 group, in contrast to more distorted tetrahedra reported in earlier PXD studies.122,123 Powder neutron diffraction of the triple isotopically substituted o-7Li11BD4 at 3.5 K reveals boron–hydrogen bond lengths (B–H) of 1.208–1.225 Å, and bond angles (H–B–H) in the range 107.2–111.7°.177

Orthorhombic o-LiBH4 transforms to a hexagonal wurtzite-like polymorph h-LiBH4 (P63mc) at ∼110 °C. PXD and PND studies reveal large and anisotropic displacements of hydrogen atoms.177,178 The observed atomic displacement ellipsoids may indicate orientational disorder in addition to thermal vibrations of the BH4 group. The large vibrational amplitudes of BH4 in the hexagonal polymorph agree with an apparent shortening of the B–H bonds to ∼1.07 Å. An entropy contribution from this disorder is considered to be a factor in stabilizing the hexagonal structure.170,176 Two high pressure polymorphs of LiBH4 are also observed at room temperature. One polymorph is observed at a pressure of 1.2–18 GPa, which is pseudo-tetragonal (Amma2) with Li tetrahedrally coordinated by four BH4 groups and the BH4 groups in a nearly square-planar coordination by four Li atoms.131 A more complex ordering of the BH4 groups, showing repulsive interactions, was ﬁrst suggested in the \[\sqrt{2}a \times c\] supercell of the Amma2 structure theoretically79 and then shown experimentally.180 At high pressure a cubic LiBH4 polymorph forms, which is isostructural to cubic NaNH2 (Pm3n) at 4.4 GPa. In general, the four polymorphs of lithium borohydride primarily show coordination between lithium and the borohydride complex anion by edge sharing, but h-LiBH4 and o-LiBH4 appear to have face sharing for the shortest Li–B contact (2.37 Å). The structural distortions in LiBH4 polymorphs have been analysed by group-theoretical and crystal-chemical considerations revealing the layered structure of LiBH4,181 where the deformation of layers deﬁne the structural stability of the observed polymorphs.

The heavier alkalai metals. Available p-orbitals and the increasing sizes of heavier alkali metals facilitate the formation of rock salt (NaCl, Pm3m) type structures of alkali metal borohydrides, MBH4, M = Na, K, Rb and Cs. Theoretical studies suggest that electron density deformations of the heavier alkali metals may also contribute to the formation of NaCl-type structures.176 Additional studies at low temperature and high pressures have discovered several other structural polymorphs.18,19,133,135,182
<table>
<thead>
<tr>
<th>Cation</th>
<th>Polymorph</th>
<th>( \rho_m ) (wt% H)</th>
<th>Stability</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>α-LiBH(_4)</td>
<td>18.5</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Pnma</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>h-LiBH(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hp-LiBH(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(^+)</td>
<td>γ-Mg(BH(_4))(_2)</td>
<td>14.9</td>
<td>RT</td>
<td>Hexagonal</td>
<td>P6(_{3})mc</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>β-Mg(BH(_4))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>γ-RbBH(_4)</td>
<td>7.5</td>
<td>&lt;70 K or RT, 3.8–6.8 GPa</td>
<td>Tetragonal</td>
<td>P4(_{4})/nmc</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>β-RbBH(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(^+)</td>
<td>γ-Ca(BH(_4))(_2)</td>
<td>11.6</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Pnma</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>α-Ca(BH(_4))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(^+)</td>
<td>γ-Mn(BH(_4))(_2)</td>
<td>9.5</td>
<td>RT</td>
<td>Hexagonal</td>
<td>P3(_1)2(_1)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>α-Mn(BH(_4))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>α-RbBH(_4)</td>
<td>6.9</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Fd(_3)m</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>β-RbBH(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm(^+)</td>
<td>α-Sm(BH(_4))(_3)</td>
<td>4.5</td>
<td>~500 K</td>
<td>Tetragonal</td>
<td>P4(_{2})2(_1)</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>β-Sm(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu(^+)</td>
<td>α-Eu(BH(_4))(_3)</td>
<td>4.4</td>
<td>~430 K</td>
<td>Tetragonal</td>
<td>P4(_{2})2(_1)</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>β-Eu(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd(^+)</td>
<td>Gd(BH(_4))(_3)</td>
<td>6.0</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Fm(_3)m</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>Tb(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy(^+)</td>
<td>Dy(BH(_4))(_3)</td>
<td>5.9</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Pm(_3)m</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>Ho(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er(^+)</td>
<td>Er(BH(_4))(_3)</td>
<td>5.7</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Pm(_3)m</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>Yb(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>α-Yb(BH(_4))(_2)</td>
<td>4.0</td>
<td>RT</td>
<td>Tetragonal</td>
<td>P4(_{2})2(_1)</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>β-Yb(BH(_4))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf(^+)</td>
<td>Hf(BH(_4))(_3)</td>
<td>6.8</td>
<td>&gt;523 K</td>
<td>Hexagonal</td>
<td>P4(_{2})2(_1)</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>α-Hf(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>β-Hf(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Th(^+)</td>
<td>Th(BH(_4))(_3)</td>
<td>5.5</td>
<td>473–573 K</td>
<td>Tetragonal</td>
<td>P4(_{2})2(_1)</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>α-Th(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>β-Th(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U(^+)</td>
<td>α-U(BH(_4))(_3)</td>
<td>5.4</td>
<td>RT</td>
<td>Orthorhombic</td>
<td>Cm(_{2})m</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>β-U(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Np(^+)</td>
<td>Np(BH(_4))(_3)</td>
<td>5.5</td>
<td>~130 K</td>
<td>Tetragonal</td>
<td>P4(_{2})2(_1)</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>α-Np(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>β-Np(BH(_4))(_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cations</td>
<td>Polymorph</td>
<td>(\rho_m) (wt% H)</td>
<td>Crystal system</td>
<td>Space group</td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>------------------</td>
<td>----------------</td>
<td>-------------</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>Li⁺</td>
<td>K⁺</td>
<td>LiK(BH₄)₂</td>
<td>10.6</td>
<td>Orthorhombic</td>
<td>Pnma</td>
<td>130</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Rb⁺</td>
<td>m-LiK(BH₄)₂</td>
<td>6.6</td>
<td>Monoclinic</td>
<td>C2/m</td>
<td>156</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Cs⁺</td>
<td>o-LiK(BH₄)₂</td>
<td>6.6</td>
<td>Orthorhombic</td>
<td>Cmc2 (_1)</td>
<td>156</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Yb⁺</td>
<td>h-LiK(BH₄)₂</td>
<td>8.4</td>
<td>Hexagonal</td>
<td>P₆(_3),22</td>
<td>156</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Sc⁺</td>
<td>LiSc(BH₄)₂</td>
<td>4.8</td>
<td>Orthorhombic</td>
<td>Cmc2 (_1)</td>
<td>156</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Y⁺</td>
<td>LiY(BH₄)₂</td>
<td>10.4</td>
<td>Tetragonal</td>
<td>P4(_2) (_2)c</td>
<td>150</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Yb⁺</td>
<td>LiY(BH₄)₂</td>
<td>6.7</td>
<td>Tetragonal</td>
<td>P4(_2) (_2)c</td>
<td>150</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Lu⁺</td>
<td>LuLu(BH₄)₂</td>
<td>6.7</td>
<td>Tetragonal</td>
<td>P4(_2) (_2)c</td>
<td>147</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Zn⁺</td>
<td>LiZn(BH₄)₂</td>
<td>9.5</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>159 and 160</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Al⁺</td>
<td>LiAl(BH₄)₂</td>
<td>17.4</td>
<td>Cubic</td>
<td>P(_{4}) (_3) (_n)</td>
<td>160</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Cs⁺</td>
<td>LiCs(BH₄)₂</td>
<td>17.3</td>
<td>Monoclinic</td>
<td>P(_2) (_1) /c</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sc⁺</td>
<td>NaSc(BH₄)₂</td>
<td>12.7</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>150</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Y⁺</td>
<td>NaY(BH₄)₂</td>
<td>9.4</td>
<td>Orthorhombic</td>
<td>C22(_2), (_2)</td>
<td>63 and 161</td>
</tr>
<tr>
<td>Na⁺</td>
<td>La⁺</td>
<td>NaLa(BH₄)₂</td>
<td>7.3</td>
<td>Orthorhombic</td>
<td>Pbcn</td>
<td>162</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Yb⁺</td>
<td>NaYb(BH₄)₂</td>
<td>6.3</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>163</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Zn⁺</td>
<td>NaZn(BH₄)₂</td>
<td>9.1</td>
<td>Monoclinic</td>
<td>P(_2) (_1) /c</td>
<td>70 and 157</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Al⁺</td>
<td>NaAl(BH₄)₂</td>
<td>8.8</td>
<td>Monoclinic</td>
<td>P(_2) (_1) /c</td>
<td>70 and 157</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Mg⁺</td>
<td>K₂Mg(BH₄)₂</td>
<td>10.0</td>
<td>Monoclinic</td>
<td>P(<em>4)</em>(<em>2)</em>(<em>m)</em>(_bc)</td>
<td>164</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Mg⁺</td>
<td>K₂Mg(BH₄)₂</td>
<td>9.3</td>
<td>Tetragonal</td>
<td>P(<em>4)</em>(<em>2)</em>(<em>m)</em>(_bc)</td>
<td>164</td>
</tr>
<tr>
<td>K⁺</td>
<td>Ca²⁺</td>
<td>KCa(BH₄)₂</td>
<td>9.8</td>
<td>Orthorhombic</td>
<td>P(_b) (_a)</td>
<td>1</td>
</tr>
<tr>
<td>K⁺</td>
<td>Sr²⁺</td>
<td>SrSr(BH₄)₂</td>
<td>7.1</td>
<td>Orthorhombic</td>
<td>Pna(<em>2)</em>(_1) (_2)</td>
<td>165</td>
</tr>
<tr>
<td>K⁺</td>
<td>Sc²⁺</td>
<td>ScSc(BH₄)₂</td>
<td>11.2</td>
<td>Orthorhombic</td>
<td>Pmc(<em>2)</em>(_1)</td>
<td>166</td>
</tr>
<tr>
<td>K⁺</td>
<td>Y²⁺</td>
<td>o-KY(BH₄)₂</td>
<td>8.6</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>167</td>
</tr>
<tr>
<td>K⁺</td>
<td>Ce³⁺</td>
<td>K₀Ce(BH₄)₂</td>
<td>8.6</td>
<td>Orthorhombic</td>
<td>Cmcm</td>
<td>167</td>
</tr>
<tr>
<td>K⁺</td>
<td>Gd³⁺</td>
<td>K₀Gd(BH₄)₂</td>
<td>6.3</td>
<td>Monoclinic</td>
<td>C(_2) /c</td>
<td>78</td>
</tr>
<tr>
<td>K⁺</td>
<td>Ho³⁺</td>
<td>K₀Ho(BH₄)₂</td>
<td>6.3</td>
<td>Monoclinic</td>
<td>C(_2) /c</td>
<td>78</td>
</tr>
<tr>
<td>K⁺</td>
<td>Yb³⁺</td>
<td>K₀Yb(BH₄)₂</td>
<td>8.4</td>
<td>Monoclinic</td>
<td>P(<em>4)</em>(<em>2)</em>(<em>m)</em>(_bc)</td>
<td>164</td>
</tr>
<tr>
<td>K⁺</td>
<td>Mn²⁺</td>
<td>K₀Mn(BH₄)₂</td>
<td>8.7</td>
<td>Tetragonal</td>
<td>P(<em>4)</em>(<em>2)</em>(<em>m)</em>(_bc)</td>
<td>164</td>
</tr>
<tr>
<td>K⁺</td>
<td>Cd²⁺</td>
<td>K₀Cd(BH₄)₂</td>
<td>6.2</td>
<td>Monoclinic</td>
<td>C(_2) /c</td>
<td>46</td>
</tr>
<tr>
<td>K⁺</td>
<td>Zn²⁺</td>
<td>K₀Zn(BH₄)₂</td>
<td>6.5</td>
<td>Monoclinic</td>
<td>C(_2) /c</td>
<td>46</td>
</tr>
<tr>
<td>K⁺</td>
<td>Al³⁺</td>
<td>K₀Al(BH₄)₂</td>
<td>7.9</td>
<td>Monoclinic</td>
<td>P(_2) (_1) /c</td>
<td>146</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Mg²⁺</td>
<td>Rb₂Mg(BH₄)₂</td>
<td>12.9</td>
<td>Orthorhombic</td>
<td>F(_d) (_d) (_d)</td>
<td>169</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Ca²⁺</td>
<td>Rb₂Ca(BH₄)₂</td>
<td>12.9</td>
<td>Orthorhombic</td>
<td>F(_d) (_d) (_d)</td>
<td>169</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Sr²⁺</td>
<td>Rb₂Sr(BH₄)₂</td>
<td>5.6</td>
<td>Monoclinic</td>
<td>Pna(<em>2)</em>(_1)</td>
<td>1 and 165</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Y²⁺</td>
<td>o-RbY(BH₄)₂</td>
<td>6.9</td>
<td>Orthorhombic</td>
<td>Pna(<em>2)</em>(_1)</td>
<td>165</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>Al³⁺</td>
<td>Rb₂Al(BH₄)₂</td>
<td>9.4</td>
<td>Orthorhombic</td>
<td>F(_d) (_d) (_d)</td>
<td>160</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Mg²⁺</td>
<td>Cs₂Mg(BH₄)₂</td>
<td>6.0</td>
<td>Monoclinic</td>
<td>C(_2)</td>
<td>1</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Ca²⁺</td>
<td>Cs₂Ca(BH₄)₂</td>
<td>4.1</td>
<td>Monoclinic</td>
<td>C(_2)</td>
<td>1</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Sr²⁺</td>
<td>Cs₂Sr(BH₄)₂</td>
<td>5.6</td>
<td>Monoclinic</td>
<td>C(_2)</td>
<td>1</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>Y²⁺</td>
<td>Cs₂Y(BH₄)₂</td>
<td>5.7</td>
<td>Monoclinic</td>
<td>C(_2)</td>
<td>1</td>
</tr>
</tbody>
</table>
Alkaline earth metal borohydrides. The monometallic alkaline earth metal borohydrides show increasingly covalent and directional bonding with decreasing ionic radius and increasing electronegativity and charge density, in the series, Be > Mg > Ca > Sr > Ba. Indeed, the number of polymorphs (in parentheses) of composition M(BH₄)₂ show decreasing trends in the series Mg (7) > Ca (4) > Sr (3) > Ba (4). Porosity in the solid state is also observed in frameworks with the highest covalence, namely x- and 𝛾-Mg(BH₄)₂, with 6 and 30% of open space in the structures, respectively.

Strontium and barium borohydrides. Sr(BH₄)₂ and Ba(BH₄)₂ are the most ionic of the alkaline earth metal borohydrides. Barium borohydride is synthesised as an orthorhombic polymorph (α₁), which transforms to another orthorhombic polymorph (α₂) at T ~ 395 °C, which is isostructural to α-M(BH₄)₂, M = Sr, Sm, Eu, 68,142,143,147 o2-Ba(BH₄)₂ transforms to t- and c-Ba(BH₄)₂ polymorphs at 445 and 460 °C. Similarly, o-M(BH₄)₂, M = Sr, Eu also transform to t- and c-M(BH₄)₂ polymorphs upon heating. These polymorphs are structurally related, α₁- to CaCl₂-type, α₂- to α₂- to α-PbO₂, t- to h₄-ZrO₂, and c- to CaF₂. 143 In fact, the CaCl₂ structure type is an orthorhombic deformation of the tetragonal rutile type (TiO₂), which is based on hcp packing of BH₄⁻ anions, i.e. metal ions placed in octahedral positions. The α-PbO₂ structure is then related to the rutile type by a well-known phase transition which may be induced by applying pressure. The t-polymorph is a superstructure (doubled c-axis) of the h₄-ZrO₂ type which is a deformation of cubic CaF₂ structure type. The orthorhombic structures of the α-PbO₂-type likely form due to the similar cation sizes, Sm²⁺ (r = 1.22 Å), Eu²⁺ (r = 1.25 Å), Sr²⁺ (r = 1.26 Å), Ba²⁺ (r = 1.42 Å).

Calcium borohydride. Four distinct polymorphs of calcium borohydride, denoted x-, x’, β- and 𝛾-Ca(BH₄)₂, are described, which are structurally related to polymorphs of TiO₂. 183-185 The orthorhombic polymorph, stable at RT, is α-Ca(BH₄)₂ (P2/dd). A second order phase transition at ~ 220 °C was described as a group–subgroup transition from P2/dd to P2/dd for the polymorphs x- to x’-Ca(BH₄)₂. 137 At higher temperatures, the polymorphs x- and x’-Ca(BH₄)₂ transform to β-Ca(BH₄)₂ with a more complex structure described by two similar models P4_2/m1 and P4_1/m, 137 combining diffraction data and DFT optimization. The β-Ca(BH₄)₂ polymorph may have some dynamic motion of the BH₄ groups in the solid state, e.g. similar to the high-temperature h-LiBH₄ polymorph. 9,101 The high-temperature β-Ca(BH₄)₂ polymorph is 4–6% denser than x- and x’-Ca(BH₄)₂, and at room temperature it slowly converts back to orthorhombic x-Ca(BH₄)₂. 186 Solvent based synthesis methods provide another orthorhombic polymorph, γ-Ca(BH₄)₂, which irreversibly transforms to β-Ca(BH₄)₂ at ~ 320 °C. 139 The crystal structures of all four Ca(BH₄)₂ polymorphs contain calcium cations coordinated by six borohydride anions forming octahedra, which suggests ionic bonding. However, the existence of non-densely packed polymorphs points towards some degree of directionality in the Ca–BH₄ bonding.

Magnesium borohydride. The extreme structural flexibility observed for metal borohydrides is highlighted in magnesium borohydride for which seven very different crystalline polymorphs are known: x-, β-, β’, γ-, δ- and δ-Mg(BH₄)₂. 5,106,128,129,134,168-189 The x-Mg(BH₄)₂ polymorph crystallizes in a large hexagonal unit cell a = 10.354 and c = 37.055 Å (originally reported in P6₁), confirmed by DFT and single-crystal diffraction. 106,192 Analysis of the initial P6₁ models shows that the determination of H-atom locations from powder data posed the main problem for identification of the correct symmetry. Solid x-Mg(BH₄)₂ contains an unoccupied volume of 6.4% within the structure. 106 These voids are, in principle, large enough.
The ζ-polymorph transforms to an orthorhombic β-Mg(BH₄)₂ polymorph at T > 220 °C, which can be described in a super cell with Fddd symmetry, a = 37.072 Å, b = 18.6476 Å and c = 10.9123 Å. The high-temperature ξ-polymorph is ~3% less dense and contains no unoccupied voids.

Solvent based synthesis using triethylamine borane or dimethyl sulfide borane complexes provide two different crystalline magnesium borohydride solvates. The monoclinic solvate structure of Mg(BH₄)₂·1/2S(CH₃)₂ is a 3D framework containing two Mg sites: one Mg is tetrahedrally coordinated to four BH₄ groups, and the other to four BH₄ groups and one S(CH₃)₂ ligand forming a trigonal bipyramid. The S(CH₃)₂ ligand can be extracted at moderate conditions (T < 100 °C), which provides the highly symmetric cubic structure of γ-Mg(BH₄)₂ (Ia3d) (see Fig. 1), where a single Mg site is tetrahedrally coordinated to the BH₄ groups. The structure has a 3D network of interpenetrated channels and γ-Mg(BH₄)₂ is the first hydride to have a large permanent porosity. The empty volume in the structure amounts to ~33%. The narrowest part of the pore channel is defined by a 5.8 Å distance between hydrogen atoms, but in contrast, a point at (1/8, 1/8, 1/8) in the structure is 3.56 Å away from the nearest H-atom, 4.12 Å from B and 4.82 Å from Mg. The framework topology of γ-Mg(BH₄)₂ is isomorphic to both a hypothetical zeolite type polymorph of SiO₂ and to a porous zinc imidazolate framework ZIF-72. This is illustrated by the amorphisation of porous γ-Mg(BH₄)₂ at RT over time and recrystallization of γ-Mg(BH₄)₂ upon heating at T = 80 °C. Amorphisation of porous materials, e.g. metal organic frameworks (MOF) is a well-known feature, but recrystallization of a porous framework upon heating has possibly not been observed for any other material.

Powder X-ray diffraction experiments conducted at elevated pressures, using diamond anvil cells, reveal extreme collapse of the ζ- and γ-Mg(BH₄)₂ structures upon compression, equating to a ~20% and ~44% volume contraction, respectively. The compression of γ-Mg(BH₄)₂ displays the largest volume contraction observed, or predicted, for a hydride material. ζ-Mg(BH₄)₂ transforms to a new high pressure polymorph of magnesium borohydride denoted δ-Mg(BH₄)₂ at 1.1–1.6 GPa. Whereas highly porous γ-Mg(BH₄)₂ transforms to an X-ray amorphous material at 0.4–0.9 GPa and then to crystalline δ-Mg[BH₄]₂ at ~2 GPa. The polymorph δ-Mg(BH₄)₂ has a tetragonal structure consisting of two interpenetrated Mg[BH₄]₂ frameworks (Fig. 1). Each framework resembles the cristobalite structure (a polymorph of SiO₂), whilst their doubly interpenetrated arrangement has a Cu₃O₂ topology, which is typical for MOFs. This structural organization is stable on compression up to ~15 GPa, upon decompression to 1 bar, and even on heating up to ~100 °C at ambient pressure, where it then transforms to ζ-Mg(BH₄)₂.

All experimentally discovered Mg(BH₄)₂ polymorphs, and the lowest-energy theoretical structures, contain BH₄ coordinated by two Mg cations via opposite tetrahedral edges [Mg–B–Mg angles deviating by 3–20° from linearity]. The Mg⋯BH₄ interaction is highly directional and the Mg⋯B–Mg fragments can be considered fundamental building units in all the structures. Magnesium atoms coordinate four BH₄ tetrahedra in a strongly deformed tetrahedral environment. Interestingly, Mg atoms only form a limited set of MgH₈ polyhedra where only the less uniform Johnson solids are found in the experimental structures. The ¹H and ¹¹B spin–lattice relaxation NMR studies of the BH₄ reorientational motion support the highly anisotropic BH₄⋯⋅Mg interaction in ζ-Mg(BH₄)₂. This contrasts the theoretically predicted structures, which always contain MgH₈ cubes. The predicted Mg(BH₄)₂ structures also tend to be either highly porous or dense, e.g. the low-density Iαm2 (ρ = 0.56 g cm⁻³) and F222 (ρ = 0.54 g cm⁻³) structures, containing a single porous framework or a dense, doubly interpenetrated framework I₄₁/amd (ρ = 1.01 g cm⁻³). Although these predicted structures are topologically similar to γ- and δ-Mg(BH₄)₂ (Fig. 1), they have not yet been observed experimentally.

Both experiments and theoretical predictions suggest vast polymorphism of Mg(BH₄)₂. Moreover, all the experimentally observed polymorphs are stable at ambient conditions and in relatively wide temperature and pressure ranges indicating that the reconstruction of strongly bound Mg(BH₄)₂ coordination frameworks is kinetically hindered. This may be due to the high stability of the linear Mg⋯BH₄⋯Mg units, linking the MgH₈ nodes into various framework structures, similar to partly covalently-bonded MOFs. The stability of Mg(BH₄)₂ polymorphs

Fig. 1. The crystal structure of (a) porous γ-Mg[BH₄]₂, ρ = 0.550 g mL⁻¹ and (b) the high-pressure δ-Mg[BH₄]₂, ρ = 0.987 g mL⁻¹.
may also be related to the relative stability of the MgH4 polyhedra. Clearly, the BH4 complexes act as directional ligands, similar to organic ligands (“linkers”) with partly covalent coordination to metals in MOFs. The Mg–BH4 interaction is directional and partly covalent and is essentially the reason for the MOF-like behaviour of Mg(BH4)2, i.e. the rich polymorphism and their relatively high stability, the large pressure-induced volume collapses, the amorphisation under pressure and the surprising recrystallization of porous structures from amorphous material. The unusual crystal chemistry and high structural complexity of Mg(BH4)2 is the most extreme case for metal borohydrides, but is typical for coordination polymers, such as MOFs.

3.2 Monometallic borohydrides with the d- and f-block
Stable metal borohydrides with the d-block metals can be prepared for metals, which in a low oxidation state, have the d-electron configurations, d5, d6 or d7. Scandium borohydride has not yet been obtained in pure form, but a series of alkali scandium bimetallic borohydrides, MSc(BH4)2, M = Li, Na, K, Rb, Cs are discussed in Section 3.5 of this review. Titanium borohydride, Ti(BH4)3 with d4 configuration appears as an exception to this trend, but it is a molecular borohydride (see Section 3.3), with limited stability, decomposing at T < 0 °C. Transition metal borohydrides, M(BH4)2, M = Cr2+ (d4), Fe2+ (d6) and Co2+ (d7) are stable in solution (c10). The high-temperature polymorph is stable on cooling. Yttrium borohydride. Y(BH4)3, has received significant interest as a hydrogen storage material due to the high gravimetric hydrogen content, ρH2(Y(BH4)3) = 9.07 wt% H2, and moderate decomposition temperature, T ~ 270 °C. Y(BH4)3 exists as two polymorphs, α- and β-Y(BH4)3, both stable at ambient conditions. Mechanocatalytic treatment of LiBH4 and YCl3 yields α-Y(BH4)3, and in some cases small amounts of β-Y(BH4)3. Solvent-based methods may provide a solvate Y(BH4)3(S(CH3)2), which transforms to α-Y(BH4)3 during desolvation at T ~ 140 °C. Transformation from α- to β-Y(BH4)3, is observed when heating in a narrow temperature interval, 190–200 °C, as decomposition begins at higher temperatures. The high-temperature polymorph is stable on cooling.

α-Y(BH4)3 crystallizes in a cubic unit cell a = 10.7445 Å (Pn3m), whilst β-Y(BH4)3, crystallizes in a slightly larger cubic unit cell a = 11.0086 Å (Pm3c). The structure of β-Y(BH4)3 was initially suggested to be disordered primitive cubic, a = 5.4547 Å (Pm3m), based on SR-PXD data, but later defined as ordered in an orthorhombic cell using powder neutron diffraction data. The major difference between the two powder diffraction patterns is that the strongest reflection in PND data (531), which is the only reflection defining the doubled lattice parameter, is practically invisible in PXD data. The cubic framework structures of the two polymorphs are closely related, yttrium being octahedrally coordinated to six BH4 anions. In β-Y(BH4)3, the octahedral coordination of Y is regular but is somewhat distorted in α-Y(BH4)3. The [Y(BH4)3] octahedra share corners and coordinate via Y–B–Y bridges where BH4 units share edges (η2) to yttrium, i.e. resulting in a 12-fold coordination of yttrium to hydrogen. Furthermore, the high-temperature β-polymorph structure is 4.6% less dense than α-Y(BH4)3, and contains relatively large unoccupied voids of 39 Å3, which are smaller in the low-temperature polymorph. The H···H repulsion seems to be at the origin of the polymorphic transition. The orientation of BH4 groups in β-Y(BH4)3, slightly expands the structure and maximizes the H···H contacts, whereas half of the BH4 complexes in α-Y(BH4)3, are flipped, allowing for a more densely packed structure, but with shorter H···H contacts (Fig. 2). This situation is somewhat similar to the disordered cubic alkali borohydrides, MBH4 (M = Na–Cs), where the number of repulsive H···H contacts is minimized via a local ordering of the BH4 groups at low temperatures. Manganese borohydride. Mn(BH4)2, (Mn2+, d5) was the first transition metal borohydride to be described, in 2009, denoted α-Mn(BH4)2, and is one amongst a total of four manganese borohydride polymorphs known to date. The polymorph, α-Mn(BH4)2, was originally prepared mechanochemically from MnCl2 and LiBH4. A different manganese borohydride solvate can be obtained using dimethylsulfide as the solvent, Mn(BH4)2·1/2S(CH3)2, which is isostructural to the magnesium analogue, Mg(BH4)2·1/2S(CH3)2. Gentle removal of the solvent provides a porous polymorph, γ-Mn(BH4)2, that is isostructural to the magnesium analogue, γ-Mg(BH4)2. The unit cell volume of γ-Mn(BH4)2 is ~ 8.8% larger than that of the Mg-counterpart, which corresponds well to the radius of Mn2+ (r = 0.80 Å) being larger than that of Mg2+ (r = 0.71 Å). Furthermore, SR-PXD data indicate one or more unidentified compounds, which may be a manganese analogue of α-Mg(BH4)2. Thus, the structural chemistry of manganese borohydride resembles that of the magnesium analogue.

The structure of α-Mn(BH4)2 contains two independent Mn atoms both surrounded by four BH4 units in a deformed tetrahedral coordination, whilst each BH4 is nearly linearly coordinated by two Mn atoms via the opposite tetrahedral edges (η1), exactly as observed for magnesium borohydrides. The structure of α-Mn(BH4)2, is also isostructural to α-Mg(BH4)2. The structures of α-Mn(BH4)2, as shown in Fig. 2, reveal the order of the BH4 groups at low temperatures. The high-temperature polymorph shows a regular octahedral coordination around yttrium, whereas the low-temperature polymorph has a distorted octahedral around yttrium.
and $\alpha$-Mg(BH$_4$)$_2$ show similarity and both contain similar chiral layers, stacked along the $c$-axis, and rotated by $120^\circ$ by the $3_1$ axis in $\alpha$-Mn(BH$_4$)$_2$ and by $60^\circ$ by the $6_1$ axis in $\alpha$-Mg(BH$_4$)$_2$. Existence of a solid solution Mg$_2$Mn$_{1-n}$(BH$_4$)$_3$ further illustrates the close similarity between manganese and magnesium borohydrides. Similar to $\alpha$-Mg(BH$_4$)$_2$, $\alpha$-Mn(BH$_4$)$_2$ also has some degree of porosity in the structure and contains isolated voids with an estimated volume of 21 Å$^3$, occupying 6% of the structure volume.

At pressures above ~1 GPa, $\alpha$-Mn(BH$_4$)$_2$ transforms into the high-pressure $\delta$-phase having either $\overline{P}$n2$_1$ or $I$4$_1$/a$\overline{c}$d space group symmetry. The latter shows the same ordering pattern for the BH$_4$ group as suggested by Yao and Klug for high-pressure LiBH$_4$. $\delta$-Mn(BH$_4$)$_2$ is quenchable to ambient pressure and shows a volumetric hydrogen density of 125 g H$_2$ L$^{-1}$ at ambient conditions but turns back into the $\alpha$-phase on heating to 67–109 °C. At pressure above 8.6 GPa, a $\delta$-phase with $F\overline{d}d$ structure forms reversibly.

**Cadmium borohydride.** Cd(BH$_4$)$_2$ ($\text{Cd}^{2+}$, d$^{10}$) is another recently characterized monometallic borohydride with low and high temperature polymorphs, $\alpha$- and $\beta$-Cd(BH$_4$)$_2$, and the first order polymorphic transition at $T \sim 55$ °C. Both polymorphs consist of two identical interpenetrated three-dimensional frameworks built from Cd coordinated to four BH$_4$ units by edge sharing ($\Pi_1$). Each Cd atom is coordinated almost linearly by two BH$_4$ complexes. The [Cd(BH$_4$)$_4$] tetrahedra are slightly distorted in tetragonal $\alpha$-Cd(BH$_4$)$_2$ whilst exhibiting ideal tetrahedral geometry in cubic $\beta$-Cd(BH$_4$)$_2$. The cubic $\beta$-Cd(BH$_4$)$_2$ has a Cu$_2$O-antitype structure with B and Cd on the positions of Cu and O, respectively, while $\alpha$-Cd(BH$_4$)$_2$ has a tetragonally distorted structure, identical to the tetragonal high-pressure polymorph of magnesium borohydride $\delta$-Mg(BH$_4$)$_2$. The parent cubic structure has also been mentioned as a possible high-symmetry polymorph of Mg(BH$_4$)$_2$.

**Monometallic rare-earth borohydrides.** Synthesis of La(BH$_4$)$_3$ and Ce(BH$_4$)$_3$ was initially conducted by mechanochemically facilitated metathesis reactions but without structural characterization. A number of other monometallic rare-earth borohydrides are reported, which can be subdivided into two groups, those with oxidation state (II), isostructural to Sr(BH$_4$)$_2$ or Ca(BH$_4$)$_2$. Existence of a solid solution Mg$_2$Mn$_{1-n}$(BH$_4$)$_3$ further illustrates the close similarity between manganese and magnesium borohydrides. Similar to $\alpha$-Mg(BH$_4$)$_2$, $\alpha$-Mn(BH$_4$)$_2$ also has some degree of porosity in the structure and contains isolated voids with an estimated volume of 21 Å$^3$, occupying 6% of the structure volume.

3.3 Strongly covalent molecular monometallic borohydrides

Several monometallic borohydrides appear to have prevailingly covalent bonding and directionality in the M–BH$_4$ coordination. The first example is beryllium borohydride, Be(BH$_4$)$_2$, known in one very unique structural form. The tetragonal structure was investigated by single-crystal X-ray diffraction and reveals trigonal-planar coordinated beryllium by three edge-sharing BH$_4$ groups, i.e. beryllium has an unusually high coordination number of six hydrogen atoms in the nearest coordination sphere. Two borohydride complexes are bridging beryllium with linear Be–B–Be geometry and edge sharing (111) coordination. Another borohydride anion also coordinates to Be by edge sharing (111) but is terminal with two dangling hydrogen atoms. The structure is built from one-dimensional polymeric chains held together by weak interactions. This is illustrated by the fact that beryllium borohydride is reported to have a significant vapour pressure at RT and readily sublimes, which illustrates that there are weak intermolecular interactions and that the polymeric chains dissociate easily. In the gas phase, beryllium borohydride Be(BH$_4$)$_2$ may be a molecular compound, with face-sharing BH$_4$ (111) and the same coordination of beryllium, CN(Be) = 6. Furthermore, the compound is unusually reactive and pyrophoric due to the characteristic three-centre-two-electron bonds in the Be–H–B contacts, similar to diborane, B$_2$H$_6$. Be(BH$_4$)$_2$ is also extremely poisonous like other beryllium compounds. The highest gravimetric hydrogen density of a metal borohydride is observed for Be(BH$_4$)$_2$, $\rho_\text{H}(\text{Be(BH}_4)_2)=20.8$ wt% H$_2$ (Table 2), which also has the second-highest volumetric hydrogen density for metal borohydrides, $\rho_\text{H}(\text{Be(BH}_4)_2)=127$ g H$_2$ L$^{-1}$.

The most strongly polarizing cations form molecular monometallic borohydride structures, e.g. Ti$^{3+}$, Al$^{3+}$ with electronegativity $\chi_P \sim 1.5$ and Zr$^{4+}$ and Hf$^{4+}$ with $\chi_P \sim 1.3$. The structures of both zirconium and hafnium borohydride are isosstructural, molecular metal borohydrides and consist of isolated neutral M(BH$_4$)$_4$ units (Fig. 3) having low sublimation temperatures, $T_{\text{sub}}(\text{Zr(BH}_4)_4)=29$ °C. The tetrahedral molecules of Zr and Hf borohydrides are analogous to the methane molecule where each BH$_4$ complex coordinates via face sharing (111) to the metal with one dangling hydrogen atom and the solids have primitive cubic unit cells. The experimental structural data clearly supports previous assumptions that solid Zr(BH$_4$)$_4$ consists of discrete neutral molecules interacting mainly by weak van der Waals and dispersion interactions.
**Aluminum borohydride.** Aluminum borohydride is another molecular metal borohydride, consisting of discrete Al(BH₄)₃ units, that was characterized in 1997.¹⁰⁷ Aluminum borohydride has a high gravimetric hydrogen content, ρₘ = 16.8 wt% H₂, but is volatile and pyrophoric with a tendency to release diborane at RT and therefore very challenging to handle and utilize in practical applications.²⁰⁵

**Titanium borohydride.** Titanium borohydride, Ti(BH₄)₃, is of high interest as the only genuine transition metal borohydride with an open set of d-orbitals (d¹ electron configuration), and despite many published reports on this compound the solid state structure remains unknown.¹⁵¹,²⁰⁶ However, the gas phase structure has been characterized by electron diffraction,²⁰⁷ which reveals monomeric Ti(BH₄)₃ species with BH₄⁻ face sharing to the metal center (η¹) with an overall C₃h symmetry. The tridentate bonding in volatile Ti(BH₄)₃ has been confirmed by vibrational spectroscopy²⁰⁸ and calculated structural optimizations.²⁰⁷,²⁰⁸ Though following a tridentate coordination-scheme in the gas phase, in some molecular compounds such as [Li(Et₂O)₂]-[Ti₂(BH₄)₆(PMe₂Ph)₄]²⁰⁹ titanium centres are bridged by bidentate BH₄⁻ (η²), thus forming one dimensional chains of linked metal centres. These chains can be considered as dimers [Ti₂(BH₄)₆] being linked by Li, also via bidentate BH₄⁻ (η²). Pronounced aggregation of Ti(BH₄)₃ molecules has also been suggested to occur in the solid state for titanium borohydride implying that the predominant species is the dimer [Ti₂(BH₄)₆]²⁻.²⁰⁰ Titanium borohydride rapidly decomposes at room temperature but has recently been stabilized through incorporation into a metal–organic framework (MOF).²¹⁰

### 3.4 Bimetallic s-block borohydrides

The majority of the recently discovered bimetallic borohydrides consist of complex metal borohydride anions counter-balanced by alkali cations. In all these structures the more electronegative metal constitutes the central atom in the complex anion by coordination to a number of borohydride units, as for instance [Mg(BH₄)₄]²⁻. The formation of discrete complex anions can be considered as a consequence of the electronegativity difference between the two metals in the structures, which causes formation of partly covalent bonds between the more electronegative metal and the BH₄⁻ units. This contrasts bi-alkali metal borohydrides where the interaction is rather ionic. Series of bimetallic borohydrides have been discovered and are subdivided here in three groups, those based on s-block metals only, those based on a d- or f-block metal and typically an alkali metal and those based on a p-block metal and an alkali metal. This review focuses on series of compounds in order to aim at analyzing trends in structures and properties.

**Bi-alkali metal borohydrides.** The first bimetallic borohydride was discovered in 2008, lithium potassium borohydride, LiK(BH₄)₂, which has an ionic structure due to similarities in electronegativity of the two metals.¹³⁹ Lithium and potassium coordinate to four and seven BH₄⁻ tetrahedra, respectively. The structure can be regarded as built from anionic layers [Li(BH₄)₂]⁻ cut from an o-LiBH₄ framework and intercalated by K⁺ cations. The decomposition temperature for this compound is nearly an average of those for the two individual borohydrides.

Sodium potassium borohydride, NaK(BH₄)₂, was initially described as a stoichiometric compound,²¹¹ but was later shown to be a solid solution NaₓK₁₋ₓBH₄, 0 < x < 1, stable in the temperature range 200 < T < 450 °C. The solid solution, NaₓK₁₋ₓBH₄, 0 < x < 1, is metastable at RT and phase-separates into the monometallic borohydrides at RT within 24 h.³³

**Lithium rubidium and lithium cesium borohydrides.** The phase diagram LiBH₄–ABH₄ (A = Rb, Cs) has to date revealed ten compounds LiₐAⱼ(BH₄)ⱼ₋ᵢ (A = Rb, Cs), with i, j ranging between 1 and 3. Amongst these, eight new structure types of homoeptic borohydrides are found. The Li–BH₄⁻ substructure adopts various topologies as a function of the compound’s Li content, ranging from one-dimensional isolated chains to three-dimensional networks. The coordination environment around the Li-node is either triangular or tetrahedral in these sublattices, and various compounds of this series contain the rare connectivity of edge-sharing Li(BH₄)₄-tetrahedra, following the building principle of LiKMG[BH₄]₄,¹⁷² where a charged, layered, honeycomb-like substructure LiₘMG[BH₄]ₙ⁻ is charge-balanced by the larger K⁺ counter-cation. Such substructures may suggest that, next to Mg²⁺, Li⁺ may have potential to participate in framework building with the tetrahydroborate anion, BH₄⁻, as a linker, if the framework is stabilized by large electropositive counter-cations.

**Alkali and alkaline earth bimetallic borohydrides.** No bimetallic borohydrides between Li or Na and Mg have been observed. This may be understood when considering the preferred coordination polyhedra of the different cations. (4,4)-Connected tetrahedral Li–Mg frameworks cannot form without counter-cations, i.e. other than as trimetallic borohydrides.¹⁷² Sodium cations are readily accommodated in octahedral coordination but do not adopt higher coordination numbers, which explains why the structural analogues to K–Mg borohydrides do not exist for sodium.

Two bimetallic potassium magnesium borohydrides have been discovered in the KₓMg(BH₄)₂ system, namely K₂Mg(BH₄)₄
and K₃Mg(BH₄)₅. The structure of K₂Mg(BH₄)₄ is isostructural to K₅Mn(BH₄)₄ and built from distorted tetrahedral [Mg(BH₄)₄]⁻ complex anions. The BH₄ anions share an edge with Mg (η³) similar to all polymorphs of Mg(BH₄)₂. Potassium ions form a K₁₁ cage (Edshammar polyhedron) around the complex anions. Structural similarities for the series of isostructural bimetallic borohydrides KₓM(BH₄)₅ (M = Mg, Mn, Zn, Cd) are discussed later in this section of the review.

The structure of K₃Mg(BH₄)₅ is orthorhombic (P₄/2bc) and has an intriguing nature that can be described as an intergrowth of KBH₄ and K₂Mg(BH₄)₄. Interestingly, the BH₄ complexes occur in two different environments, forming complex anions [Mg(BH₄)₄]⁻ similar to those observed in the structure of K₅Mg(BH₄)₅, and with a second boron position only coordinating to potassium. This latter BH₄ is octahedrally coordinated, strongly resembling the local environment of BH₄ in KBH₄ which crystallizes in the rock salt prism of K₈, surrounding the composite anions of [Mg(BH₄)₄]⁻ and interconnected via common edges.

**Alkalai metal calcium borohydrides.** The heavier alkalai metal borohydrides, MBH₄, M = K, Rb and Cs, readily react with calcium borohydride and form perovskite-type metal borohydrides (Fig. 4). The compounds all have the same composition MCa(BH₄)₃, M = K, Rb, Cs, and each exists in at least two polymorphs, see Fig. 4. Furthermore, a perovskite-type solid solution is also described, RbCa_Mg₁₋ₓ(BH₄)₃.¹

**Alkalai metal strontium borohydrides.** Alkalai metal strontium borohydrides are also found to form perovskite-type compounds, M Sr(BH₄)₃, M = K, Rb, Cs.¹⁵ The alkalai-Ca and alkalai-Sr borohydrides are the only two series where all three metal cations (K, Rb, Cs) stabilize the perovskite structure type. Interestingly, the Ca-compounds reveal decreasing symmetry across their high temperature polymorphic transitions.¹ In contrast, the Sr-perovskites have increasing symmetry and the ambient temperature Sr-polymorphs are lower in symmetry than their Ca-analogues. This suggests that the Sr cation is too large to stabilize the ideal cubic perovskite type structure, and that the Ba-cation will come to lie outside the stability criteria of this structure type amongst borohydrides.

### 3.5 Bimetallic d- and f-block borohydrides

**Alkalai metal scandium borohydrides.** The structure of LiSc(BH₄)₄ was the first bimetallic borohydride containing discrete anions to be characterized in 2008, while two other members of the series, NaSc(BH₄)₄ and KSc(BH₄)₄, were described in 2010 (Fig. 5).¹⁸⁰,¹⁶⁶ Mono-metallic scandium borohydride, Sc(BH₄)₄, has not yet been prepared nor structurally characterized. LiSc(BH₄)₄ is tetragonal (P42c),¹⁸¹ NaSc(BH₄)₄ is orthorhombic (Cmm) with the HT-CrVO₄ structure type and KSc(BH₄)₄ is also orthorhombic (Pnma) but with a BaSO₄ type structure.¹⁸⁰,¹⁶⁶ Scandium–boron distances and B–Sr–B angles in the tetrahedral geometry of [Sc(BH₄)₄]⁻ in NaSc(BH₄)₄ are relatively regular and resemble the almost ideal tetrahedral [Sc(BH₄)₄]⁻ anion, found by DFT optimization.¹⁸¹ The [Sc(BH₄)₄]⁻ anion is slightly distorted in KSc(BH₄)₄ and more deformed in the structure of LiSc(BH₄)₄. The Sc–B distances (2.27–2.50 Å) are similar in all three known alkalai metal scandium borohydrides and compare well to those in the tetrahedral molecular compounds Zr(BH₄)₄ and Hf(BH₄)₄.¹⁸⁹,¹⁰⁹,¹₂⁶,¹₂⁷ In all three scandium-based compounds, the [Sc(BH₄)₄]⁻ anion is located inside alkalai metal cages, i.e. tetragonal Li₈ prisms (all prisms occupied) in LiSc(BH₄)₄, slightly deformed trigonal Na₈ prisms (each second prism occupied) in NaSc(BH₄)₄ and monocapped trigonal K₈ prisms (all prisms occupied) in KSc(BH₄)₄. Note that the Li position is disordered along the c-axis in LiSc(BH₄)₄ and therefore the exact shape of the Li₈ polyhedra cannot be determined. The primary building principle in NaSc(BH₄)₄ and KSc(BH₄)₄ consists of packing Na⁺/K⁺ cations and [Sc(BH₄)₄]⁻ anions. The BH₄ complex coordinates to Sc by edge sharing (η²) forming a dominantly covalent bond whereas alkalai metal ions tend to coordinate to the complex anions with a dominantly ionic coordination.

**Alkalai metal yttrium borohydrides.** Discrete complex [Y(BH₄)₄]⁻ ions have been shown to exist in MY(BH₄)₄, produced by ball milling Y(BH₄)₃–3LiCl mixtures and MBH₄ (M = K, Rb or Cs).¹⁶⁷,¹⁷¹ KY(BH₄)₄ is isostructural to NaSc(BH₄)₄ (Cmcm) whereas RbY(BH₄)₄ and CsY(BH₄)₄ form unique structures.¹⁷¹ RbY(BH₄)₄ crystallizes in monoclinic unit cell (P2₁/c) with a AgMnO₄ structure type, which is a deformation of the BaSO₄-type structure. There are seven Rb⁺ cations located around each [Y(BH₄)₄]⁻ and seven

---

**Fig. 4** Crystal structure of (a) the ordered room temperature polymorph of CsCa(BH₄)₃ and (b) of the modulated high temperature polymorph of RbCa(BH₄)₃. Ca (brown), Rb, Cs (blue), BH₄ (green).
[Y(BH4)4]− ions around Rb+ forming slightly distorted monocapped trigonal prisms. CsY(BH4)4 is tetragonal (I4/m) with a CaWO4-scheelite structure type. Cs+ is surrounded by eight BH4 groups forming a distorted dodecahedron (snub disphenoid). While these structures were originally studied on chloride-containing samples, hence the solution of chloride on borohydride sites cannot be excluded, chlorine-free samples later allowed for additional analysis. It was found that KY(BH4)4 also crystallizes in a monoclinic (C2/c) structure with an octahedral coordination of Y, and RbY(BH4)4 crystallizes in the regular BaSO4 structure type. Double perovskites A3Y(BH4)6 (A = Rb, Cs) were also prepared. Recently, also LiY(BH4)4 and NaY(BH4)4 have been prepared by thermal treatment and the two compounds were found to be isostructural to LiSc(BH4)4 and NaSc(BH4)4, respectively.

**Alkaline metal manganese borohydrides.** A bimetallic potassium manganese borohydride was synthesized in the KBH4–Mn(BH4)2 system, K2Mn(BH4)4, which is isostructural to K2Mg(BH4)4 and is indexed in a monoclinic cell as discussed above. Structural similarities between the series of isostructural bimetallic borohydrides K2M(BH4)4 (M = Mg, Mn, Cd) are discussed later in this section. The decomposition of K2Mn(BH4)4 has been shown to generate KBH4 and a new compound KMn(BH4)3 identified as a perovskite type metal borohydride. Later, the compound CsMn(BH4)3 (Cc) was also noticed to have the perovskite type structure.

**Alkaline metal zinc borohydrides.** Several alkaline metal zinc borohydrides have been characterized in which zinc coordinates trigonally, in a planar fashion, to three BH4 units forming complex discrete anions, as for example MZn(BH4)3 (M = Na or K) containing [Zn(BH4)3]−. The Zn–BH4 (η3) coordination is significantly more directional and covalent in contrast to the alkaline metal Na+ or K+ coordination. The trigonal coordination in [Zn(BH4)3]− anions in KZn(BH4)3 is more regular than those in NaZn(BH4)3. Interestingly, the Zn–B distance of 2.573 Å in KZn(BH4)3 is similar to the average of the three shortest Zn–B distances of 2.56 Å in NaZn(BH4)3. In both compounds the [Zn(BH4)3]− anions are located in Na8 or K8 cubes and the alkalai cations coordinate to six BH4 units in a trigonal prism. However, the coordination of the BH4 unit by the cations differs in these two compounds, i.e. in NaZn(BH4)3 the BH4 units coordinate either almost linearly to one Na and one Zn atom, triangular planar to one Zn and two Na atoms or to one Zn and three Na atoms in a tetrahedral geometry, while in KZn(BH4)3 only the triangular coordination is observed.

The more zinc-rich alkaline zinc borohydrides, MZn2(BH4)5 (M = Li or Na) also exhibit similar general structural topologies consisting of two identical interpenetrated three-dimensional frameworks. This type of structural topology is common for the coordination polymers involving organic ligands, such as MOFs, however observed for the first time in hydrides in this case. Alternatively, the structures of MZn2(BH4)5 (M = Li or Na) can be considered to be built from dinuclear complex ions, [Zn2(BH4)5]− and alkalai metal ions. The MZn2(BH4)5 structures reveal strong and directional Zn–BH4 bonding by edge sharing (η2) that defines the structural architecture. The Zn atoms in both compounds have a triangular, nearly planar, coordination by three BH4 groups, similar to Zn in NaZn(BH4)3 and KZn(BH4)3. These structures are almost linearly coordinated by two metal atoms, either bridging the two zinc atoms in [Zn2(BH4)5]− or coordinating to one Zn and one M atom. Furthermore, LiZn2(BH4)5 has been studied by PND, revising the orientation of one of the BD4 groups, revealing that the coordination mode for the BD4 units to both Zn and Li corresponds to the cation–D–D (η2) coordination scheme, which is supported by DFT calculations.

**Alkaline metal cadmium borohydrides.** The potassium cadmium borohydride, KCd(BH4)3, has an interesting 3D polymeric framework topology and contains a complex anion, [Cd(BH4)3]n−, built from corner-sharing [Cd(BH4)4] tetrahedra and [Cd(BH4)6] octahedra. All six BH4 units in the [Cd(BH4)6] octahedra are coordinated almost linearly by another Cd atom from the neighbouring Cd(BH4)4 tetrahedra, whereas two of the four BH4 units within the [Cd(BH4)4] tetrahedra are terminal. The structure of KCd(BH4)3 can also be described as a garnet, with K on dodecahedral and octahedral sites, and Cd on octahedral and tetrahedral sites. In contrast, the structure of K2Cd(BH4)4 is built from discrete [Cd(BH4)4]2− anions counter-balanced by K+ cations. In the complex anion the Cd atom is coordinated to four BH4 units in a distorted tetrahedral geometry. The structure of K2Cd(BH4)4 resembles that of MSc(BH4)3 (M = Li, Na and K) and K2M(BH4)4 (M = Mg, Mn, Cd) discussed below.

**Electronic and size effects stabilizing tetrahedral complex anions based on bivalent metals.** The compounds containing tetrahedral complex anions of the type [M(m)m−1(BH4)4]m−1 (m = 2, 3) are based either on a trivalent cation M such as Sc3+, Y3+, Al3+, Ho3+, Yb3+, Lu3+ or on a bivalent cation such as Mg2+, Mn2+, Zn2+, Cd2+,...
and have already been discussed. Alkali metals often act as counterions in these compounds and stabilise the composite anions with a metal center.

The compounds $K_2M[BH_4]_4$ (M = Mg, Mn, Zn, Cd) all represent monoclinically distorted variants of $\beta-K_2SO_4$, i.e. M and BH$_4^-$ occupying the S- and O-positions, respectively and thus replacing the sulphate tetrahedron by a complex anion $[MBH_4]^{2-}$, with consistently bidentate bonding scheme M⋯BH$_2$ (η$_2$). DFT calculations performed on $K_2M[BH_4]_4$ (M = Mg), suggest high stability of the complex anion. DFT structural optimizations reveal that the inner B–H distances are longer than the outer ones, while the H–B–H angle is smaller on the BH$_4^-$ edge facing the Mg metal centre. As discussed above, the coordination environment of the complex anion, is positionally and orientationally disordered. A repulsive interaction between this BH$_4^-$ and the terminal ones complex anion, is positionally and orientationally disordered.

### Table 5
Comparison of the local environments of the complex tetrahedral anions $[MBH_4]^{2-}$ with M = Mg, Mn, Zn and Cd

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average M–B (Å)</th>
<th>B–K/M–B (Å)</th>
<th>$V(MK_{11})/V(MB_4)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2Mg[BH_4]_4$</td>
<td>2.4544(51)</td>
<td>1.41</td>
<td>36.61</td>
</tr>
<tr>
<td>$K_2Mg[BH_4]_4$</td>
<td>2.5027(31)</td>
<td>1.38</td>
<td>34.33</td>
</tr>
<tr>
<td>$K_2Zn[BH_4]_4$</td>
<td>2.466(17)</td>
<td>1.33</td>
<td>31.85</td>
</tr>
<tr>
<td>$K_2Cd[BH_4]_4$</td>
<td>2.881[10]</td>
<td>1.11</td>
<td>24.02</td>
</tr>
<tr>
<td>$K_2Sc[BH_4]_4$</td>
<td>2.3204(3)</td>
<td>1.64</td>
<td>31.56</td>
</tr>
<tr>
<td>$K_2Mg[BH_4]_4$</td>
<td>2.4369(77)</td>
<td>1.45</td>
<td>38.23</td>
</tr>
</tbody>
</table>

Analysis of the relative interatomic distances K–B/M–B in the above mentioned compounds provides some insight to the structural differences caused by differences in metal Pauling electronegativity and ionic radii. A general trend shows that ‘the degree of isolation’ (i.e. the extent to which the crystal should be described on the basis of the complex anion rationalization rather than a framework), as defined by the K–B/M–B ratio, decreases from 1.41 in the Mn compound to 1.11 in the Cd compound.

<table>
<thead>
<tr>
<th>RE ion</th>
<th>Ion radius (Å)$^{211}$</th>
<th>$LiRE[BH_4]_4$</th>
<th>$NaRE[BH_4]_4$</th>
<th>$KRE[BH_4]_4$</th>
<th>$z$-$RE[BH_4]_4$</th>
<th>$\beta$-$RE[BH_4]_4$</th>
<th>$LiRE[BH_4]_4$Cl</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$^{3+}$</td>
<td>0.885</td>
<td>$P4_{2}2_{1}$ (CuAlCl$_4$)</td>
<td>$Pmmn$ (ht-CrVO$_4$)</td>
<td>$Pma$ (BaSO$_4$)</td>
<td>80, 81 and 166</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu$^{3+}$</td>
<td>1.001</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>1.008</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>150 and 163</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>1.03</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>1.04</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>1.041</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>148</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>1.052</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>144</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>1.063</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>1.078</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>1.098</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>1.123</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>1.13</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>1.15</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>1.172</td>
<td>$P4_{2}2_{1}$ (CuCl$_4$)</td>
<td>$Pmcm$ (ht-CrVO$_4$)</td>
<td>$Pnma$ (ht-CrVO$_4$)</td>
<td>147</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
to crystallize as double-perovskites with the formula A₃RE[BH₄]₉. Different stoichiometries such as K₂Gd[BH₄]₉ with square pyramidal and trigonal double pyramidal complex cations have also been observed. As for bivalent RE such as Sm²⁺, Eu²⁺ and Yb²⁺ they adopt the structures of alkali-earth borohydrides: the one of Sr[BH₄]₂ for the larger Sm²⁺ and Eu²⁺ whilst that of Ca[BH₄]₂ for the smaller Yb²⁺.

3.6 Binmetallic p-block borohydrides

**Alkali p-block borohydrides.** Mechaenochmical treatment of AlCl₃−LiBH₄ and AlCl₃−NaBH₄ produce chloride containing alkali aluminium borohydrides Li₄Al[BH₄]₃−Cl − ₄ and NaAl[BH₄]₃−Cl − ₃, which are further discussed in Section 4.2.²⁰⁻²¹ The chloride-free synthesis by the spontaneous reaction of aluminium borohydride with alkali borohydrides results in different structures that are, however, based on the same tetrahedral complex anion [Al(BH₄)₄]⁻ with tridentate binding as seen in the chloride syntheses (with the exception of lithium).¹⁶⁹,²⁰⁵ The reaction between LiBH₄ and Al[BH₄]₃ produces a framework structure LiAl[BH₄]₃ with both cations tetrahedrally coordinated and resembling the framework of R₉−LiBH₄. The sodium compound NaAl[BH₄]₃ crystallizes with a monoclinic structure that is a deformation of the orthorhombic type ht-CrVO₄ also known for NaSc(BH₄)₄. Larger alkali metals K and Rb crystallize with the orthorhombic structure type of TbAsO₄, observed for potassium for the first time.²⁰⁶ The larger CsAl[BH₄]₃ crystallizes with the CaWO₄-scheelite type known from CsY(BH₄)₄. Cesium lead borohydride, CsPb(BH₄)₃, is hitherto the compound observed for potassium for the first time.¹⁶⁰ The larger CsAl(BH₄)₄ crystallizes with the CaWO₄-scheelite type known from CsY(BH₄)₄. As for bivalent RE such as Sm²⁺, Eu²⁺ and Yb²⁺ they adopt the structures of alkali-earth borohydrides: the one of Sr[BH₄]₂ for the larger Sm²⁺ and Eu²⁺ whilst that of Ca[BH₄]₂ for the smaller Yb²⁺.

3.7 Trimetallic borohydrides

**Trimetallic borohydrides with cation disorder.** The first trimetallic homoleptic borohydride compounds, Li₃MgZn₃[BH₄]₁₅, M = Mg and Mn, were presented in 2013 and are also new cationic solid solutions (see Table 4).³⁳ The two compounds are isostructural and were structurally investigated using in situ SR-PXD and PND, which provides an average view of the structure as hexagonal, a = 15.371, and c = 8.586 Å, (P6/mmc) for the Mg-compound at RT. Interestingly, DFT optimization suggests locally ordered models in an ortho-hexagonal unit cell, which maximize Mg–Mg separation. Thus, the hexagonal structure observed by diffraction may be a superposition of three such orthorhombic structures in three orientations along the hexagonal c-axis. The framework in Li₃MgZn₃[BH₄]₁₅ is of the neo-topological type, and contains channels built from face sharing [M(BH₄)₆] octahedra with triangularly coordinated lithium occupying the faces, and consists of two interpenetrated frameworks of tfa-type (Fig. 6). The framework type is related to binmetallic LiZn₃[BH₄]₉ with cation disorder (Li/Mg) on the Li-position. The new borohydrides Li₃MgZn₃[BH₄]₁₅ are potentially interesting as solid state electrolytes, if the lithium mobility within the octahedral channels is improved by disordering the site via heterovalent substitution. The two compounds decompose via formation of the more stable mono- and binmetallic borohydrides.⁸³

**Alkaline earth alkali trimetallic borohydrides.** The five trimetallic compounds ALiM[BH₄]₄ (A = K or Rb; M = Mg or Mn) and KₓLiₓMgₓ[BH₄]₄, represent the first two-dimensional topologies amongst homoleptic borohydrides. The layered substructure is formed from negatively charged Li–Mg 4-connected networks (Fig. 7), which can be rationalized as a honeycomb-like sheet of edge- and corner-sharing tetrahedra. On their basis, the general chemistry of hypothetical, long sought-after, binmetallic Li–Mg borohydrides has been discussed and the results have been put into context with the end-members Mg[BH₄]₂ and LiBH₄. The crystal structures of these trimetallic compounds reveal interesting structural relationships to aluminosilicates such as KAl₂Si₂O₆ (feldspar) and may be exploited by using them as precursors in an attempt to produce zeolite-like metal borohydrides, since zeolite contains three-dimensional negatively charged Al–Si–O networks, which could be rebuilt by their Li–Mg–BH₄ analogues. The double-sheets found in KₓLiₓMgₓ[BH₄]₄ of type [LiₓMgₓ(BH₄)₄]⁻ are fragments similar to the structure of [β-Mg[BH₄]₂] and could provide a new route to design nanoporous open-structured materials with new host–guest adsorption properties.¹⁷²

---

Fig. 6  Structural projections of hexagonal Li₃MgZn₃[BH₄]₁₅ along the c₉₀−axis (left), and of orthorhombic LiZn₃[BH₄]₉ along the a₉₀−axis (right). A structural fragment with an ideal hexagonal symmetry in Li₃MgZn₃[BH₄]₁₅ and pseudo-hexagonal symmetry in LiZn₃[BH₄]₉ is clearly visible and underlines the similarity of both structures built from similar frameworks.
Double perovskite and garnet trimetallic borohydrides. Double perovskites LiA\textsubscript{M}(BH\textsubscript{4})\textsubscript{2}, have been observed for large alkali metals A = Rb, Cs and M = Y, Ce, Gd while the smaller alkali metal A = K stabilizes the garnet-type structure Li\textsubscript{3}K\textsubscript{2}M(BH\textsubscript{4})\textsubscript{12} for M = La, Ce.\textsuperscript{168}

3.8 General trends in the structural chemistry of metal borohydrides

Metals with increasing Pauling electronegativity have increasing degrees of directionality in the M–BH\textsubscript{4} coordination, in particular alkaline earth and d-block metals, which mostly form framework structures. These structures may have unexpected structural topologies and contain interpenetrated frameworks or some degree of porosity. These metal borohydrides often exist as several polymorphs (metastable in a wide range), with the extreme case of Mg(BH\textsubscript{4})\textsubscript{2} showing at least seven polymorphs. These observations highlight the structural flexibility mainly assigned to directionality and some degree of covalence in the M–BH\textsubscript{4} interaction.

The majority of the bimetallic compounds containing an alkali metal and an alkaline earth metal, or a d-block metal, tend to form structures built from discrete composite complex anions formed by a metal and BH\textsubscript{4}, which is due to a significant difference in Pauling electronegativity. In all cases, the more electronegative metal coordinates relatively strongly to BH\textsubscript{4} with a dominantly covalent interaction, while the less electronegative metal, usually an alkali, acts as a charge-balancing ion.

The number of BH\textsubscript{4} complexes in the first coordination sphere of metals, in the structures of metal borohydrides, appears to correlate with the ionic radius of the metal, M. As expected, the number of BH\textsubscript{4} complexes increases with the increasing cationic radius of the metal and the number varies from three to thirteen in o-RbY(BH\textsubscript{4})\textsubscript{3}.\textsuperscript{193} In general, the M–BH\textsubscript{4} distances also increase with increasing cationic radii of the metal. The number of BH\textsubscript{4} units coordinating to the same metal vary as shown in Table 7.

3.9 Comparisons between metal borohydrides and metal oxides

Structural relationship between metal borohydrides and metal oxides. This section provides numerous examples of structural similarities of metal borohydrides and metal oxides, which has been reported recently.\textsuperscript{193} This similarity may be due to the fact that the tetrahydridoborate, BH\textsubscript{4}\textsuperscript{−}, and the oxide, O\textsuperscript{2−}, anions are isoelectronic, both carrying 10 electrons. However, the main reason is probably due to the fact that both borohydrides and oxides are ionocovalent compounds following similar rules on structure stability such as those dictated by the Pauling rules. The structural similarities are notable for $\beta$- and $\gamma$-Mg(BH\textsubscript{4})\textsubscript{2}, where frameworks built from corner-sharing [Mg(BH\textsubscript{4})\textsubscript{4}] tetrahedra are related to SiO\textsubscript{2} structure types.\textsuperscript{188}

Another polymorph, $\delta$-Mg(BH\textsubscript{4})\textsubscript{2}, was described as a Cu\textsubscript{2}O-type framework, i.e. as two interpenetrated $\beta$-crystobalite-type frameworks (crystobalite is a polymorph of SiO\textsubscript{2}). Analogous similarities between the polymorphs of $\alpha$/$\alpha'$-, $\beta$- and $\gamma$-Ca(BH\textsubscript{4})\textsubscript{2} and the TiO\textsubscript{2} polymorphs anatase, rutile and brookite, respectively, were also described\textsuperscript{185} and are illustrated in Fig. 8. The similarities between borohydride and oxide structures reveal that the homolectic solid metal borohydrides are, like oxides, structures with partly ionic and partly covalent bonding having different degrees of electron transfer between a metal cation and borohydride anion. Consequently, the Pauling rules\textsuperscript{215} can rationalize the crystal structures of borohydrides.\textsuperscript{216}

Structural differences between metal borohydrides and oxides. There are differences between the coordination of borohydride, BH\textsubscript{4}−, and oxide, O\textsuperscript{2−}, anions to metal cations, resulting in structural differences between metal borohydrides and oxides. The negative charge of the oxide O\textsuperscript{2−} has twice the charge of the borohydride BH\textsubscript{4}−, which allows for more structural flexibility in oxides, e.g. incorporation of metal ions with mixed oxidation states. This can lead to charge-ordering related phenomena such as magnetism or ferroelectricity. The oxide anion also contains electron lone pairs, which decrease the sphericity in case of coordination numbers lower than four. In contrast, the borohydride anion has a more pronounced non-spherical tetrahedral shape. Therefore, metal borohydride crystal structures often have lower symmetry when compared to the symmetry of the related oxides.

Furthermore, the borohydride anion is rather large \( r(\text{BH}_4^-) = 2.03 \) Å,\textsuperscript{192,217} being nearly twice as large as the radius of oxide anion \( r(\text{O}^{2-}) = 1.24 \) or 1.28 Å for tetrahedral or octahedral coordination, respectively. As a consequence, the charge density of the oxide ion is more than eight times larger than that of the borohydride ion. Secondly, the Pauling electronegativity is 3.44 for oxygen and only 2.13 (group electronegativity)\textsuperscript{215} for the borohydride anion. This illustrates that the BH\textsubscript{4}− anion is more

| Table 7 | Coordination number of metal and ligand in bimetallic compounds. The hapticity, \( \eta \), is given in the last column if determined by neutron diffraction or periodic DFT calculations |
|---|---|---|---|---|
| Borohydrides of metal, M′ | \( r(M^\text{M′}) \) | CN(M′) | CN(BH\textsubscript{4}) | Hapticity, \( \eta \) BH\textsubscript{4}−·M′ |
| Ba | 1.38 | 6 | 3 | — |
| Sr | 1.18 | 6 | 3 | — |
| Gd | 0.94 | 5 | 2, 3, 4 | 2, 3 |
| Y | 0.90 | 6, 4 | 2 | 2, 3 |
| Cd | 0.78 | 4 | 2, 4 | — |
| Sc | 0.75 | 4 | 2, 3, 4 | 3 |
| Zn | 0.60 | 3 | 2, 3, 4 | 2 |
reducing than $\text{O}^{2-}$. Therefore, stable oxides are often formed by metal ions with a high oxidation state, small radius and, thus, high charge density. This section shows that the opposite is valid for the metal borohydrides, which are often formed by the larger metal ions with lower oxidation state and lower charge density, e.g. potassium tetraoxoferrate(vi), $K_2\text{FeO}_4$ ($\text{Fe}^{\text{VI}}$, $d^0$), is stable at RT whereas $\text{Fe}([\text{BH}_4]_2)$ ($\text{Fe}^{2+}$, $d^6$) exists in solution at $T < -30$ °C, or stabilized with ammonia at RT as $[\text{Fe}([\text{NH}_3]_6)][\text{BH}_4]_2$. Structures of metal oxides are often considered as a close packing of anions with cations filling octahedral or tetrahedral sites. This structural view holds less convincingly for the metal borohydrides, which often have a structural packing deviating significantly from the close packing of anions. This may be ascribed to higher ‘softness’ and polarizability, which introduces more directionality and covalence in the $\text{M–BH}_4$ bonding compared to metal oxides.\textsuperscript{218}

**Role of $\text{H}^+ \cdots \text{H}^-$ interactions.** The repulsive $\text{H}^+ \cdots \text{H}^-$ interaction between neighbouring borohydride groups is another structure-determining parameter. The Switendick limit of 2.1 Å for a minimal $\text{H} \cdots \text{H}$ distance known from metallic hydrides also seems to hold approximately for borohydrides. An illustrative example of the role of the repulsive $\text{H} \cdots \text{H}$ interaction is the RT to HT polymorphic transition from $\alpha$- to $\beta$-$\text{Y(BH}_4)_3$). While the RT polymorph allows for more dense packing, three $\text{H} \cdots \text{H}$ distances around each Y are close to Switendick limit of 2.1 Å. The HT $\beta$-polymorph is less dense, and by reorientation of three out of six borohydrides in the Y coordination, the shortest $\text{H} \cdots \text{H}$ distance becomes 2.6 Å (Fig. 2). Interestingly, DFT calculations suggest the HT phase to be the ground state, indicating the overestimation of the $\text{H} \cdots \text{H}$ repulsion in the calculation. In $\text{ReO}_3$, the oxide equivalent of $\text{Y(BH}_4)_3$ is indeed the equivalent to $\beta$-$\text{Y(BH}_4)_3$, and the oxide equivalent to the RT $\alpha$-$\text{Y(BH}_4)_3$ is obtained by applying the pressure. The flipping of three borohydride groups also straightens the Y-$\text{BH}_4$-Y bridges in the HT-polymorph, which allows maximizing the $\text{H} \cdots \text{H}$ distances. A similar behaviour was observed for $\alpha$- and $\beta$-$\text{Cd(BH}_4)_3$ with a tetrahedral coordination of Cd. While the RT-polymorph is a distorted anti-Cu$_2$O-type structure, the HT-polymorph crystallizes in the regular cubic anti-Cu$_2$O type. Whether the flipping of $\text{BH}_4$ groups is at the origin of this phase transformation remains controversial, since the hydrogen positions have not been reliably determined. The repulsive $\text{H}^+ \cdots \text{H}^-$ interaction is also likely at the origin of the pressure-induced phase transitions in $\text{Mg(BH}_4)_2$ and $\text{Mn(BH}_4)_2$. These compounds change their structure with pressure from a more porous $\alpha$- to more dense $\delta$- or $\delta'$-polymorphs, which are also deformation variants of anti-Cu$_2$O-type.

The repulsive $\text{H}^+ \cdots \text{H}^+$ interaction is naturally expected to be more pronounced for higher partial hydrogen charges, $\delta$. Indeed, $\delta$ varies from $-0.86$ in $\alpha$-$\text{LiBH}_4$\textsuperscript{175} (and even closer to $-1$ for heavier alkali metals) to values much closer to zero for more covalent borohydrides such as $\text{Mg(BH}_4)_2$, where only a partial charge transfer occurs from the metal cation to the $\text{BH}_4$ anion. The limiting case is $\text{Cd(BH}_4)_2$, as Cd is the most electropositive metal forming a borohydride at ambient conditions without stabilization by alkali metal ions. The deformations of the Cu$_2$O-antitype $\text{Mg(BH}_4)_2$ and $\text{Cd(BH}_4)_2$ with pressure and temperature\textsuperscript{3,146} is determined by $\text{H} \cdots \text{H}$ interactions driven by different values of $\delta$, as well as by different radii of the metal atoms. Thus, the strength of the repulsive $\text{H} \cdots \text{H}$ interactions depend on the charge transfer from the counter ion and this influences the stability of some polymorphs.

**4. Structure of anion substituted metal borohydrides.** Metal borohydrides have diverse compositions and rich and fascinating structural chemistry, as discussed in the previous section of this review. The metal borohydrides have been mainly prepared mecanochemically during the past decade, which often produced a variety of metal borohydride halides. Halide substitution in metal borohydrides is a valuable approach for tailoring physical and chemical properties. Metal borohydride halides have either fully ordered, partly ordered or disordered structures (Fig. 9 and Table 8), which is the major focus of this section. Another class of anion substituted metal borohydrides contains both the borohydride, $\text{BH}_4^-$, and the amide, $\text{NH}_2^-$, anions. These boron–nitrogen compounds are also investigated intensively due to their hydrogen storage and ion conductivity properties. In cases where metal borohydrides are contaminated by oxygen containing impurities, e.g. water or solvents, they may partly decompose to metal borohydride borates, $\text{BO}_3^{3-}$. Recently, borohydride $\text{closo}$-boranes, i.e. $\text{B}_3\text{H}_12\text{^2-}$,
were discovered to host fast ion conduction. These new classes of materials, metal borohydride amides, borates and closo-boranes are discussed in the last part of this section.

### 4.1 Metal borohydride halides – fully ordered structures

Strontium borohydride chloride, Sr(BH₄)Cl, is a stoichiometric, ordered compound, which crystallizes in the orthorhombic crystal system at RT (Pnma) with the structure type of Sr(OH)₂.

#### Potassium zinc borohydride chloride

The first mixed-anion mixed-cation borohydride, K₂Zn(BH₄)Cl₂, characterized in 2010, has a structure with crystallographic sites fully occupied by BH₄⁻ or chloride anions and consists of isolated heteroleptic [Zn(BH₄)Cl]⁻ anions charge balanced by K⁺ cations. The [Zn(BH₄)Cl]⁻ anion is built from Zn in a trigonal-planar orientation to two Cl atoms and one BH₄ unit, similar to zinc in the structures of Na₂Zn(BH₄)₃ and KZn(BH₄)Cl. The BH₄⁻ complex coordinates to Zn by edge sharing (e.g.), which then has coordination number four, CN(Zn) = 4. The potassium atom has an unusual coordination number of eight, with a distorted square antiprismatic coordination, formed by five Cl atoms and three BH₄ groups. In agreement with the high coordination number of K, the K–Cl (3.159–3.66 Å) and K–B (3.274–3.781 Å) distances in K₂Zn(BH₄)Cl₂ are slightly longer than in KC (3.130 Å) and KBF₄ (3.364 Å), where the K⁺ ion has an octahedral environment coordinated by six Cl⁻ or BH₄⁻, respectively. This coordination difference underlines that the structure is not directly related to that of KBF₄ and cannot be considered a simple composite of the starting materials.

#### Lithium rare-earth metal borohydride chlorides

A series of alkali rare-earth metal borohydride chlorides with fully anion-ordered structures, LiRE[RE₂(BH₄)₉Cl]₃, RE = La, Ce, Pr, Nd, Sm or Gd crystallize in cubic unit cells with space group symmetry I₄/m. A combination of X-ray diffraction (SR-PXD), neutron diffraction (PND) and density functional theory (DFT) optimization of structural models reveals that the structure contains isolated tetranuclear anionic clusters [RE₂Cl₄(BH₄)₁₂]⁻ with a distorted cubane-like [RE₂Cl₄] core, known from coordination chemistry. The complex anions [RE₂Cl₄(BH₄)₁₂]⁻ are charge balanced by discrete Li⁺ ions. Each rare-earth metal atom, RE, coordinates to three chloride ions and three borohydride groups forming an octahedron, but the BH₄⁻ tetrahedra coordinates to the large rare-earth ions by face sharing (e.g.). Li⁺ ions are disordered, occupying 2/3 of the 12d Wyckoff site, leading to fast lithium ion conduction, further discussed in Section 7. DFT calculations indicate that the structure of LiCe(BH₄)₃Cl is stabilized by entropy, in accordance with the disorder on Li⁺ positions. This complicated structure type, containing both light and heavy atoms, could not be resolved by any two of the three methods, SR-PXD, PND and DFT calculations, and it was only possible to...
solve with the combined use of all three methods. Alternatively, the structure may be rationalized from the borohydride-oxide similarity (Section 3.9) as derived from spinel. If the anions, $\text{BH}_4^-$ or $\text{Cl}^-$, are considered to be close packed then rare-earth metals occupy the octahedral sites, and lithium atoms occupy the tetrahedral sites (similar to those in spinel, but in a ratio 1:1 instead of 2:1 as in spinels).

### 4.2 Metal borohydride halides – partly ordered structures

**Barium borohydride chloride.** Mechanochemical treatment of $\text{LiBH}_4$-$\text{BaCl}_2$ in molar ratios 1:1 and 2:1 produces two new barium borohydride chlorides with different structures.$^{220}$ An orthorhombic chloride-rich compound, $\alpha$-$\text{Ba(BH}_4)_0.16\text{Cl}_1.84$, is obtained using the reactant ratio 1:1 and a borohydride-rich hexagonal compound, $\text{h-Ba(BH}_4)_{0.85}\text{Cl}_1.15$, using molar ratio 2:1. The structures of $\alpha$-$\text{Ba(BH}_4)_0.16\text{Cl}_1.84$ and $\text{h-Ba(BH}_4)_{0.85}\text{Cl}_1.15$ were described on the basis of SR-PXD data using Rietveld refinement and structural similarities to orthorhombic barium chloride, $\text{BaCl}_2$ (Pnma)$^{222}$ and the hexagonal high temperature barium chloride polymorph, $\text{h-BaCl}_2$ (P6$_2$mm).$^{233}$ Respectively. Boron and chlorine atoms occupy the two Cl positions in the $\text{BaCl}_2$ polymorphs with the overall occupancy of B and Cl constrained to one. A third anion position in each structure, $\alpha$-$\text{Ba(BH}_4)_0.16\text{Cl}_1.84$ and $\text{h-Ba(BH}_4)_{0.85}\text{Cl}_1.15$, can be regarded as $\text{H}_4^-$ free.

**Sodium yttrium borohydride chloride.** Mechanochemical synthesis produces a mixed-cation mixed-anion borohydride chloride with the ideal composition $\text{NaY(BH}_4)_2\text{Cl}_2$. The compound crystallizes in a polymeric pseudo-orthorhombic unit cell (P2/c), only slightly distorted from the orthorhombic metrics (with $\beta = 90^\circ$).$^{87,167}$

However, Rietveld refinements suggest some Cl-substitution on the $\text{BH}_4$ site, resulting in a partly ordered structure with the composition, $\text{NaY(BH}_4)_2\text{Cl}_2x$, with $x = 0.21$ at RT.$^{87}$ Interestingly, both experimental and theoretical results reveal two anion sites with different sizes in the structural model. The $\text{BH}_4^-$ anions clearly have a preference for the larger of the two sites, whereas the chloride anion prefers the smaller, due to the size difference of the two anions, $r(\text{Cl}^-) = 1.81$ and $r(\text{BH}_4^-) = 2.03$ Å. Both the yttrium and sodium atoms in $\text{NaY(BH}_4)_2\text{Cl}_2$ have slightly distorted octahedral coordination environments consisting of two $\text{BH}_4$ sites and four Cl atoms for yttrium (i.e. $\text{Y(BH}_4)_2\text{Cl}_4$) and two Cl atoms and four $\text{BH}_4$ sites for sodium atoms (i.e. $\text{Na(BH}_4)_4\text{Cl}_2$). DFT optimization of the experimental structure and Raman spectroscopy suggests that the $\text{BH}_4$ units coordinate by face-sharing ($\eta^3$) towards yttrium and by a combination of edge and face-sharing to sodium.$^{87}$

The existence of one larger and one smaller anionic site is analogous to oxides. The structure of $\text{NaY(BH}_4)_2\text{Cl}_2$ is related to $\text{MgWO}_4$, which again is a cation substitution variant of the $\alpha$-$\text{PbO}_2$ structure. The latter is the structure type observed for $\text{Sr(BH}_4)_2$. There is only one anion site in $\alpha$-$\text{PbO}_2$ but two in $\text{MgWO}_4$ with different sizes due to the size difference of the cations, $\text{Mg}^{2+}$ and $\text{W}^{6+}$. Interestingly, the cations’ coordination number increases from six to seven for the borohydride free compound $\text{NaYCl}_4$. However, the triclinic structure of $\text{NaYCl}_4$ has similar packing and connectivity of the cation coordination polyhedra as observed for the $\text{MgWO}_4$ and $\text{NaY(BH}_4)_2\text{Cl}_2$ type structures.

**Lithium aluminum borohydride chloride.** The first example of a bimetallic borohydride based on s- and p-block metals has the ideal composition $\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}$.$^{159}$ The structure is built from cationic, $[\text{BH}_4]^-$ and an anionic, $[\text{Al(BH}_4)]^{-}$, complexes. However, these units are not isolated, i.e. the Li–B distances within $[\text{BH}_4]^-$ and between the Li atom and B within $[\text{Al(BH}_4)]^{-}$ are similar. Hence this structure can be described as a 3D framework. On the other hand, the structure of $\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}$ can be related to that of the anti-$\text{Cr}_3\text{Si}$ type, by rationalizing it as close packing of complex anions and cations. Detailed structural analysis reveals chloride substitution mainly in the anion-centered complex, $[\text{BH}_4]^-$, providing Li–Cl coordination similar to that observed in $\text{LiBH}_4$–$\text{LiCl}$ solid solutions (see Section 4.4.1).$^{9,214}$ Rietveld refinements of SR-PXD data measured for $\text{AlCl}_3$–$\text{NaBH}_4$ 1:4 and 1:5 samples reveal the presence of $\sim 27$ mol% and $\sim 46$ mol% chloride anions in the compositions $\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}$–$\text{LiCl}$ 21/3.2 and $\text{Li}_4\text{Al}_3(\text{BH}_4)_{13}$–$\text{LiCl}$ 7.5Cl–5.5.

**Sodium aluminum borohydride chloride.** $\text{NaAl(BH}_4)_2\text{Cl}_2$–$x$ with a partly ordered orthorhombic (Pnma) structure is also described. The highest yield of $\text{NaAl(BH}_4)_2\text{Cl}_2$–$x$, $\sim 86$ mol% together with $\text{NaAlCl}_4$, $\sim 14$ mol%, was obtained by mechanochemical treatment of a $\text{AlCl}_3$–$\text{NaBH}_4$ 1:2 sample. The structure consists of one Na, one Al, one Cl and two $\text{BH}_4$ sites. There is no indication of any borohydride substitution on the general position occupied by Cl. The borohydride anions appear to prefer two sites with higher local symmetry on the mirror plane. However, Rietveld refinement indicates Cl-substitution on the $\text{BH}_4$ site. The structure contains complex tetrahedral anions of $[\text{Al(BH}_4)_2\text{Cl}_2]^{-}$ which form in a relatively narrow composition range $1 < x < 1.43$, counter balanced by $\text{Na}^+$ cations. The highest borohydride content (x = 1.43) is obtained from a sample with composition $\text{AlCl}_3$–$\text{NaBH}_4$ 1:3 relative anion occupancies $\text{BH}_4^-$/Cl$^- = 0.82/0.18$ and 0.61/0.39 on each boron site.$^{159,214}$

Contrary to the complex anions $[\text{M(BH}_4)_4]^-$ ($\text{M = Mg, Sc, Mn, Cd}$), $[\text{Zn(BH}_4)_5]^-$ and $[\text{Zn}_2(\text{BH}_4)_5]^-$ the complex anion $[\text{Al(BH}_4)_4]^-$ appears to be more difficult to stabilize (see the discussion in Section 3.5), requiring a certain extent of partial substitution of $\text{BH}_4^-$ units by the smaller $\text{Cl}^-$ ligand.$^{214}$

### 4.3 Metal borohydride halides – fully disordered structures

Compounds with fully disordered anion positions in the structures have statistical distributions of $\text{BH}_4$ and the heavier halide anion on all anionic sites. The section after this one, 4.4, is devoted to compounds, which may be classified as solid solutions of two compounds.

**Potassium zinc borohydride chloride.** A fully disordered monoclinic bimetallic borohydride chloride, $\text{K}_2\text{Zn(BH}_4)_2\text{Cl}_4$–$x$ (P2$_1$/n) has been identified where all four anionic sites are partly occupied by $\text{BH}_4^-$ and $\text{Cl}^-$. The structure of $\text{K}_2\text{Zn(BH}_4)_2\text{Cl}_4$–$x$ consists of $[\text{Zn(BH}_4)_4\text{Cl}_4-x]^-$ anions with Zn coordinating to four $\text{BH}_4$/Cl groups, forming a somewhat distorted tetrahedron. The compound $\text{K}_2\text{Zn(BH}_4)_2\text{Cl}_4$–$x$ is isosstructural to the series of bimetallic borohydrides $\text{K}_2\text{M(BH}_4)_2\text{Cl}_4$, $\text{M = Mg, Mn, Cd}$, discussed in Section 3.5.
In fact, $K_2Zn(BH_4)_xCl_{4-x}$ is a monoclinic distortion of the high temperature $K_2ZnCl_4$ polymorph observed at $T > 315$ °C with a $K_2SO_4$ type structure ($Pnam$). Interestingly, the volume per formula unit ($V/Z$) for $K_2Zn(BH_4)_xCl_{4-x}$ measured at RT is almost identical to that of the high temperature polymorph of $K_2ZnCl_4$ at 315 °C. This indicates that the unit cell volume expansion caused by the incorporation of BH$_4^-$ is similar to the thermal expansion causing the polymorphic phase transformation from the RT polymorph of $K_2ZnCl_4$ (Pna2$_1$) to the high temperature polymorph ($Pnam$).

$K_2Zn(BH_4)_xCl_{4-x}$ is formed after prolonged ball milling of KBH$_4$–ZnCl$_2$ (2:1), and the structure is not fully characterized but may crystallize in the tetragonal space group $P4_2/mnc$ and contains the complex anion $[Zn(BH_4)_xCl_{4-x}]^z^2$ making it a substitutional and deformation variant of the tetragonal ($I4/mcm$) $Cs_3CoCl_5$ structure type.

**Lithium ytterbium borohydride chloride.** The compound LiYb(BH$_4$)$_{2-x}$Cl$_x$ can also be formed, which crystallizes in a primitive tetragonal structure with $x \approx 1.0$ ($P4_2/c$), which is isostructural to LiSc(BH$_4$)$_4$ during heating, ytterbium is also reduced, similar to samarium borohydrides, forming Yb(BH$_4$)$_{2-x}$Cl$_x$. This compound exists with two different compositions depending on both temperature and synthesis conditions. Yb(BH$_4$)$_{2-x}$Cl$_x$, $x = 0.76$, crystallizes in a primitive tetragonal unit cell ($P4_1$), whilst Yb(BH$_4$)$_{1-x}$Cl$_x$, $x = 0.3$, crystallizes in a primitive orthorhombic unit cell ($Pbcn$).

### 4.4 Metal borohydride halides forming solid solutions

Compounds with statistically distributed anions in their structures are denoted fully disordered and may be classified as solid solutions of two compounds. This will be further discussed in the following section. Anion substitution is a method for tailoring the properties of known metal borohydrides. Substitution of BH$_4^-$ or H$^+$ by anions with the same charge and comparable size may lead to formation of solid solutions (see Table 9). The first part of this subsection is devoted to investigations regarding substitution of the BH$_4^-$ complex anion with the heavier halides, Cl$^-$, Br$^-$ or I$^-$. Fluorine substitution has also been attempted, which is discussed in the end of this section, see Section 4.4.2.

In some cases, full solubility between a metal borohydride and the halide salt can be observed, e.g. Na(BH$_4$)$_{1-x}$Cl$_x$. General rules for anion substitution are derived from the numerous examples presented in the following section and are described in the end of this section.

#### 4.4.1. Metal borohydride halides, the s-block

**Lithium borohydride–lithium iodide.** Initially, anion substitution was observed by *in situ* diffraction experiments during heating a sample of LiBH$_4$–LiCl 0.85–0.15. Diffraction data suggest that solid LiCl dissolves into the structure of the solid hexagonal polymorph, h-LiBH$_4$, at $T > 110$ °C, obtaining a maximum chlorine substitution of 42 mol%, i.e. h-Li(BH$_4$)$_{0.58}$Cl$_{0.42}$ The hexagonal solid solution, h-Li(BH$_4$)$_{0.58}$Cl$_{0.42}$, obtained using thermal treatment is stable upon cooling to RT, however slow segregation of LiCl is observed and o-Li(BH$_4$)$_{0.91}$Cl$_{0.09}$ is obtained after several months. The mechanism for anion substitution in the system LiBH$_4$–LiCl is described in reaction scheme (4.1), i.e. one solid, LiCl, dissolves in another solid, LiBH$_4$.

\[
xLiCl + (1-x)LiBH_4 \rightarrow Li(BH_4)_{1-x}Cl_x \quad (4.1)
\]

**Lithium borohydride–lithium bromide.** The mechanism for anion substitution in LiBH$_4$–LiBr, facilitated by mechanochemical or thermal treatment, has been investigated by *in situ* SR-PXD and the formation of two solid solutions is observed. Mechanochemical treatment, or just hand mixing, of a sample of LiBH$_4$–LiBr leads to formation of a hexagonal solid solution h-Li(BH$_4$)$_{1-x}$Br$_x$ with a unit cell volume similar to β-LiBr. This indicates that the first step in the anion substitution process is a dissolution of small amounts of LiBH$_4$ into γ-LiBr (β-LiBr and h-LiBH$_4$ are isostructural). Heating the sample to elevated temperatures, $T > 112$ °C, also enables dissolution of LiBr in h-LiBH$_4$ forming a lithium borohydride rich solid solution with unit cell volume similar to LiBH$_4$. Two solid solutions can be observed at $T > 112$ °C and the dissolution process is further accelerated resulting in a single solid solution at elevated temperatures and full solubility in the system LiBH$_4$–LiBr.

Cooling such a solid solution of h-Li(BH$_4$)$_{1-x}$Br$_x$ should finally lead to crystallization of γ-LiBr, o-Li(BH$_4$)$_{1-x}$Br$_x$ and/or a hexagonal solid solution h-Li(BH$_4$)$_{1-x}$Br$_x$. The composition of the solid solution h-Li(BH$_4$)$_{1-x}$Br$_x$ appears to remain constant ($x \approx 0.5$) upon storage at RT for several months, but γ-LiBr and presumably amorphous o-LiBH$_4$ are slowly segregated. Bromide substitution stabilizes the hexagonal structure of LiBH$_4$ to RT as a solid solution with composition h-Li(BH$_4$)$_{0.5}$Br$_{0.5}$. The solid solutions of Li(BH$_4$)$_{1-x}$J$_x$ have been obtained by reacting LiBH$_4$ with γ-LiJ.

**Lithium borohydride–lithium iodide.** Solid solutions of Li(BH$_4$)$_{1-x}$J$_x$ have been obtained by reacting LiBH$_4$ with γ-LiJ. The substitution process can be induced either by heat treatment at $T \approx 245$ °C or by mechanochemical treatment. In *in situ* SR-PXD has demonstrated that anion substitution initially forms two solid solutions, which at elevated temperatures merge into one containing up to 62 mol% LiJ. Two solid solutions may occur due to substitution of γ for BH$_4^-$ in LiBH$_4$ and substitution of BH$_4^-$ for γ in LiJ. The structures of the two solid solutions are identical to the hexagonal structures of h-LiBH$_4$ and β-LiJ. The solid solutions of Li(BH$_4$)$_{1-x}$J$_x$ have a broader stability range (from RT to the melting at 330 °C) compared to that of both h-LiBH$_4$ and β-LiJ.

**Sodium borohydride–sodium chloride.** The mechanism for anion substitution, facilitated by annealing, was investigated by *in situ* SR-PXD during three consecutive cycles of heating to 300 °C, annealing for 30 min and cooling to RT for a sample of NaBH$_4$–NaCl (1:1), see Fig. 10. The unit cell volume of NaCl increases and decreases linearly due to thermal expansion and contraction, respectively (linear thermal expansion coefficients, $z_{NaCl} = 2.562 \times 10^{-5}$ K$^{-1}$ for $T = 32–300$ °C). No changes are observed in the unit cell volume of NaCl before and after the three annealing cycles, *i.e.* no dissolution of NaBH$_4$ into NaCl.

<table>
<thead>
<tr>
<th>Table 9 Ionic radii of selected anions</th>
<th>F$^-$</th>
<th>H$^-$</th>
<th>NH$_4^-$</th>
<th>Cl$^-$</th>
<th>Br$^-$</th>
<th>BH$_4^-$</th>
<th>I$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (Å)</td>
<td>1.33</td>
<td>1.40</td>
<td>1.68</td>
<td>1.81</td>
<td>1.96</td>
<td>2.03</td>
<td>2.20</td>
</tr>
</tbody>
</table>
observed as a continuous change in the position of KBH₄
diffraction peaks toward higher 2θ values, i.e., the unit cell of
KBH₄ contracts upon heating. This suggests two simultaneous
and coupled chemical reactions taking place. (a) The ternary
chloride K₅ScCl₄ reacts with KBH₄ to form potassium chloride,
KCl, and possibly also amorphous scandium borides, boron,
and/or higher boranes and (b) simultaneously, KCl dissolves in
the remaining KBH₄ and forms a solid solution K[KBH₄]ₓ-Clₓ,
with increasing amounts of KCl, see reaction scheme (4.2).

\[
(1 - x)\text{KBH}_4 + x\text{KCl} \rightarrow \text{K[KBH}_4]_x-\text{Cl}_x
\]  

(4.2)

Magnesium borohydride–magnesium halide. Anion substitution
in Mg[BH₄]ₓ is observed after annealing a milled mixture of
\(x\)-Mg[BH₄]ₓ-MgXₓ (X = Cl or Br). The substitution is identified
from the shift of Bragg peaks from \(x\) to \(\beta\)-Mg[BH₄]ₓ, i.e. anion
substitution only occurs in the \(\beta\)-Mg[BH₄]ₓ polymorph. Structure
refinement revealed that unit cell parameters decreased by about
0.1–0.2 Å for \(\beta\)-Mg[BH₄]ₓ in the mixtures, which corresponds to a
volume contraction of the unit cell of about 2%. A combined
experimental and theoretical approach for the Cl substitution in
Mg[BH₄]ₓ has shown that the enthalpy gain is more favourable for
the \(\beta\)-solid solution than for the \(x\)-solid solution.²²₅

Calcium borohydride–calcium chloride and bromide. Halide
substitution in Ca[BH₄]ₓ-CaClₓ and Ca[BH₄]ₓ-CaBrₓ was also
investigated.²²₆,²²₇ Chlorine substitution was not observed after
BM of the samples but readily occurs after the transition from
\(x\)- to \(\beta\)-Ca(BH₄)ₓ upon heating above ~250°C. Rietveld analysis
of the obtained \(\beta\)-Ca[BH₄]ₓ-Clₓ phases indicates compositions
from \(x = 0.3\) to 0.7 depending on the amount of CaCl₂ in the
mixtures. No anion substitution with CaF₂ or CaBr₂ is observed.²²₆

Calcium borohydride–calcium iodide. Anion substitution
in the system Ca[BH₄]ₓ-CaIₓ resulted in the formation of three
new compounds, which are solid solutions with BH₄⁻ and I⁻
ions sharing the same positions in the structures.²²₈ Sample
preparation methods have a significant influence on the reaction
pathway. Mechanochemical synthesis (ball milling) mediates a
significant degree of dissolution of Ca[BH₄]ₓ into CaI₂ (~70 mol%)
yielding a CaI₂-type trigonal solid solution, tri-Ca[(BH₄)ₓ-Iₓ]₂
(\(x \approx 0.7\)). Upon heating, tri-Ca[(BH₄)ₓ-Iₓ]₂ transforms to a
CaCl₂-type orthorhombic structure, o-Ca[(BH₄)ₓ-Iₓ]₂ (\(x \approx 0.3\)),
which is structurally related to \(\beta\)-Ca(BH₄)ₓ. Upon further heating
(at 335 °C), the sample partly transforms to a more iodide-rich
dodecagonal solid solution, tet-Ca[(BH₄)ₓ-Iₓ]₂ (\(x \approx 0.6\)), with
a novel structure type. This compound decomposes to CaI₂
and CaBr₂ (at T > 345 °C). Apparently, minor amounts of CaI₂
also dissolve into \(\beta\)-Ca[BH₄]ₓ forming a solid solution, which is
structurally similar to o-Ca[(BH₄)ₓ-Iₓ]₂, i.e. \(\beta\)-Ca[(BH₄)ₓ-Iₓ]₂
with \(x \sim 0.05\).²²₈

4.4.2 Fluoride substitution in metal borohydrides. The smaller
halide ion, F⁻ (1.33 Å), has a similar size to the hydride ion, H⁻
(1.40 Å) and metal hydrides and fluorides share many properties,
et.g. the ionic compounds are often found to be isostructural.
This suggests that hydrogen and fluorine may substitute for
each other in both ionic and covalently bonded compounds.

Potassium borohydride–potassium chloride. Anion substitution
in potassium borohydride has been observed during the decom-
position of K₅Sc[BH₄]₄.¹⁶⁶ The mechanochemically produced
sample originally contained the three compounds: K₅Sc[BH₄]₄,
K₅ScCl₄, and KBH₄. The amount of KBH₄ increases during the
decomposition of K₅Sc[BH₄]₄ in the temperature range 150 to 230 °C
and further reacts with K₅ScCl₄ at T > 230 °C. The reaction is
takes place during the short time of the experiment (only 90 min
at 300 °C).

At T ~ 240 °C the unit cell volume of Na[BH₄]ₓ-Clₓ decreases
rapidly and continues to do so for approximately 20 min. On this
time scale the unit cell parameter is found to decrease from
6.2099–6.1295 Å, while the degree of substitution, \(x\) changes from
approximately 0.15 to 0.50. During the second and third annealing
periods at T = 300 °C the unit cell volume of Na[BH₄]ₓ-Clₓ decreases
linearly due to anion substitution. Furthermore, the fact that the
decline in unit cell volume of Na[BH₄]ₓ-Clₓ is linear upon cooling
suggests that NaCl does not segregate from NaBH₄ on the time
scale of the experiment and the final composition is found to be
Na[BH₄]₁₋₀.₄₃Cl₀.₇₇.²²²

Dissolution of 10 mol% NaCl into NaBH₄, forming Na[BH₄]ₓ-Clₓ,
takes place during relatively mild ball milling, i.e. 60 × 2 min
with 2 min breaks to restrict sample heating (total BM time
120 min). A higher degree of dissolution of NaCl into NaBH₄ is
obtained by more harsh BM (e.g. 24 h) in some cases combined
with sample heating by the reaction heat from decomposition of
metal borohydrides. These investigations suggest full solubility
in the system NaBH₄–NaCl, i.e. one solid solution.²¹,²² This is
expected because NaCl and NaBH₄ are both isomorphous.
Investigations reveal a linear correlation between the compositions
of the solid solutions and the unit cell volume, in agreement with
Vegard’s law.²¹,²² Chlorine substitution for the larger iodide
anion also occurs readily and stoichiometrically during relatively
mild ball milling.
The most significant difference between the two lies in the electronegativity, which is 2.1 and 4.0 for hydrogen and fluorine, respectively. Therefore, fluorine substitution is expected to lead to significant thermodynamic changes in metal hydrides. The first fluorine-substituted complex hydride was prepared by hydrogenation of the system NaF-Al-H₂, which yielded the complex hydride Na₃AlH₆·Fₓ, i.e. fluoride substitution of the complex anion [AlH₆·Fₓ]⁻. The substitution of fluoride into NaMgH₂, forming NaMgH₂F, has been shown to stabilize the structure and increase the enthalpy of hydrogen absorption/desorption, a desirable property for concentrating solar thermal energy storage applications.

Fluoride substitution in the BH₄⁻ complex anion, i.e. H⁻ → F⁻, is also possible. The system NaBH₄–NaBF₄ provided the first fluoride substituted borohydride, NaBH₂₁F₉, observed in a narrow temperature range of 200 to 215 °C by SR-PXD. However, the obtained materials MBHₓ(Fₓ)₄ appear to have relatively low thermal stability and the released hydrogen can be contaminated with significant amounts of boronfluorides and/or borane gases and may lead to the formation of significant amounts of unwanted MgₓH₃H₁₂. The system KBH₄–KBF₄ was investigated by solid state ¹¹B and ¹⁹F NMR, which appear more consistent with a statistical distribution of fluoride substituted [B(H,F)]₄⁻ tetrahedra rather than a mix of discreet BH₄⁻ and BF₄⁻ tetrahedra.

Hydrogen substitution by fluorine in orthorhombic α-LiBH₄ has been investigated with quantum-mechanics calculations aiming to describe thermodynamic properties of LiBH₄, for hydrogen storage applications. Excess enthalpies of the mixed compounds were computed, suggesting that fluorine atoms tend to agglomerate on the same boron atoms rather than be homogeneously dispersed over all the available BH₄ tetrahedra. These data show that, at room temperature, the formation of solid solutions between lithium borohydride and borofluoride is thermodynamically unfavoured, so the fluorine substitution destabilizes the pure hydride. A number of reactive hydride composites (further discussed in Section 6.8) containing metal fluorides have been successfully hydrogenated and in some cases cycled with hydrogen release and uptake, (CaH₂/CaF₂)–MgB₂, Mg–LiBH₄ composites catalysed by FeF₃, LiH–LiF–MgB₂ system, Ca(BH₄)₂–MgF₂, and Ca(BH₄)₂–MgF₂. A drawback is the high stability of both ionic metal fluorides MF and molecular covalent borontrifluoride, BF₃.

4.5 General trends for halide substitution in metal borohydrides

Metal borohydrides and the heavier halides. The above Section 4.4 provides a range of examples of halide substitution in stable monometallic alkali and alkaline earth metal borohydrides and some trends in the structural chemistry of anion substitution are observed. Anion substitution by the heavier halides, i.e. Cl⁻, Br⁻ or I⁻, of borohydrides:

(i) The solid containing the smaller anion tends to dissolve into the compound containing the larger anion, and the structure of the latter tends to be preserved in the obtained solid solution. This trend can be interpreted as a contraction of the structure providing shorter average bond lengths and therefore larger lattice energy.

(ii) Some polymorphs of metal borohydrides are more prone to perform anion substitution than others. This effect is illustrated by the high temperature polymorphs, e.g. h-LiBH₄, β-Mg[BH₄]₂ and β-Ca[BH₄]₂, which more readily dissolve solid metal halides into their structures. Investigations using diffraction and solid state MAS NMR reveal that anion substitution is facilitated by structural dynamics and an orientational disorder, i.e. entropy effects, in particular related to the BH₄ unit, which possibly make the BH₄ tetrahedra appear more spherical and similar to halides.

(iii) In the case where the metal borohydride and the metal halide are isostructural, anion substitution may occur in both compounds, which can lead to two solid solutions. This effect is observed during moderate heat treatment of mechanochemically treated mixtures of various borohydrides and halides, leading to two solid solutions and indicating non-equilibrium conditions. Thus, mechanochemical treatment facilitates formation of the solid solution with larger volume, compared to the parent compound, due to thermal expansion. Such binary solid solutions tend to merge to a single solid solution after prolonged heating, i.e. a solid solution exists in the full concentration range at higher temperatures (and can be quenched to RT). This is observed for LiBH₄–LiBr, LiBH₄–LiI and NaBH₄–NaCl systems, and notice that β-LiBr, β-LiI and h-LiBH₄ and also NaBH₄ and NaCl are isostructural.

Reactions during mechanochemical treatment appear to be promoted by elevated pressure, i.e. by compression of materials, therefore all anion substitutions obtained by BM appear to follow (i). In contrast, thermal treatment (annealing) tends to facilitate increased mobility, e.g. of BH₄⁻, and thermal expansion of the structures. Therefore, initially rule (i) appears to be violated in cases where (iii) is valid, but prolonged heating will eventually lead to chemical equilibrium and appear to follow (i), i.e. two solid solutions tend to merge to one. In the cases where anion substitution occurs at elevated temperature (ii) the high temperature polymorph is often stabilised to lower temperatures. Here the dissolution of a metal halide at elevated temperatures appears to be a fast process but segregation of the metal halide at lower temperatures is often a slower process.

Thus, in conclusion, anion substitution and anion disorder is a well-known property of metal borohydrides that has been exploited to tailor hydrogen release properties, and more recently to develop ionic conductors. Cation disorder, on the other hand, has not been observed very often, with some examples being, Mₓ₃Mₓ₂(BH₄)ₓ, and LiₓZnₓ[BH₄]₁₅, M = Mg and Mn. Only very recently have some researchers started to consider the functional design of physical properties by means of cation substitution, which in turn is the most dominant tool to tailor transition metal oxides. Cation disorder may occur for structures containing very large anions dominating structural organization, or when the cations are very similar in size, such as for Mg⁷⁺ and Mn⁷⁺ with identical charge and similar ionic radius, r(Mg⁷⁺) = 0.71 Å and r(Mn⁷⁺) = 0.80 Å. However, cation substitution can also occur for cations that have the same preferred coordination sphere such
as Li⁺ and Mg²⁺ that both prefer tetrahedral coordination. Therefore the tri-metallic compound Li₃Mzn₃(BH₄)₁₅, M = Mg and Mn may be considered as being derived from the bimetallic compound LiZn₃(BH₄)₂ by Li-Mg cation substitution.⁸³

Fluorine substitution in hydridocomplexes is clearly possible, however the stability of the produced compounds is limited due to the formation of very stable ionic solids or molecular gases. The system Na–Al–F–H can provide the complex Na₃AlF₆...F₇, which has a strong tendency to form fully fluorine substituted octahedral complexes [AlF₆]³⁻.²³⁸ Recall the composition of the rather stable mineral cryolite, Na₃AlF₆. The metal borohydride–borofluorides, NaBH₄–NaBF₄ and KBH₄–KBF₄, provide some new and partly fluorine substituted borohydride complexes, NaBH₂₋₁Fₓ₋₁ built from [B(H,F)₄]⁻.²²³,²²⁴ However, their stability is rather limited and these systems have a strong tendency to decompose to significantly more stable ionic metal fluorides or possibly the molecular compound, BF₃.

4.6 Trends in series of bimetallic borohydride halides

In some cases, series of bimetallic alkali metal–d-block metal borohydride halides have been investigated. The monometallic borohydrides are described as two different polymorphs for yttrium and cadmium. The existence of monometallic scandium and zinc borohydrides has been suggested, but they have not been observed experimentally. For the bimetallic systems containing lithium, only cadmium forms a ternary halide, Li₆CdCl₆.¹⁴⁶ For the tri-metallic systems containing lithium, synthesis of Li₃Mzn₃(BH₄)₁₅ also yields some Li₆MCl₆, M = Mg or Mn.¹⁴³ However, ternary halides are formed in most cases for sodium and potassium systems.

The systems MBH₄–ZnCl₂ (M = Rb, Cs) and MBH₄–ScCl₄ (M = Rb, Cs) remain incompletely characterised due to their complexity. Thus, there is a tendency for more complex structural chemistry, higher numbers of compounds and solid solutions in the phase diagrams and more diverse compositions for heavier alkali metals.

4.7 Metal borohydride closo-boranes

There are a few examples of mixed borohydride closo-boranes.¹,²²² Both Cs₃BH₄B₁₂H₁₂ and Rb₃BH₄B₁₂H₁₂ were thought to be by-products from the pyrolysis of their respective B₁₂H₁₄ compounds in 1990,²³⁵ which can also be formed as decomposition products from bi- and trimetallic borohydride-perovskites.⁷⁸ The compound Cs₃BH₄B₁₂H₁₂ was presented in 2003 (see Fig. 11),²⁴⁵ which can be precipitated from water. This compound crystallizes in a trigonal (R₃m) anti-perovskite structure type, where Cs⁺ is considered as a shared vertex of two [BH₄Cs₆]⁻ octahedra. Interestingly there is dynamic disorder of the BH₄⁻ anion at room temperature, whereas a further structural transition is believed to occur near 305 °C, which could involve rotation of the B₁₂H₁₄²⁻ anions. This was also suggested by a more detailed study of the decomposition of borohydride-perovskites, and the symmetry of the high temperature cubic anti-perovskite polymorph was identified as P2₃.²₅⁵

More recently Na₃BH₄B₁₂H₁₂ and (Li₀.₇Na₀.₃)BH₄B₁₂H₁₂ were synthesized by mechanical milling followed by heat treatment and investigated for their ion conductivity properties.²₅₆ Na₃BH₄B₁₂H₁₂ is orthorhombic Omc2₁ and (Li₀.₇Na₀.₃)BH₄B₁₂H₁₂ is orthorhombic Pna₂₁. Filling the interstitial sites of Na₃BH₄B₁₂H₁₂ with Li⁺ affords (Li₀.₇Na₀.₃)BH₄B₁₂H₁₂, where both compounds appear to have ordered B₁₂H₁₄²⁻ and BH₄⁻ anions, though no conclusions can be drawn on low frequency reorientations.

4.8 Metal borohydride amides

The first composite of a metal borohydride and a metal amide, LiBH₄–LiNH₂ (1 : 2), was reported in 2005²⁵⁷ with the aim of improving H₂ desorption temperatures, owing to partly negatively and positively charged H atoms present in the composite. In addition, it was shown in 2009 that composites of LiBH₄–LiNH₂ are good lithium ion conductors.⁸⁹ These two factors have inspired research into various other borohydride–amide composites, e.g. Mg(BH₄)₂–LiNH₂,²⁵⁸ and Mg(BH₄)₂–Mg(NH₂)₂ see Table 10.⁹⁰ As described earlier in Section 4, halides may directly substitute for BH₄⁻ on the same crystallographic position. On the other hand, due to difference in size and coordination, the complex NH₂⁻ anion always has unique crystallographic sites compared to BH₄⁻ in borohydride-amide structures.

The first reported crystal structure of a borohydride–amide was Li₄(BH₄)(NH₂)₃, cubic (I2₁3), with three independent lithium positions that all are coordinated by four ligands, i.e. three BH₄⁻ and one NH₂⁻; one BH₄⁻ and three NH₂⁻; and four NH₂⁻ (Fig. 12).²⁶₃,²⁶₄ The rhombohedral structure (R3) of Li₄(BH₄)(NH₂)₃ was later determined with two independent lithium positions that are coordinated by three BH₄⁻ and one NH₂⁻; and one BH₄⁻ and three NH₂⁻.²⁵⁹,²⁶⁰ To our knowledge, the LiBH₄–LiNH₂ system is unique compared to the other metal borohydride amide systems in the way that new compounds are readily formed by mechanochemical treatment. In all other systems, mechanochemical treatment only leads to physical mixtures of the starting reactants.
A high temperature polymorph, α-Na\(_2\)(BH\(_4\))(NH\(_2\))\(_2\), was prepared by heating NaBH\(_4\)–NaNH\(_2\) to the melting point, 219 °C, for 1 h and subsequently cooling to RT.\(^{99}\) After longer annealing times (10 days) at lower temperatures, 98 °C, α-Na\(_2\)(BH\(_4\))(NH\(_2\)) transforms into the low temperature polymorph, β-Na\(_2\)(BH\(_4\))(NH\(_2\)). The cubic α-Na\(_2\)(BH\(_4\))(NH\(_2\)) crystallizes in the K\(_3\)SO\(_4\)F structure type (Pm\(_3\)m), whereas β-Na\(_2\)(BH\(_4\))(NH\(_2\)) has an orthorhombic structure (Pb\(_{\text{cm}}\)). Both structures can directly be derived from the anti-perovskite type structure ABO\(_3\), with the [BH\(_4\)]\(^-\) and [NH\(_3\)]\(^-\) moieties in the A and B sites, respectively. The charge balancing Na\(^+\) ions occupy 2/3 of the O positions.

Mg(BH\(_4\))(NH\(_2\))\(_2\) has been prepared by thermal treatment of Mg(BH\(_4\))\(_2\)–Mg(NH\(_2\))\(_2\) at 180 °C.\(^{90}\) The structure is tetragonal (I\(_4\)1) with the Mg\(^{2+}\) ions tetrahedrally coordinated by two BH\(_4\)\(^-\) and two NH\(_2\)\(^-\) ligands. This material exhibits relatively high Mg\(^{2+}\) ion conductivity of 10\(^{-6}\) S cm\(^{-1}\) at 150 °C.\(^{270}\)

LiCa[BH\(_4\)\(_2\)](NH\(_2\)) and NaCa[BH\(_4\)\(_2\)](NH\(_2\)) are suggested to form by ball milling of Ca(BH\(_4\)\(_2\))–MNH\(_2\) (M = Li, Na),\(^{268}\) however, structure determination is not reported.\(^{266,267}\)

### 5. Derivatives of metal borohydrides with neutral molecules

Metal borohydrides have diverse compositions with rich and fascinating structural chemistry, which may be further expanded by the inclusion of other negatively charged anions, discussed in the previous sections of this review. Furthermore, a wide range of metal borohydrides containing neutral molecules have been discovered during the past few years that are the topic of the present section. The introduction of nitrogen in metal borohydrides has received significant interest owing to the possible inclusion of dihydrogen bonding via partly positively charged hydrogens, e.g. B–H\(^+\)…H–N. Dihydrogen bonding is considered a new valuable approach for tailoring a material’s physical and chemical properties. A high number of new ammine, NH\(_3\), metal borohydrides have been discovered and trends in composition, structure and properties are first discussed in this section, followed by hydrazine, N\(_2\)H\(_2\) and ammonia borane, NH\(_3\)BH\(_3\) derivatives. Solvent molecules with nitrogen, oxygen or sulphur as donor atoms may also crystallize with metal borohydrides depending on synthesis conditions.

#### 5.1 Ammine metal borohydrides

Ammine metal borohydrides, M(BH\(_4\))\(_n\) nNH\(_3\), have been known since the 1950’s, but the number of new compounds has increased tremendously during the past ~5 years having received interest as both ammonia and hydrogen stores (Table 11). The number of BH\(_4\)\(^-\) anions (n) in the compounds is fixed and determined by the oxidation state of the metal, whereas the number of NH\(_3\) ligands (n) may range from 1 to 8. Compared to the borohydride anions, NH\(_3\) coordinates more strongly and less flexibly to the metal, i.e. always via an electron pair donated by N, and acts as a terminal ligand.

##### 5.1.1 Mono-metallic ammine metal borohydrides

Mono-ammine lithium borohydride. LiBH\(_4\)–NH\(_3\), is the only reported ammine alkali metal compound stable at RT. Monoammine lithium borohydride crystallizes in an orthorhombic unit cell with symmetry \(Pm\(_{\text{cm}}\)\).\(^{271}\) Each Li atom is tetrahedrally coordinated by three BH\(_4\)\(^-\) units and one NH\(_3\) molecule, while each BH\(_4\)\(^-\) unit is linked to three Li atoms and four NH\(_3\) molecules via dihydrogen interactions.

Ammine magnesium borohydrides. Mg(BH\(_4\)\(_2\)) nNH\(_3\), are known for n = 1, 2, 3 and 6, while the crystal structure for n = 1 remains
Table 11 Ammine metal borohydrides, M(BH₄)ₓₜₙNH₃, with known crystal structures

<table>
<thead>
<tr>
<th>Compounds</th>
<th>n</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-metallic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li[BH₄]₂·nNH₃</td>
<td>1</td>
<td>271</td>
</tr>
<tr>
<td>Mg[BH₄]₂·nNH₃</td>
<td>1, 2, 3, 6, 9</td>
<td>54, 272 and 273</td>
</tr>
<tr>
<td>Ca[BH₄]₂·nNH₃</td>
<td>1, 2, 4, 6b</td>
<td>54 and 274-277</td>
</tr>
<tr>
<td>Sr[BH₄]₂·nNH₃</td>
<td>1, 2, 4b</td>
<td>277 and 278</td>
</tr>
<tr>
<td>Al[BH₄]₂·nNH₃</td>
<td>1, 6</td>
<td>279-281</td>
</tr>
<tr>
<td>V[BH₄]₂·nNH₃</td>
<td>3</td>
<td>282</td>
</tr>
<tr>
<td>Cr[BH₄]₂·nNH₃</td>
<td>6b</td>
<td>94</td>
</tr>
<tr>
<td>Mn[BH₄]₂·nNH₃</td>
<td>1, 2, 3, 6</td>
<td>54</td>
</tr>
<tr>
<td>Fe[BH₄]₂·nNH₃</td>
<td>6b</td>
<td>94</td>
</tr>
<tr>
<td>Co[BH₄]₂·nNH₃</td>
<td>6b</td>
<td>94</td>
</tr>
<tr>
<td>Zn[BH₄]₂·nNH₃</td>
<td>2, 4a</td>
<td>119 and 283</td>
</tr>
<tr>
<td>Y[BH₄]₂·nNH₃</td>
<td>1, 2, 4, 5, 6, 7</td>
<td>53</td>
</tr>
<tr>
<td>Zr[BH₄]₂·nNH₃</td>
<td>8</td>
<td>284</td>
</tr>
<tr>
<td>La[BH₄]₂·nNH₃</td>
<td>4, 6</td>
<td>285</td>
</tr>
<tr>
<td>Ce[BH₄]₂·nNH₃</td>
<td>4, 5, 6</td>
<td>285</td>
</tr>
<tr>
<td>Gd[BH₄]₂·nNH₃</td>
<td>4, 5, 6, 7</td>
<td>53</td>
</tr>
<tr>
<td>Dy[BH₄]₂·nNH₃</td>
<td>4, 5, 6, 7</td>
<td>53</td>
</tr>
<tr>
<td>Bimetallic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiMg[BH₄]₂·nNH₃</td>
<td>2</td>
<td>286</td>
</tr>
<tr>
<td>Li₂Mg[BH₄]₂·nNH₃</td>
<td>6</td>
<td>54 and 287</td>
</tr>
<tr>
<td>Li₂Al[BH₄]₂·nNH₃</td>
<td>6</td>
<td>288</td>
</tr>
<tr>
<td>Li₃Sc[BH₄]₂·nNH₃</td>
<td>4</td>
<td>282</td>
</tr>
<tr>
<td>Li₂Mn[BH₄]₂·nNH₃</td>
<td>6</td>
<td>54</td>
</tr>
<tr>
<td>Li₂Fe[BH₄]₂·nNH₃</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>Na₂Zn[BH₄]₂·nNH₃</td>
<td>2</td>
<td>289</td>
</tr>
<tr>
<td>Solid solutions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn₁₋₂Mg₂[BH₄]₂·nNH₃</td>
<td>6</td>
<td>54</td>
</tr>
<tr>
<td>Co[BH₄]₂₋₂Cl₂·nNH₃</td>
<td>6b</td>
<td>94</td>
</tr>
</tbody>
</table>

* Detailed crystal structure remains unknown. b Unstable at RT.

unknown.²⁷²,²⁷³ Mg[BH₄]₂·6NH₃ is isostuctural to MgCl₂·6NH₃ (if the hydrogen atoms are not considered) and crystallizes in a cubic unit cell (Pm3m), where Mg is octahedrally coordinated by six NH₃ molecules, forming [Mg(NH₃)₆]²⁺ complexes, while BH₄⁻ act as counter ions in the crystalline solid.²⁷² Mg[BH₄]₂·3NH₃ crystallizes in an orthorhombic unit cell with space group Pmma.²⁴ Here, Mg coordinates to two terminal BH₄⁻ anions and three NH₃ molecules, forming neutral molecular complexes [Mg(BH₄)₂(NH₃)]₂⁻ connected by dihydrogen bonds between H⁺ from BH₄⁻ and H⁻ from NH₃. Similarly, Mg[BH₄]₂·2NH₃ forms neutral complexes of [Mg(BH₄)₂(NH₃)]₂⁻ where Mg is tetrahedrally coordinated by two BH₄⁻ anions and two neutral NH₃ ligands.²⁷²

Ammine calcium borohydrides. Ca[BH₄]₂·nNH₃ are known for n = 1, 2, 4 and 6, where n is isostuctural to Mg[BH₄]₂·6NH₃ and consists of octahedral complexes [Ca(NH₃)₆]²⁺ charge balanced by BH₄⁻. A monoclinic (P2₁/c) Ca[BH₄]₂·4NH₃ has Ca octahedrally coordinated by four equatorial NH₃ groups and two axial terminal BH₄⁻ groups forming neutral [Ca(NH₃)₄][BH₄]₂ complexes.²⁷⁷ The structure is composed of hep octahedra layers in the bc-plane stacked along the a-axis in the order AAA, which are connected by dihydrogen bonds. Ca[BH₄]₂·2NH₃ has an orthorhombic structure (Pbcn) in which Ca is coordinated octahedrally by four bridging BH₄⁻ groups and two terminal NH₃ groups. Ca and the four BH₄⁻ groups form a 2D layer stacked in the order ABAB.²⁷³ Ca[BH₄]₂·NH₃ has an orthorhombic unit cell (Pna2₁) with Ca octahedrally coordinated by one NH₃ group and five bridging BH₄⁻ ligands, creating zig-zag chains of edge sharing octahedra running along the c-axis forming a 3D network.²⁷⁴

Ammine strontium borohydrides. Sr[BH₄]₂·nNH₃ (n = 1, 2, 4), have been reported with Sr[BH₄]₂·4NH₃ being isostuctural to Ca[BH₄]₂·4NH₃.²⁷²²²² Sr[BH₄]₂·2NH₃ (orthorhombic, Pnca2₁) consists of Sr octahedrally coordinated by four bridging BH₄⁻ groups in-plane and by two axial NH₃ groups. Similar to Ca[BH₄]₂·2NH₃, the four BH₄⁻ groups and the metal create a two-dimensional layer in the bc-plane stacked in the sequence AAA along the a-axis. The NH₃ groups are terminal ligands pointing between the layers. Sr[BH₄]₂·NH₃ (orthorhombic, Pbna) has Sr coordinated octahedrally by five BH₄⁻ groups and one NH₃ group similar to Ca in Ca[BH₄]₂·NH₃.²⁷⁴ There are two different types of BH₄⁻ groups in the structure of Sr[BH₄]₂·NH₃, one BH₄⁻ is bridging between three Sr atoms by the edge of the tetrahedron (η₃), while one BH₄⁻ group is bridging two Sr atoms by edge (η₂) and face (η₁) sharing. Sr[BH₄]₂·NH₃ is a double layered structure in the ab-plane, where the identical layers are shifted by an n-glide plane. The layers are stacked along the c-axis in the sequence ABAB and connected by dihydrogen bonds.

Ammine aluminum borohydride. Al[BH₄]₂·nNH₃, have been known for n = 1 since 1974,²⁹⁰ whereas the structure of n = 6 was reported more recently.²⁸¹ Al[BH₄]₂·3NH₃ crystallizes in a monoclinic unit cell (P2₁/n) and consists of tetrahedral neutral complexes of [Al(BH₄)₂(NH₃)]₄⁻ and [Al(BH₄)₄]⁻ as counter ions in the crystalline solid.

Ammine vanadium borohydride. V[BH₄]₃·3NH₃, crystallizes in a cubic system (F23) and consists of neutral [V[BH₄]₃(NH₃)]₃⁻ complexes, where V is octahedrally coordinated.²⁸²

Hexaammine chromium, iron and cobalt borohydride. M[BH₄]₂·6NH₃ (M = Cr, Fe, Co) with the metals in the oxidation state (n), are all isostuctural and are also isostuctural to Mo[BH₄]₂·6NH₃ (M = Mg, Ca), i.e. consisting of [M(NH₃)₄]²⁻ and [BH₄⁻]⁻ complexes.²⁹⁴

Ammine manganese borohydrides. Mn[BH₄]₂·nNH₃, are known for n = 1, 2, 4 and 6, while the crystal structure for n = 4 remains unknown, and n = 2, 3 and 6 are all isostuctural to the magnesium analogues.²⁵⁴ Thus, Mn[BH₄]₂·6NH₃ forms [Mn(NH₃)₆]³⁻ complexes with BH₄⁻ as counter ions, while Mn[BH₄]₂·3NH₃ and Mn[BH₄]₂·2NH₃ contain neutral molecular complexes.

Tetraammine zinc borohydride. Zn[BH₄]₄·4NH₃ is one of the first reported ammine metal borohydrides, but the crystal structure remains unknown.¹¹⁰ More recently, Zn[BH₄]₂·2NH₃, monoclinic (P2₁), was discovered and consists of neutral [Zn(BH₄)₂(NH₃)]₂⁻ complexes connected by dihydrogen bonds.²⁸³

Ammine yttrium borohydrides. Y[BH₄]₂·nNH₃ (n = 1, 2, 4, 5, 6 and 7), form the most extensive ammine metal borohydride series.³³ Y[BH₄]₃·7NH₃ (orthorhombic, Pca2₁) contains cation complexes of Y surrounded by seven NH₃ molecules, forming a monocapped trigonal prism. The [Y(NH₃)₇]³⁺ prism forms a hexagonal pattern in the ab-plane, which are stacked in the order ABAB along the c-axis. The structure of Y[BH₄]₃·6NH₃ (Pn3) is built from Y octahedrally coordinated by six ammonia molecules producing octahedral complexes [Y(NH₃)₆]³⁺. The [Y(NH₃)₆]³⁺
octahedra are ordered in a hexagonal pattern in (111) layers, which are stacked in the sequence ABC along the [111] direction. Compared to the other ammine yttrium borohydrides, Y(BH$_4$)$_3$·6NH$_3$ has a low density and the BH$_4^-$ may be relatively mobile. Y(BH$_4$)$_3$·5NH$_3$ has a hexagonal unit cell (P6$_3$) with Y eight-fold coordinated by five NH$_3$ molecules and three terminal BH$_4^-$ groups in molecular complexes [Y(NH$_3$)$_5$(BH$_4$)$_3$]. The complexes [Y(NH$_3$)$_5$(BH$_4$)$_3$] are packed in the $ab$-plane in a hexagonal pattern, which are stacked in the order ABAB along the $c$-axis. Y(BH$_4$)$_3$·4NH$_3$ crystallizes in an orthorhombic unit cell (P$\text{na}2_1$) and Y is seven-fold coordinated by four NH$_3$ and three BH$_4^-$, creating neutral molecular complex [Y(NH$_3$)$_4$(BH$_4$)$_3$]. The molecular complexes are packed in $ab$-layers in a hexagonal pattern, which are stacked in the order ABAB along the $c$-axis. Y(BH$_4$)$_3$·2NH$_3$ (orthorhombic, $Pbca$) with Y$^{3+}$ coordinated to two NH$_3$ and to four BH$_4^-$ groups in an octahedron, where two of the BH$_4^-$ groups are bridged to other yttrium atoms. Thus, the solid Y(BH$_4$)$_3$·2NH$_3$ consists of one-dimensional zig-zag ribbons running along the $a$-axis. Y(BH$_4$)$_3$·4NH$_3$ is orthorhombic (Cmcm) with Y$^{3+}$ coordinated by one NH$_3$ and five BH$_4^-$ groups, where four of the BH$_4^-$ groups are bridging other yttrium atoms, forming 2D layers stacked in the order ABAB.

Ammine zirconium borohydride. Zr(BH$_4$)$_4$·$n$NH$_3$, has the highest number of coordinated NH$_3$, i.e. $n=8$, and crystallizes in an orthorhombic unit cell ($Pmna$). The structure is built from complex cations [Zr(NH$_3$)$_8$]$^{4+}$ charge balanced by BH$_4^-$.

Ammine lanthanum borohydrides. La(BH$_4$)$_3$·$n$NH$_3$ ($n=2, 4, 5, 6$), have recently been reported. La(BH$_4$)$_3$·6NH$_3$ crystallizes in an orthorhombic unit cell ($P2_12_12_1$) with La$^{3+}$ coordinated by six NH$_3$ ligands and two terminal BH$_4^-$ groups, creating a large complex cation [La(BH$_4$)$_3$·(NH$_3$)$_2$] that is charged balanced by one BH$_4^-$ (Fig. 13) α-La(BH$_4$)$_3$·4NH$_3$, and $\beta$-La(BH$_4$)$_3$·4NH$_3$ are, together with the cerium analogues, the only examples of ammine metal borohydrides having two polymorphs. α-La(BH$_4$)$_3$·4NH$_3$ crystallizes in a monoclinic unit cell ($P2_1$), where La$^{3+}$ is coordinated by four NH$_3$ groups and three BH$_4^-$ groups, creating molecular clusters [La(BH$_4$)$_3$·(NH$_3$)$_2$]. $\beta$-La(BH$_4$)$_3$·4NH$_3$ are isostuctural to M(BH$_4$)$_3$·4NH$_3$ (M = Y, Gd, Dy).

*Ceberium lanthanum borohydrides. Ce(BH$_4$)$_3$·$n$NH$_3$ ($n=2, 4, 5, 6$), have been reported. Ce and $\beta$-Ce(BH$_4$)$_3$·4NH$_3$ are isostuctural to $\alpha$- and $\beta$-La(BH$_4$)$_3$·4NH$_3$, while Ce(BH$_4$)$_3$·5NH$_3$ and Ce(BH$_4$)$_3$·6NH$_3$ are isostuctural to M(BH$_4$)$_3$·5NH$_3$ (M = Y, Gd, Dy) and La(BH$_4$)$_3$·6NH$_3$, respectively.

5.1.2 Bimetallic ammine metal borohydrides. Seven ammine bimetallic borohydrides have been reported in the scientific literature. Here, NH$_3$ always coordinates to the metal with the highest charge density, which also has the higher oxidation number, while the metal with lower charge density, typically Li or Na, only coordinate to BH$_4^-$.

Diammine lithium magnesium borohydride. LiMg(BH$_4$)$_2$·2NH$_3$ has a hexagonal unit cell (P6$_3$), where Mg is five-fold coordinated and resides in triangular-bipiramidal coordination, with the N atoms located at the axial positions of this polyhedron and the BH$_4^-$ groups at the equatorial positions. Li atoms are located in a triangular antiprism formed by six BH$_4^-$ groups.

Hexaammine dilithium magnesium borohydride. Li$_2$Mg(BH$_4$)$_3$·6NH$_3$, tetragonal, $P4_2/mnm$ is another known ammine bimetallic borohydride based on lithium and magnesium built from distinct [Mg(NH$_3$)$_6$]$^{2+}$ complex ions counter-balanced by one-dimensional [Li$_2$(BH$_4$)$_4$]$_n$ polymers.

Hexaammine dilithium aluminum borohydride. Li$_2$Al(BH$_4$)$_3$·6NH$_3$, was the first ammine bimetallic borohydride reported and reveals a promising hydrogen storage capacity and thermal decomposition temperature. The structure of Li$_2$Al(BH$_4$)$_3$·6NH$_3$ is hexagonal (P6$_3$), where Al is octahedrally coordinated by NH$_3$ forming complex cations [Al(NH$_3$)$_6$]$^{3+}$, as in Al(BH$_4$)$_3$·6NH$_3$. Li is tetrahedrally coordinated by BH$_4^-$, and the Li[BH$_4$]$_4$ tetrahedra are then vertex-linked through three bridging BH$_4^-$ units with the fourth BH$_4^-$ in the trans position, leading to the formation of a two-dimensional honeycomb-patterned sheet that spreads along the $ab$ plane.

Tetraammine lithium scandium borohydride. LiSc(BH$_4$)$_4$·4NH$_3$, crystallizes in an orthorhombic unit cell (Pc2$_1$), where Sc is octahedrally coordinated by three NH$_3$ ligands and three BH$_4^-$ groups.

Hexaammine dilithium manganese borohydride. Li$_2$Mn(BH$_4$)$_3$·6NH$_3$, and hexaammine dilithium iron borohydride, Li$_2$Fe(BH$_4$)$_3$·6NH$_3$, are isostuctural to Li$_2$Mg(BH$_4$)$_3$·6NH$_3$ and consist of [M(NH$_3$)$_6$]$^{2+}$ complexes and [Li$_2$(BH$_4$)$_4$]$_n$ polymers.

Diammine sodium zinc borohydride. NaZn(BH$_4$)$_2$·2NH$_3$, crystallizes in an orthorhombic unit cell ($P2_1$), and consists of large complex bimetallic cations [NaZn(BH$_4$)$_2$·(NH$_3$)$_2$] charge balanced by BH$_4^-$. Two solid solutions of ammine metal borohydrides have been reported, which are Mn$_{1-x}$Mg$_x$(BH$_4$)$_3$·6NH$_3$ where the metal cation site is statistically disordered, and Co(BH$_4$)$_2$·$x$Cl$_2$·6NH$_3$, where the anion site is partially occupied by Cl$^-$ and BH$_4^-$. Both Mn$_{1-x}$Mg$_x$(BH$_4$)$_3$·6NH$_3$ and Co(BH$_4$)$_2$·$x$Cl$_2$·6NH$_3$ have the cubic symmetry $Pm3m$. 

5.1.4 Structural trends for ammine metal borohydrides. Ammine metal borohydrides are represented by a range of
different structure types and an overview is provided in Table 12. The structures of magnesium, calcium, strontium, manganese and yttrium borohydrides consist of three-dimensional networks of \([\text{MBH}_4]_n\) octahedra or \([\text{MBH}_4]_n\) tetrahedra, where each BH\(_4^-\) group bridge between two metal atoms with edge \((\eta^2)\) coordination.\(^{129,137,142,145,197}\) Introduction of NH\(_3\) molecules interrupts these frameworks. For the series of ammine yttrium borohydrides, the structures vary from two-dimensional layers \((n = 1)\), one-dimensional chains \((n = 2)\), molecular compounds \((n = 4)\) and 5) to those containing large complex cations \((n = 6\) and 7), see Fig. 14. Similar structural variations appear for the other series of compounds. In general, molecular structures appear when the total number of ligands \((\text{NH}_3 + \text{BH}_4^-)\) match the preferred coordination number of the cations, e.g. \([\text{Mn(BH}_4]_2(\text{NH}_3)_3\)] and \([\text{Sr(BH}_4]_3(\text{NH}_3)_3\]). For compounds with higher numbers of coordinated NH\(_3\) molecules, BH\(_4^-\) becomes a counter ion, e.g. \([\text{Ca(NH}_3]_6[\text{BH}_4]_2\) and \([\text{Y(NH}_3]_5[\text{BH}_4]_3\) \((n = 6\) and 7), whereas one- or two-dimensional structures are formed for compounds with lower numbers of coordinated NH\(_3\) molecules.

The NH\(_3\) coordinated metal cations may be described as complex cations, and the complete structure may be illustrated as a packing of the complex cations (relatively close to being spherical) and borohydride anions. The dihydrogen contacts between them lower the symmetry compared to the simple packing of spheres.

Metal–nitrogen bond distances for selected ammine metal borohydrides plotted as a function of the ionic radius are shown in Fig. 15. As expected, the M–N bond distances increase approximately linearly with increasing ionic radius, and the M–N bond distances do not vary significantly for varying numbers of NH\(_3\) ligands, e.g., the Sr–N bond lengths only varies from 2.69–2.70 Å for \([\text{Sr(BH}_4]_2(\text{NH}_3)_5\) \((n = 1, 2\) and 4). However, the Zr–N interactions are outliers for this trend with bond

### Table 12  Structural trends of ammine mono-metallic and bimetallic borohydrides

<table>
<thead>
<tr>
<th>M</th>
<th>Composition</th>
<th>Space group</th>
<th>Coordination environment of the metal</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>(\text{MBH}_4\cdot\text{NH}_3)</td>
<td>(\text{Pnma})</td>
<td>(\text{Li}^+): coordinated by one \text{NH}_3 and three \text{BH}_4^-)</td>
<td>271</td>
</tr>
<tr>
<td>Y</td>
<td>(\text{MBH}_4\cdot2\text{NH}_3)</td>
<td>(\text{Pbca})</td>
<td>(\text{Y}^{3+}): coordinated by two \text{NH}_3 and four \text{BH}_4^-)</td>
<td>53 and 291</td>
</tr>
<tr>
<td>Ca</td>
<td>(\text{MBH}_4\cdot\text{NH}_3)</td>
<td>(\text{Pnca})</td>
<td>(\text{Ca}^{2+}): coordinated by one \text{NH}_3 and five \text{BH}_4^-)</td>
<td>274</td>
</tr>
<tr>
<td>Ca</td>
<td>(\text{MBH}_4\cdot2\text{NH}_3)</td>
<td>(\text{Pmc}2_1)</td>
<td>(\text{Ca}^{2+}): coordinated by two \text{NH}_3 and four \text{BH}_4^-)</td>
<td>275</td>
</tr>
<tr>
<td>Sr</td>
<td>(\text{MBH}_4\cdot\text{NH}_3)</td>
<td>(\text{Pnma})</td>
<td>(\text{Sr}^{2+}): coordinated by one \text{NH}_3 and five \text{BH}_4^-)</td>
<td>277</td>
</tr>
<tr>
<td>Sr</td>
<td>(\text{MBH}_4\cdot2\text{NH}_3)</td>
<td>(\text{Pmc}2_1)</td>
<td>(\text{Sr}^{2+}): coordinated by two \text{NH}_3 and four \text{BH}_4^-)</td>
<td>277</td>
</tr>
<tr>
<td>Y</td>
<td>(\text{MBH}_4\cdot\text{NH}_3)</td>
<td>(\text{Cmc}2_1)</td>
<td>(\text{Y}^{3+}): coordinated by one \text{NH}_3 and five \text{BH}_4^-)</td>
<td>53</td>
</tr>
<tr>
<td>Mg, Mn</td>
<td>(\text{MBH}_4\cdot2\text{NH}_3)</td>
<td>(\text{Pcab})</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>54 and 272</td>
</tr>
<tr>
<td>Mg, Mn</td>
<td>(\text{MBH}_4\cdot3\text{NH}_3)</td>
<td>(\text{Pnma})</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>54</td>
</tr>
<tr>
<td>Ca, Sr</td>
<td>(\text{MBH}_4\cdot4\text{NH}_3)</td>
<td>(\text{Pn}2_1/c)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>277</td>
</tr>
<tr>
<td>Al</td>
<td>(\text{MBH}_4\cdot\text{NH}_3)</td>
<td>(\text{P}2_1/n)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>290</td>
</tr>
<tr>
<td>Y, Gd, Dy, Ce</td>
<td>(\text{MBH}_4\cdot4\text{NH}_3)</td>
<td>(\text{Pn}2_1)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>53 and 285</td>
</tr>
<tr>
<td>Y, Gd, Dy, Ce</td>
<td>(\text{MBH}_4\cdot5\text{NH}_3)</td>
<td>(\text{Pn}2_1)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>53 and 285</td>
</tr>
<tr>
<td>V</td>
<td>(\text{MBH}_4\cdot3\text{NH}_3)</td>
<td>(\text{P}2_3)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>282</td>
</tr>
<tr>
<td>Zn</td>
<td>(\text{MBH}_4\cdot2\text{NH}_3)</td>
<td>(\text{P}2_1)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>119</td>
</tr>
<tr>
<td>Ce, La</td>
<td>(\text{MBH}_4\cdot4\text{NH}_3)</td>
<td>(\text{I}2)</td>
<td>([\text{MBH}_4]_2(\text{NH}_3)_3]</td>
<td>285</td>
</tr>
</tbody>
</table>
lengths ranging 2.15–2.67 Å observed in the [Zr(NH₃)₆][BH₄]₂⁺ side-bicapped trigonal prism for [Zr(NH₃)₆][BH₄]₂.⁶²⁴

On the other hand, the coordination of BH₄⁻ tetrahedra to a metal is more flexible, illustrated by the range of M–B distances and varying hapticities from η¹ to η³ (Fig. 16), i.e. BH₄⁻ can be either a terminal or bridging ligand or act as a counter-ion. As expected, when BH₄⁻ coordinates to a metal in a partly covalent manner, i.e. η¹ to η³ then bond distances increase for increasing ionic radii of the metal, which is also observed for metal borohydrides.⁶²⁹ M–B distances substantially increase for decreasing hapticities in the yttrium based series Y(BH₄)₃.nNH₃ where Y–B is in the range of 4–5 Å when BH₄⁻ has dominantly ionic interactions with ammine yttrium complexes (η⁰) for n = 6, 7 (see Table 13). In ammine bimetallic borohydrides, NH₃ coordinates to the metal with the highest charge density, whereas BH₄⁻ may coordinate to both metals.

The unit cell volumes per formula unit (V/Z) at RT as a function of the number of NH₃ molecules, n, in the formula unit for M[BH₄]₃.nNH₃ (M = Ca, Sr, Mn and Y, Fig. 17) reveals an approximately linear relationship for each series. For the manganese-based series, Mn[BH₄]₃.nNH₃, the slope of the straight line is 34.0 Å³ per molecule (R² = 0.9998) corresponding well to the size of one ammonia molecule, which in solid NH₃ at −80 °C is V[NH₃] = 33.9 Å³.²₉³ In order to include Li₂Mn[BH₄]₆ in the plot, the volume of two LiBH₄ ([LiBH₄] = 54.2 Å³)²⁴ has been subtracted from V[Li₂Mn[BH₄]₆.nNH₃], which has a slightly lower V/Z than Mn[BH₄]₃.nNH₃. Similarly, the DFT optimized structures of Y[BH₄]₃.nNH₃ increase linearly as a function of n (37.3 Å³, R² = 0.9916), whereas the experimental values deviate slightly from the linear trend.

All ammine metal borohydride structures contain dihydrogen H₂⁺ contacts between partly positively charged hydrogen, H⁺ bonded to N and partly negatively charged hydrogen, H⁻ bonded to B. The shortest distance, 1.850 Å, between [Y(NH₃)₇]³⁺ and BH₄⁻ is determined by X-ray diffraction. However, as discussed in Section 5.1.5, the strength of the dihydrogen bonds do not play a significant role for the composition of the released gases on thermal decomposition.

Structural analogies between ammine metal borohydrides and chlorides or bromides exist, considering only heavier atoms, i.e. neglecting hydrogen atoms. For example, M[BH₄]₃.nNH₃ (M = Mg and Ca) and MgX₂.nNH₃ (X = Cl and Br) are isostructural, and Sr[BH₄]₂.nNH₃ and MCl₂.nNH₃ (M = Ca and Sr) are structurally similar. The borohydride complex, BH₄⁻, is a non-spherical anion in contrast to the halide anions; therefore crystal structures of ammine metal borohydrides often have lower symmetry than their halide analogues, as usually observed when comparing metal borohydrides and metal halides. A high degree of structural similarity is observed between compounds with high numbers of coordinated ammonia (n), where both the BH₄⁻ anion and the halides, X⁻, act as counter ions with a predominantly ionic bonding, η⁰.

5.1.5 Thermal properties of ammine metal borohydrides

The research of ammine metal borohydrides as potential hydrogen storage materials was initiated by Soloveichik et al. in 2008, studying Mg[BH₄]₃.nNH₃, which mainly releases H₂ upon decomposition, whereas Mg[BH₄]₃.nNH₃ mainly releases NH₃.²⁷² Since then, ammine metal borohydrides have attracted attention as promising hydrogen storage materials, e.g., the compounds Al[BH₄]₃.nNH₃, Li₃Al[BH₄]₆.nNH₃ and Zn[BH₄]₂.nNH₃ release 9–12 wt% H₂ in the temperature range 115–170 °C with traces of NH₃.²₇⁹,²₈₃,²₈₈ In comparison, the decomposition of metal borohydrides, M[BH₄]₃.mH₂0 below 200 °C is always accompanied by the release of diborane, B₂H₆.

Interestingly, ammine metal borohydrides with low electronegativities (ξp < 1.6) often display reduced temperatures for gas release when compared to the pure metal borohydride. On the other hand, ammine metal borohydrides with high electronegativities (ξp > 1.6) are often more thermally stable than...
Table 13 Overview of the coordination of Y, CN(Y), and selected bond lengths for Y(BH₄)₃·nNH₃. The distances and hapticities (η*) are obtained from DFT optimized crystal structures with experimental unit cell parameters.

<table>
<thead>
<tr>
<th>n</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN(Y)</td>
<td>6</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Y–N (Å)</td>
<td>—</td>
<td>2.48</td>
<td>2.50</td>
<td>2.77</td>
<td>2.80</td>
<td>2.80</td>
</tr>
<tr>
<td>Y–B₁ (Å)</td>
<td>2.74 (η²)</td>
<td>2.50 (η²)</td>
<td>2.77 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
</tr>
<tr>
<td>Y–B₂ (Å)</td>
<td>2.75 (η²)</td>
<td>2.77 (η²)</td>
<td>2.53 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
</tr>
<tr>
<td>Y–B₃ (Å)</td>
<td>2.80 (η²)</td>
<td>2.79 (η²)</td>
<td>2.79 (η²)</td>
<td>2.83 (η²)</td>
<td>2.83 (η²)</td>
<td>2.83 (η²)</td>
</tr>
<tr>
<td>Y–B₄ (Å)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
<td>2.80 (η²)</td>
</tr>
</tbody>
</table>

Structure type: 3D-framework 2D-layers 1D-chains Molecular Molecular Ionic complexes Ionic complexes

a Number of BH₄⁻ and NH₃ ligands coordinated to Y. b Number of H (from BH₄⁻) and N (from NH₃) atoms coordinated to Y.

Fig. 17 Unit cell volumes (V) at RT divided by the number of formula units (Z) plotted as a function of the number of ammonia molecules, n, in the formula unit, M(BH₄)ₙ·nNH₃. The dashed and solid line correspond to linear fit to the DFT optimized values for Y(BH₄)₃·nNH₃ and the experimental values for Mn(BH₄)₂·nNH₃, respectively. The unit cell volume of Li₂Mn(BH₄)₄·6NH₃ subtracted the volume of two formula units of LiBH₄ is also included.

Their respective metal borohydride is significantly more stable than the corresponding metal borohydride (Fig. 18). Ca(BH₄)₂·nNH₃ and Sr(BH₄)₂·nNH₃ clearly become more stable for lower n/m ratios, however, they still decompose at significantly lower temperatures than M(BH₄)₂, M = Ca, Sr, and they release NH₃ only. At higher temperatures the remaining M(BH₄)₂, M = Ca, Sr, decompose and release hydrogen. Similarly, Y(BH₄)₃·nNH₃, n = 7, 6 and 5, release NH₃ at significantly lower temperatures than the decomposition temperature of Y(BH₄)₃, T_{dec}(Y(BH₄)₃) ~ 200 °C, whereas the compounds Y(BH₄)₃·nNH₃, n = 4, 2 and 1 release decreasing amounts of NH₃ in the gas mixture consisting of NH₃ and H₂ in the temperature range, T ~ 160–200 °C, approaching T_{dec}(Y(BH₄)₃) ~ 200 °C. Ammine metal borohydrides based on less stable metal borohydrides, e.g. M = Al, Zn, Zr and Y, do not release pure NH₃ gas, possible because of the lower decomposition temperature of the respective metal borohydrides.

As an example, Al(BH₄)₃·6NH₃ releases H₂ and small amounts of NH₃ at ~165 °C, where Al(BH₄)₃ is unstable, T_{dec}(Al(BH₄)₃) ~ 25 °C.
(Fig. 18). This hydrogen release can be decreased even lower (~120 °C) by encapsulating Al(BH₄)₃·6NH₃ within a nanoporous polymer. ²⁹⁴

(ii) The partial pressure of ammonia. In a closed system, the partial pressure of ammonia increases upon ammonia release, p(NH₃) > 0, during thermolysis of LiBH₄·NH₃, Ca(BH₄)₂·nNH₃ and Sr(BH₄)₂·nNH₃. At higher temperatures, the released ammonia gas reacts with the metal borohydride, releasing hydrogen exothermically in a solid gas reaction.²⁷⁵,²⁹⁵

5.1.6 Mechanism for gas release of ammine metal borohydrides. Hydrogen release from ammine metal borohydrides appears always to be exothermic, which indicates that a chemical reaction is responsible for the gas release. This may suggest that hydrogen is released in an elimination reaction between H⁺ and H₂.⁷⁵.⁷⁶ Furthermore, we notice that the thermal stability for ammine metal borohydrides and ammine metal chlorides are similar when comparing the peak temperature of NH₃ release, T_{dec}(NH₃). As examples, Y(BH₄)₂·7NH₃ (T_{dec}(NH₃) ~ 80 °C) is slightly less stable than YCl₃·7NH₃ (T_{dec}(NH₃) ~ 100 °C),²⁹¹ and Mg(BH₄)₂·6NH₃ (T_{dec}(NH₃) ~ 150 °C) and MgCl₂·6NH₃ (T_{dec}(NH₃) ~ 150 °C) have similar thermal stability,²⁹⁶ whereas Mn(BH₄)₂·6NH₃ (T_{dec}(NH₃) ~ 130 °C) is slightly more stable than MnCl₂·6NH₃ (T_{dec}(NH₃) ~ 105 °C).²⁹⁷ This observation may indicate that the release of ammonia is mainly determined by the strength of the metal–ammonia (M–N) bond in the complex. Thus, the above observations support that there is no direct relation between dihydrogen bond strength, N–H···H–B, in the solid state and the temperature of the released gas.

Moreover, hydrogen release from ammine metal borohydrides may in fact be due to a chemical reaction between the proposed intermediate, diboran, B₂H₆, which may take part in the decomposition of metal borohydrides and ammonia released simultaneously or at slightly lower temperatures. We note that diboran release is always suppressed for ammine metal borohydrides as compared to the respective metal borohydrides.

5.2 Hydrazine metal borohydride complexes

Six hydrazine metal borohydride complexes, M(BH₄)₃·nNH₂NH₂, are known (see Table 14) based on M = Li, Na and Mg, where LiBH₄·NH₂NH₂ and LiBH₄·2NH₂NH₂ were first reported in 2012.¹¹⁸ In 2013 four more hydrazine metal borohydride complexes were reported, i.e. NaBH₄·NH₂NH₂, Mg(BH₄)₂·3NH₂NH₂, LiBH₄·2NH₂NH₂, LiBH₄·1/3NH₂NH₂.¹¹⁷ In contrast to ammonia, NH₃, hydrazine, NH₂NH₂, is a more flexible ligand that can bridge between two metals or be a terminal ligand. The coordination to the metal is always via a lone pair donated by a nitrogen atom.

| Table 14 Metal borohydride hydrazine complexes with known crystal structures |
|----------------|----------------|----------------|
| M in M(BH₄)₃ | Composition of complex | Symmetry | Ref. |
| Li | LiBH₄·1/3NH₂NH₂ | Monoclinic, P̅2₁ | 117 |
| Li | LiBH₄·2NH₂NH₂ | Orthorhombic, P̅2₁2₁2₁ | 117 |
| Li | LiBH₄·NH₂NH₂ | Monoclinic, Cc | 118 |
| Li | LiBH₄·2NH₂ | Orthorhombic, P̅ca₂₁ | 118 |
| Na | NaBH₄·NH₂NH₂ | Monoclinic, P̅2₁/c | 117 |
| Mg | Mg(BH₄)₂·3NH₂NH₂ | Trigonal, P̅3₁ | 117 |

LiBH₄·NH₂NH₂ crystallizes in a monoclinic unit cell (Cc) with lithium tetrahedrally coordinated by two BH₄⁻ and two NH₂NH₂ groups. LiBH₄·2NH₂NH₂ crystallizes in an orthorhombic unit cell (P̅ca₂₁), where lithium coordinates four NH₂NH₂. NH₂NH₂ bridges between two lithium cations forming chain-like cationic complexes [Li(NH₂NH₂)₄]⁺, which are separated by BH₄⁻ (see Fig. 19).

LiBH₄·1/2NH₂NH₂ crystallizes in an orthorhombic unit cell (P̅2₁2₁2₁) and consists of two-dimensional layers. Li⁺ is coordinated by three BH₄⁻ ligands and one NH₂NH₂ that is bridged to the neighbouring Li⁺. There are two types of BH₄⁻ ligands that both coordinate to Li through the edge (n²). One BH₄⁻ is located in the same plane as the Li atoms and coordinates to four Li atoms, while one BH₄⁻ is positioned slightly above (or below) the plane and coordinates to two Li atoms.

LiBH₄·1/3NH₂NH₂ crystallizes in a monoclinic unit cell (P̅2₁/c). Three independent Li atoms are tetrahedrally coordinated, one by four BH₄⁻ and two by three BH₄⁻ and one hydrazine molecule. While borohydrides are shared by three or four Li atoms, the hydrazine molecule only bridges two Li atoms. Hence, the resulting 3D framework is rather complex.

NaBH₄·NH₂NH₂ crystallizes in a monoclinic unit cell (P̅2₁/c). Each Na⁺ coordinates to two bridging NH₂NH₂ leading to the formation of [Na(NH₂NH₂)₂]⁺ chains, which are separated by BH₄⁻ with Na–B distances in the range from 2.97 to 3.05 Å (see Fig. 19).

Mg(BH₄)₂·3NH₂NH₂ crystallizes in a trigonal unit cell (P̅3₁c). Each Mg²⁺ is octahedrally coordinated by six NH₂NH₂ forming [Mg(NH₂NH₂)₆]⁶⁺ complex cations that are charge balanced by BH₄⁻.

Generally, the hydrazine metal borohydride complexes have high hydrogen content and also favourable decomposition temperatures, e.g. approx. 13.0 wt% H₂ is released from LiBH₄·NH₂NH₂ at 140 °C in the presence of Fe–B catalysts.¹¹⁸ However, this leads to the formation of very stable Li₃BN₂ and BN according to reaction scheme (5.1).

3(LiBH₄·NH₂NH₂)(s) → Li₃BN₂(s) + 2BN(s) + N₂(g) + 12H₂(g)  
(5.1)

5.3 Ammonia borane metal borohydride complexes

The first ammonia borane (AB) metal borohydride complexes, LiBH₄·(NH₃BH₃)₃, Ca(BH₄)₂·(NH₃BH₃)₂ and Ba(BH₄)₂·(NH₃BH₃) were reported in 2010,¹¹⁴ whereas other ammonia borane metal borohydride complexes are now reported (Table 15). They are all prepared by mechanochemistry, except for Al(BH₄)₃·(NH₃BH₃) (where crystals are formed by reacting liquid Al(BH₄)₃ and solid NH₃BH₃) and Ca(BH₄)₂·(NH₃BH₃) (that is formed during decomposition of NH₃Ca(BH₄)₂). Complex formation is not reported for the more stable ionic alkali metal borohydrides and ammonia borane, but physical mixtures of the reactants are obtained by ball milling with M(BH₄)₃·nNH₂BH₃ (M = Na, K, Rb and Cs).²⁹⁸ NH₃BH₃ may coordinate to the metal via a lone pair donated by nitrogen, i.e. act as a terminal ligand; or it may also coordinate to the metal by H⁺– covalently bonded to B, i.e. bridge between two metal atoms; or it may even stay isolated from the metal and only coordinate via dihydrogen bonds. Ammonia borane complexes...
can also be formed from ammine metal borohydrides, resulting in framework structures, i.e. \([\text{Al(NH}_3\text{)}_6][\text{Li}_2(\text{BH}_4)_3]\cdot3\text{NH}_3\text{BH}_3\) and \([\text{Mg(NH}_3\text{)}_2(\text{BH}_4)_2]\cdot\text{NH}_3\text{BH}_3\) where AB is not coordinated to metal atoms but linked with other hydrogen-containing molecules and ions via dihydrogen bonds. The hydrogen evolution from these composites is significantly improved compared to the parent compounds containing no ammonia molecules.

The crystal structures of \(\text{Mg(BH}_4)_2(\text{NH}_3\text{BH}_3)_2\) and \(\text{Al( BH}_4)_3\)\({^{*-}}\) \((\text{NH}_3\text{BH}_3)_2\) both consist of neutral molecular units of \([\text{Mg( BH}_4)_2(\text{NH}_3\text{BH}_3)_2]\) or \([\text{Al( BH}_4)_3(\text{NH}_3\text{BH}_3)_2]\) coordinated by intermolecular dihydrogen bonds in the solid state (Fig. 20a). The four other known ammonia borane metal borohydride complexes show strikingly different connectivity, where BH\(_4\)^- complexes and NH\(_3\)BH\(_3\) molecules act as bridging ligands. The borohydride complexes bridge three lithium and two NH\(_3\)BH\(_3\) in the structure.
of LiBH₄(NH₃BH₃)₀.₅, creating a three-dimensional polymeric framework.¹¹⁴ The LiBH₄(NH₃BH₃) structure is more complex,³⁰¹ containing four independent borohydride anions and four NH₃BH₃ molecules (Fig. 20b). While the borohydride anions coordinate two to four lithium atoms, the NH₃BH₃ molecules act as a terminal ligand or even stay isolated from the metal atoms. In Ca(BH₄)₂(NH₃BH₃)₂,¹¹⁴ the borohydride groups bridge to two metal atoms, forming a two-dimensional square planar net, while the two NH₃BH₃ molecules act as terminal ligands, completing the octahedral coordination of Ca. Another ammonia borane complex, Ca[BH₄]₂(NH₃BH₃), was recently reported, containing just one NH₃BH₃ molecule per unit cell.³⁰² While structurally related to Ca[BH₄]₂(NH₃BH₃), the square planar layers in this net are buckled, and interconnected by a fifth borohydride ligand, which bridges between two Ca atoms. The octahedral coordination polyhedron is again completed by one NH₃BH₃ molecule, which is located in channels formed by the buckled Ca–BH₄ structure.

5.3.1 Thermal properties of metal borohydride ammonia borane complexes. NH₃BH₃ melts at ~110 °C and releases one equivalent of hydrogen in each of the three decomposition steps, forming polyaminoborane, [NH₃BH₃]ₙ (90–120 °C), polyiminoborane, [NHBBH]ₙ (120–200 °C) and finally boron nitride, BN (>500 °C).³⁰³–³⁰⁶ In addition, the hydrogen release is accompanied by volatile and toxic by-products, such as B₂H₆ and B₂N₂H₆. Generally, the systems M[BH₄]₃–NH₃BH₃ (M = Li, Na, K, Mg and Ca) decompose in a similar manner to NH₃BH₃ below 200 °C and do not suppress the release of the toxic gases, as observed for metal amidoamidoboranes, [M(NH₃BH₃)]₄⁻.³⁰⁴,³⁰⁶,³⁰⁷ Thus, it may be concluded that NH₃BH₃ is insufficiently modified in MBH₃–NH₃BH₃ (M = Li, Na, K, Mg and Ca), because NH₃BH₃ maintains its molecular form.³⁰⁴,³⁰⁶ This is in contrast to metal amidoamidoboranes where one hydrogen atom bonded to N is substituted by a metal atom.³⁰⁷ Al[BH₄]₃[NH₃BH₃] on the other hand, endothermically releases two moles of H₂ from NH₃BH₃ per Al at 70 °C.¹¹⁶ Thereby Al[BH₄]₃[NH₃BH₃] differs from pristine ammonia borane, metal amidoamidoboranes and other metal borohydride ammonia borane complexes, and may open up possibilities for reversible hydrogen storage. It was reported that the ability of the strong Lewis acid Al³⁺ to coordinate both the initial hydrogenated species as well as their dehydrogenation products, makes it a good template for chemical transformations involving light chemical and complex hydrides.³⁰⁹ Therefore the Al[BH₄]₃[NH₃BH₃] system can be used as a model for potentially reversible dehydrogenation of ammonia borane. Both complexes Mg[BH₄]₃[NH₃BH₃] and Al[BH₄]₃[NH₃BH₃] melt before decomposition, because of the mononuclear complexes present in the crystal structures and in the melt.¹¹⁵,¹¹⁶

5.4 Metal borohydride crystallizing with organic solvents
Solvent based synthesis methods have become more common for the synthesis of metal borohydrides during the past few years as discussed in Section 2 of this review. The solvent may coordinate strongly to the metal borohydride and form a solvate that needs further treatment in order to obtain a solvent-free product. In most cases, the solvent contains a donor atom, O, N or S that coordinates to the metal cation of the borohydride. Selected organic solvents and corresponding solvates are presented in Table 16, including bond lengths between the donor atom and the metal. M–S bonds are generally longer than M–O bonds, suggesting that sulphur based solvents are more easily removed than oxygen based solvents.

Two different structures of metal borohydrides with dimethyl sulfide, (CH₃)₂S, are known. The first is the monoclinic structure of M[BH₄]₃·2(C₂H₅)₂O (M = Mg, Mn), which is a 3D framework containing two metal atoms: one atom is tetrahedrally coordinated to four BH₄⁻ groups, and the other to four BH₄⁻ groups and one S(CH₃)₂ ligand to form a trigonal bipyramid.³⁵⁸ Sulfur coordinates relatively weakly to the metal with Mg–S and Mn–S bond lengths being 2.669 and 2.705 Å, respectively. Hence, S(CH₃)₂ is easily removed during drying without decomposing M[BH₄]₃. Similarly, halide-free and solvent-free yttrium and gadolinium borohydride may be synthesized using dimethyl sulfide with the M[BH₄]₃·S(CH₃)₂ (M = Y or Gd) solvates as intermediates, which have monoclinic structures (P2₁/c).⁶⁶

In U[BH₄]₃·2(C₂H₅)₂O, U is coordinated by four BH₄⁻ ligands coordinating by edge sharing (π⁻¹), one BH₄⁻ ligand coordinating by face sharing (π⁻¹⁻) and one O from ether, giving 14 nearest neighbours. Solvent based methods often provide the most thermodynamically stable compound, typically a monometallic borohydride or a solvate, as discussed in Section 2. Thus, very few bimetallic solvates have been discovered, e.g. LiMn₂[BH₄]₅·2(C₂H₅)₂O and NaMn₂[BH₄]₅·2(C₂H₅)₂O.⁶⁴ Here, Mn is coordinated by four bridging BH₄⁻ groups, while Li/Na is coordinated tetrahedrally by two BH₄⁻ groups and two (C₂H₅)₂O ligands Li/Na–O bond lengths ranging from 2.00 to 2.38 Å.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Selected solvates</th>
<th>Symmetry</th>
<th>M-donor atom (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfide/DMS, (CH₃)₂S</td>
<td>M[BH₄]₃·1/2(C₂H₅)₂O, M = Mg, Mn</td>
<td>Monoclinic, Cc</td>
<td>2.67–2.70</td>
<td>3 and 58</td>
</tr>
<tr>
<td>Diethyl ether/Et₂O, (C₂H₅)₂O</td>
<td>M[BH₄]₃·(C₂H₅)₂S, M = Y or Gd</td>
<td>Monoclinic, P2₁/c</td>
<td>2.89</td>
<td>66</td>
</tr>
<tr>
<td>Tetrahydrofuran/THF, C₂H₄O</td>
<td>M[BH₄]₃·2THF, M = Sr, Eu, Sm</td>
<td>Monoclinic, P2₁/c</td>
<td>2.485</td>
<td>310</td>
</tr>
<tr>
<td>Water, H₂O</td>
<td>NaBH₄·2H₂O</td>
<td>Monoclinic, C2</td>
<td>2.00</td>
<td>61</td>
</tr>
<tr>
<td>Ethylenediamine/en, C₂H₄(NH₂)₂</td>
<td>Al(en)₃[BH₄]₃, en</td>
<td>Monoclinic, C2</td>
<td>2.38</td>
<td>61</td>
</tr>
</tbody>
</table>

Table 16 Classic organic solvents and selected corresponding solvates
Similar to the metal borohydrides, THF (C₄H₈O) solvates of M(BH₄)₂·2THF are isostructural for M = Sr, Eu, Sm.¹⁰¹–¹¹¹ They crystallize in P2₁/c and form one-dimensional chains in which each metal atom is surrounded by four borohydrides and two THF molecules.

Water is a well-known inorganic solvent, but tends to react with metal borohydrides in particular for pH < 7. NaBH₄·2H₂O is the first reported metal borohydride hydrate and crystallizes in an orthorhombic unit cell (Pbcn).¹⁰⁶,¹¹¹ Na is octahedrally coordinated by four BH₄⁻ and two H₂O groups that all bridge between two Na atoms. There are three intermolecular O–H⁻···H–B dihydrogen bonds in the compound in the range 1.77–1.95 Å. Interestingly, NaBH₄·2H₂O decomposes upon heating at ~40 °C to NaBH₄ and H₂O, which at T > 40 °C slowly react to release hydrogen. Thus, the hydrate NaBH₄·2H₂O does not directly release hydrogen but decomposes into anhydrous NaBH₄ and water. This may be because NaBH₄ is stable in basic aqueous solutions. Lithium borohydride also absorbs water, forming LiBH₄·H₂O.²¹²,³¹⁶ Upon thermal treatment, LiBH₄·H₂O releases hydrogen at ~65 °C.²¹⁶ Calcium borohydride hydrate, Ca(BH₄)₂·2H₂O, has also been reported recently.¹¹³

6. Thermal properties of metal borohydrides

Metal borohydrides often have a high gravimetric and volumetric hydrogen density and have been of significant interest for many possible applications including solid-state hydrogen storage. However, the reaction mechanisms are often complex and not well understood, showing high kinetic barriers such that decomposition and hydrogen absorption often only occur at elevated temperatures, which hampers technical applications of these materials. Release and uptake of hydrogen can be denoted a chemical reaction involving two-, three- or multiple-phases such as solid–gas, solid–liquid–gas or solid–solid–gas systems. In many cases more than one possible reaction mechanism is involved, which may also change as a function of the physical conditions, e.g. partial pressures, temperature and/or stoichiometry of involved starting materials. This section focuses on general aspects regarding reaction mechanisms for hydrogen release and uptake during thermolysis, i.e. heating, also denoted pyrolysis, along with different approaches for tailoring and optimization of thermodynamic and kinetic properties. This section reveals that chemical reactions between different hydrides, i.e. reactive hydride composites, and additives can provide new perspectives for creating novel hydrogen carrier systems by tailoring physical, chemical, kinetic and thermodynamic properties. Additives have also been investigated along with their possible catalytic properties for hydrogen release and uptake reactions, as well as their function as grain refiners, and as favourable nucleation sites for the formation and decomposition of hydride compounds. Nanoconfinement is another approach that has been tested for its potential to improve both the kinetic and thermodynamic properties of metal borohydrides.

6.1 Thermodynamics of hydrogen release and uptake

There is a close correlation between the temperature of hydrogen release and uptake, at a given equilibrium pressure, and the enthalpy and entropy change for metal borohydrides, similar to metal hydrides. Consider a general reaction where a metal, M, reacts with hydrogen to form a metal hydride according to reaction scheme:

\[
M(s) + H_2(g) \leftrightarrow MH_x(s) \tag{6.1}
\]

The equilibrium constant for this reaction is,

\[
K^{-1} = \frac{p(H_2)}{p^\Theta} \quad p^\Theta \equiv 1 \text{ bar, standard pressure} \tag{6.2}
\]

The Gibbs free energy for the reaction is

\[
\Delta G_r = \Delta H_r - T\Delta S_r = -RT \ln K \tag{6.3}
\]

where \(\Delta H_r\) is the change in enthalpy, \(\Delta S_r\) is the change in entropy, \(T\) is the temperature (K), and \(R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}\). Combining (6.2) and (6.3) gives the van't Hoff equation

\[
\ln(p(H_2)/p^\Theta) = (RT)^{-1}\Delta H_r - (R)^{-1}\Delta S_r \tag{6.4}
\]

A material’s hydrogen release temperature is usually given for an equilibrium pressure of \(p_{eq}(H_2) = 1.0 \text{ bar}\) and is often denoted \(T(1 \text{ bar})\). For this special case, the van’t Hoff equation is reduced to:

\[
T(1 \text{ bar}) = \Delta H_r/\Delta S_r \tag{6.5}
\]

The major contribution to the reaction entropy change, \(\Delta S_r\), is from the change in state of hydrogen (from solid to gas phase), \(\Delta S^\Theta(H_2) = 130.7 \text{ J (K mol)}^{-1}\). Therefore, many metal hydrogen systems, but not all, have \(\Delta S_r \approx 130 \text{ J (K mol)}^{-1}\). As such, in order to reach an equilibrium pressure of \(p(H_2) = 1 \text{ bar}\) in the temperature range 50 to 200 °C the decomposition enthalpies should be in the range 40–60 kJ mol⁻¹ H₂. There is much focus in materials research aimed at identifying hydrides fulfilling this enthalpy range, which corresponds to the operational temperatures for PEM fuel cells.

For the metal borohydrides, however, entropy changes that are significantly different from 130 J (K mol⁻¹ H₂) may be observed due to more complex reaction mechanisms and, in some cases, dynamics in the solid state or liquid–solid transi-

tions. Dynamics such as ‘motion’ of BH₄⁻ complex anions may contribute to the entropy of the solid state and a lower than expected entropy of melting.³¹⁸ In addition, significantly higher temperatures for hydrogen release and uptake are often observed in order to obtain reasonable reaction kinetics as compared to the ideal temperature dictated by thermodynamics, e.g. \(T(1 \text{ bar})\). This is due to kinetic restraints in the solid state, and therefore a thermodynamic driving force is needed, i.e. \(T_{dec} > T(1 \text{ bar})\). A drawback is that higher reaction temperatures often facilitate greater chemical complexity, e.g. side-reactions, and also dynamic effects, e.g. hydrogen release from high-temperature polymorphs such as h-LiBH₄ and, in some cases, hydrogen exchange from a molten phase.

The formation enthalpy, \(\Delta H_f\), of metallic hydrides is well defined and exothermic for the stable hydrides. The enthalpy
characterizes the strength of the metal hydrogen bond and is partly determined by the local electron density on the interstitial site where hydrogen is placed.\textsuperscript{319-321} The structure of the metallic hydride is often an expanded version of the parent metal structure ($\Delta V \sim 10-20\%$) and may be considered as being derived by hydrogen intercalation.\textsuperscript{322} In contrast, the structure of a metal borohydride is much different from the structure of the residue formed by dehydrogenation of the host material. Therefore, the total reaction enthalpy, $\Delta H$, for hydrogen exchange of metal borohydrides may be considered a sum of contributions from several partial reactions. Thus, $\Delta H$, for metal borohydrides may not directly correlate with the strength of a single covalent boron hydrogen bond. The decomposition enthalpy, $\Delta H_{\text{dec}}$, is endothermic and is challenging to measure accurately.\textsuperscript{323,324} The decomposition enthalpy may often depend on the method for the measurement and the physical conditions, which may lead to alternative reaction mechanisms or a change of state, such as fusion (\textit{i.e.} then also including $\Delta H_{\text{ fus}}$). This is further discussed in the following Section 6.2.

The mechanism for hydrogen transport in metallic hydrides, \textit{e.g.} the early transition metal hydrides, is dominated by diffusion of single hydrogen atoms (or partially positively or negatively charged ions) in the solid state.\textsuperscript{325} However, more complex transport phenomena may be involved in the hydrogen release and uptake reactions in the solid state of hydrides with ionic and covalent bonds, \textit{i.e.} complex metal hydrides. There are many indications in the literature that relatively stable molecule-like units may participate in hydrogen release and uptake reactions in the solid state of boron, aluminium and nitrogen based complex hydrides, possibly BH\textsubscript{4}, AlH\textsubscript{3}, or NH\textsubscript{3}, which is further discussed in Section 6.6. Thus, the reactions that take place during hydrogen release and uptake in metal borohydrides may be significantly more complex than suggested by eqn (6.1). The thermodynamics of hydrogen release and uptake may be investigated by the Sievert's method by measurement of pressure-temperature-composition (PCT) isotherms. Generally, the published literature suggests increasing difficulty in measuring PCT-isotherms with well-defined plateau pressures for aluminium $< \text{boron} < \text{nitrogen}$ based hydrides. This may be due to increasing complexity of the involved chemistry, an increasing number of alternative reaction mechanisms, and in some cases, several simultaneous reactions.

### 6.2 Thermolysis of monometallic borohydrides

Thermolysis denotes the decomposition of a substance upon heat treatment. Monometallic borohydrides may release hydrogen and, in some cases, also diborane during the formation of higher metal boranes, metal borides or even pure boron upon thermolysis, which has been the topic of much research during the past decade. The aim of this section is to provide an overview of some of the general trends that appear in the scientific literature for the thermodynamics of hydrogen release and uptake in selected, well studied, mono-metallic borohydrides. Data collected for the same material with different methods are compared in Table 17. Additives may significantly change the reaction mechanism of decomposition. The addition of small amounts of additives in the range of a few mol\% has been considered for possible catalytic effects and is discussed in Section 6.7, whereas larger amounts may react with the metal borohydrides and form reactive hydride composites, see Section 6.8. Physical conditions such as partial pressures and temperatures also influence the mechanism of decomposition \textit{i.e.} the decomposition pathway. The presence of impurities, even in minor quantities, can also influence bubbling and frothing during melting.\textsuperscript{45}

Lithium borohydride is the most well investigated metal borohydride regarding the mechanism for hydrogen release and uptake. It undergoes a polymorphic transition from $\omega$- to $h$-LiBH\textsubscript{4} at 110 °C and melts at 280 °C.\textsuperscript{45} The polymorphic transition and melting events can be associated with minor gas release that is often attributed to impurities, \textit{e.g.} water or oxides, reacting with lithium borohydride.\textsuperscript{22,23,45,316,339} Dynamic PCT measurements under constant hydrogen flow provide thermodynamic data via the van’t Hoff equation for the decomposition reaction, $\Delta H = 74 \text{ kJ mol}^{-1} \text{H}_2$ and $\Delta S = 115 \text{ J K}^{-1} \text{mol}^{-1} \text{H}_2$ (see Table 17).\textsuperscript{326,331}

Direct decomposition without the presence of intermediate compounds, at elevated temperatures, leads to the production of boron, lithium hydride and release of 13.1 wt% hydrogen, scheme (6.6). Thermodynamic results from calorimetry provide $\Delta H = 66.6-68.9 \text{ kJ mol}^{-1} \text{H}_2$ and $\Delta S = 97.3-100.2 \text{ J K}^{-1} \text{mol}^{-1} \text{H}_2$ (see Table 17) for this suggested reaction.

$$\text{LiBH}_4(s) \rightarrow \text{LiH(s)} + \text{B(s)} + 3/2\text{H}_2(g) \quad (6.6)$$

Partial dehydrogenation can also occur, forming lithium closo-borane, Li\textsubscript{1}B\textsubscript{12}H\textsubscript{12}, \textit{via} less endothermic reactions, scheme (6.7), with a calculated reaction enthalpy of 56 kJ mol\textsuperscript{-1} H\textsubscript{2}.\textsuperscript{330}

$$\text{LiBH}_4(s) \rightarrow 5/6\text{LiH(s)} + 1/12\text{Li}_2\text{B}_2\text{H}_6(s) + 13/12\text{H}_2(g) \quad (6.7)$$

Various quantities of hydrogen in the range from 9–14 wt% are reported to be released from LiBH\textsubscript{4} under different experimental conditions, \textit{e.g.} 9 wt% H$_2$ under evolved hydrogen pressure, and 13.8 wt% H is released in flowing He by heating to 600 °C.\textsuperscript{22,340} Lithium borohydride has also been decomposed at 600 °C for 5 hours under different partial pressures of hydrogen.\textsuperscript{341} Only one-third of LiBH\textsubscript{4} transforms to Li\textsubscript{2}B\textsubscript{4}H\textsubscript{12} at $P(\text{H}_2) = 50$ bar and no amorphous boron is observed. In the pressure range, 0.1–10 bar, LiBH\textsubscript{4} nearly completely decomposes to Li\textsubscript{2}B\textsubscript{12}H\textsubscript{12} and amorphous boron. Under these physical conditions (600 °C, 5 h), LiBH\textsubscript{4} appears to decompose more efficiently to amorphous boron at lower pressure.\textsuperscript{341} Thermolysis of LiBH\textsubscript{4} under vacuum at temperatures up to 600 °C is reported to produce LiH, amorphous B (or lithium boride) \textit{via} hydrogen-poor Li\textsubscript{2}B\textsubscript{4}H\textsubscript{12}.\textsuperscript{342}

The formation of LiBH\textsubscript{4} from the elements has also been attempted, which is equivalent to rehydrogenation or reversing reaction (6.6). Amorphous boron is known as a rather inert material with a complex structure of covalently bonded boron that forms a framework containing B\textsubscript{12} clusters. Lithium hydride is expected to form readily under hydrogen pressure, but further hydrogenation can be very slow until melting, $T_m(\text{LiH}) = 689$ °C, which facilitates close contact between the reactants.\textsuperscript{343} The kinetics of hydrogen uptake reactions can be
increased by thermal treatment of lithium–boron mixtures at 330 and 450 °C in argon, which facilitates the formation of more reactive lithium borides, LiB₄ or Li₄B₁₂, respectively. The hydrogen uptake reaction has also been investigated by powder neutron diffraction starting with lithium boride. The hydrogen/deuterium absorption starts at ~200 °C with the formation of LiD, and at 350 °C LiBD₄ also starts to form. However, under the given experimental conditions, T_max = 500 °C, p[H₂] = 180 bar for ~18 hours, a complete reaction was not achieved and LiD remains.

Sodium borohydride, NaBH₄, melts at 505 °C, followed by hydrogen release at 534 °C under p[H₂] = 1 bar. However, hydrogen release can be observed at T ~ 500 °C when measured in helium or argon, p(He, Ar) = 1 bar. Sodium borohydride decomposes to the elements (Na and B), see reaction scheme (6.8), due to the lower stability of NaH, compared to LiH that is formed in the decomposition of LiBH₄. Thermal analysis of NaBH₄, however, suggests that intermediate compounds may form during the decomposition.

\[
\text{NaBH}_4(s) \rightarrow \text{Na}(l) + \text{B}(s) + 2\text{H}_2(g) \tag{6.8}
\]

Dynamic PCT measurements, under constant hydrogen flow, provide thermodynamic data via the van’t Hoff equation, \(\Delta H = 108 \pm 3 \text{ kJ mol}^{-1} \text{H}_2\) and \(\Delta S = 133 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1} \text{H}_2\), which corresponds to a decomposition temperature of \(T_{\text{dec}}(1 \text{ bar}) = 539^\circ\text{C}\). These dynamic PCT measurements are conducted at a constant temperature of 600, 650 or 700 °C and the same starting pressure, \(p(\text{H}_2) = 180 \text{ bar}\), with a mass flow controller. The decomposition appears to occur in one step with only one plateau observed on the pressure composition isotherms. The entropic component that is measured with dynamic PCT’s \(\Delta S = 133 \text{ J K}^{-1} \text{ mol}^{-1} \text{H}_2\) is rather high, and much higher than the entropic change measured by calorimetry \(\Delta S = 93.6–98.6 \text{ J K}^{-1} \text{ mol}^{-1} \text{H}_2\) (see Table 17). It is experimentally important to note the vapour pressure of Na metal is very high (0.1 bar at 675 °C) and this can result in significant Na loss at high temperature, especially under gas flow.

Potassium borohydride melts at 625 °C, followed by hydrogen release near 680 °C with a possible reaction mechanism for decomposition similar to that of NaBH₄ scheme (6.8). However, increasing evaporation of potassium from the decomposed residue is expected due to the high vapour pressure of Na metal at 672 °C. The high thermal stability of NaBH₄ and KBH₄ may be the reason for minimal scientific interest and, as such, the decomposition mechanism remains not well investigated. Although, calorimetry indicates...
that the decomposition enthalpy of KBH$_4$ is high ($\Delta H = 112.6$–$113.9$ kJ mol$^{-1}$ H$_2$) [see Table 17], which is favorable for solar thermal applications given adequate kinetics.$^{349-351}$

Magnesium borohydride, Mg(BH$_4$)$_2$, has received significant interest as a possible hydrogen storage material with a high gravimetric hydrogen content of 14.9 wt% H$_2$. Mg(BH$_4$)$_2$ can undergo an array of polymorphic transitions during heating and melting depending on gas partial pressure. $^{187,188}$ At elevated hydrogen pressures, $p$(H$_2$) $\geq$ $\sim$ 1 bar, decomposition is suppressed and the compound melts. $^{185}$ The decomposition mechanism of magnesium borohydride is also quite complex and highly dependent on reaction conditions.$^{183,187,196,333,352-355}$ An in situ SR-PXD investigation (constant heating, $\Delta T$/\$\Delta t$ = 4 °C min$^{-1}$ in $p$(H$_2$) = 1 bar) of $\gamma$-Mg(BH$_4$)$_2$ reveals melting of the $\beta$-polymorph at $T \sim$ 270 °C and observation of a broad diffraction halo at $d \sim$ 5.1 Å. $^{187}$ Ex situ visual inspection of the melting process reveals a colour change from white to yellow to brown to grey. $^{187}$ Magnesium hydride crystallizes from the melt at 320 °C and disappears at 360 °C due to the formation of Mg observed in the temperature range 340–580 °C. Boron containing compounds are not observed until the formation of MgB$_2$ at 510 °C.$^{187}$

Hydrogen release occurs in three steps and the first, 270–325 °C, is assigned to hydrogen release from molten Mg(BH$_4$)$_2$. The second, 325–360 °C, is assigned to hydrogen release from MgH$_2$ and the third, 360–410 °C, to remaining non-crystalline boranes, which may also contribute to the second release.$^{187}$ Amorphous or nanocrystalline close-borane, MgB$_2$H$_{12}$, has been reported to be a major intermediate product during decomposition of Mg(BH$_4$)$_2$ in vacuum. $^{352}$ However, when Mg(BH$_4$)$_2$ is decomposed in dynamic vacuum in the temperature range 265 to 400 °C the reaction pathway is different.$^{356}$ Here, Mg(BH$_4$)$_2$ was observed as the major decomposition product when Mg(BH$_4$)$_2$ was heated to 265 °C. Trace amounts of Mg(BH$_3$)$_2$ were observed after heating to 285 °C, and none of the boranes Mg(BH$_4$)$_2$, Mg(BH$_3$)$_2$ or MgB$_2$H$_2$ were observed in samples heated at $T > 285$ °C.$^{356}$ Recently, MgB$_{10}$H$_{10}$ was also proposed as an intermediate in the decomposition reaction. $^{355}$ Lower dehydrogenation temperatures tend to increase the amount of higher boranes and a large quantity of Mg(BH$_3$)$_2$ was obtained after 5 weeks at 200 °C in vacuum.$^{357}$ MgB$_{10}$H$_{10}$ was converted back to Mg(BH$_4$)$_2$ after 48 h at 250 °C, $p$(H$_2$) = 120 bar.$^{357}$ In a similar fashion, a mixture of Mg(BH$_3$)$_2$ + 2THF-$\rightarrow$MgH$_2$ (1:2) was heated to 200 °C under $p$(H$_2$) = 50 bar for 2 h and the product indicated a quantitative conversion to Mg(BH$_4$)$_2$. $^{358}$

Formation of magnesium borohydride from the elements by hydrogenation has also been conducted but is kinetically slow. Reactive mechanochemistry in a hydrogen atmosphere has been used successfully and $\sim$ 50% of MgB$_2$ was hydrogenated to amorphous Mg(BH$_4$)$_2$ at $p$(H$_2$) = 100 bar (ball-milling time up to 100 hours).$^{189}$ Magnesium boride, MgB$_2$, has also been hydrogenated/deuterated at 400 °C and $p$(H$_2$) = 800 bar to form $\beta$-Mg($^{11}$BD$_2$)$_2$ with a $\sim$ 43% yield.$^{134}$ A higher borohydride yield was found with pre-milled MgB$_2$ at 400 °C, $p$(H$_2$) = 950 bar for 108 h ($\sim$ 75% $\beta$-Mg(BH$_4$)$_2$).$^{365}$

A number of theoretical and experimental studies have been conducted to determine the thermodynamics of decomposition for Mg(BH$_4$)$_2$ (see Table 17). Theoretical calculations suggest a reaction enthalpy of $\Delta H =$ 38–40 kJ mol$^{-1}$ H$_2$ for reaction (6.9) or (6.10).$^{335,336}$

\[
\text{Mg(BH}_4\text{)}_2 \rightarrow \text{MgH}_2 + 2\text{B} + 3\text{H}_2 \quad (6.9)
\]

\[
\text{Mg(BH}_4\text{)}_2 \rightarrow \text{MgB}_2 + 4\text{H}_2 \quad (6.10)
\]

Experimental studies also determine similar enthalpies, with $\Delta H =$ 41 kJ mol$^{-1}$ H$_2$ from a DSC study,$^{134}$ and $\Delta H =$ 39.3–57 kJ mol$^{-1}$ H$_2$ from van’t Hoff plots.$^{196,333}$ The van’t Hoff plots were formulated from PCT isotherms in both cases, but the difference in these data could be due to one set of isotherms being measured with constant gas flow and one set being measured stepwise. This variability also demonstrates the difficulty in obtaining accurate thermodynamic data from metal borohydrides.

Calcium borohydride’s physical behaviour is similar to Mg(BH$_4$)$_2$, where a molten phase can be observed near the decomposition temperature, depending on hydrogen backpressure, which is also known to control the decomposition pathway.$^{35,361}$ The decomposition pathway is temperature dependent and may proceed through a CaB$_6$H$_x$ intermediate to either CaB$_6$ (320–350 °C) or amorphous boron (400–450 °C).$^{362,363}$ Theoretical calculations predict Ca(BH$_4$)$_2$ decomposition enthalpies to be quantitatively similar to Mg(BH$_4$)$_2$, where $\Delta H =$ 40.6–57.3 kJ mol$^{-1}$ H$_2$ for decomposition reactions (6.11) or (6.12).$^{338}$

\[
\text{Ca(BH}_4\text{)}_2 \rightarrow 2/3\text{CaH}_2 + 1/3\text{CaB}_6 + 10/3\text{H}_2 \quad (6.11)
\]

\[
\text{Ca(BH}_4\text{)}_2 \rightarrow \text{CaH}_2 + 2\text{B} + 3\text{H}_2 \quad (6.12)
\]

However, PCT measurements provide much higher thermodynamic quantities with $\Delta H =$ 87 kJ mol$^{-1}$ H$_2$ and $\Delta S =$ 158 J K$^{-1}$ mol$^{-1}$ H$_2$. Here, the entropy is much higher than all other entropies for metal borohydrides (Table 17) including theoretical calculations ($\Delta S =$ 105.7–109.3 J K$^{-1}$ mol$^{-1}$ H$_2$).$^{338}$

Strontium borohydride decomposes at 400 °C and releases $H_2$.$^{142,277}$ Crystalline SrB$_3$ is observed by in situ SR-PXD, which suggests that Sr(BH$_4$)$_2$ decomposes into SrH$_2$, SrB$_3$ and $H_2$.$^{165}$

Manganese borohydride decomposes at 160 °C with the evolution of hydrogen and large quantities of B$_2$H$_6$.$^{18}$ For a pure sample of Mn(BH$_4$)$_2$ (9.5 wt% H$_2$), a mass loss of 14.8 wt% is observed in the temperature range 125–175 °C.$^{58}$ A melting event can also be observed near this temperature but appears to be dependent on hydrogen backpressure and heating rate.$^{57}$ Temperature dependent in situ SR-PXD measured for $\alpha$-Mn(BH$_4$)$_2$ reveals that the diffraction peaks disappear and the sample turns X-ray amorphous at 140 °C or 160 °C for $p$(Ar) = 1 bar and $p$(H$_2$) = 10 bar, respectively.$^{58}$ The high-pressure polymorph, $\delta$-Mn(BH$_4$)$_2$, transforms into $\alpha$-Mn(BH$_4$)$_2$ during heating in the temperature range 67–109 °C, hence the two polymorphs decomposes similarly.$^{140}$

Yttrium borohydride forms an X-ray amorphous solid above 200 °C and decomposes near 275 °C.$^{66,98,190,364}$ When Y(BH$_4$)$_3$ is decomposed under H$_2$ back pressure, ranging from $p$(H$_2$) = 1–10 bar, Y[B$_3$H$_8$]$_3$ is observed as the main intermediate according to scheme (6.13), along with small amounts of Y$_2$(B$_3$H$_8$)$_3$.$^{60}$

\[
Y\text{(BH}_4\text{)}_3(s) \rightarrow 1/3\text{Y(B}_3\text{H}_8\text{)}_3(s) + 2/3\text{YH}_3(s) + \text{H}_2(g) \quad (6.13)
\]
The ultimate decomposition results in the formation of YH₄, YH₃, and YB₄, but does not reform the borohydride, even under 1550 bar at 300 °C. Theoretical calculations indicate that Y(BH₄)ₓ is thermodynamically unstable at room temperature with a low decomposition reaction enthalpy ΔH = 22.5–36.2 kJ mol⁻¹ H₂.⁴⁹

Cadmium borohydride's low-temperature polymorph α-Cd(BH₄)₂ transforms to β-Cd(BH₄)₂, by a first order phase transition, at ~55 °C and β-Cd(BH₄)₂ decomposes at ~75 °C into metallic Cd and likely a mixture of hydrogen and boron gases according to scheme:⁴⁶

\[ β-Cd(BH₄)₂(s) → Cd(s) + B₂H₆(g) + H₂(g) \]  (6.14)

**Molecular metal borohydride.** The decomposition mechanism for molecular metal borohydrides, such as Al(BH₄)₃, Ti(BH₄)₃, or Zr(BH₄)₄, remains not fully understood. Apparently these compounds first sublime at low temperatures: around or below 0 °C for Al(BH₄)₃,¹² and at 29 °C for Zr(BH₄)₄.¹⁰⁹,³⁶⁵ In the gas phase all three compounds tend to release diborane via polymerization reactions. The spontaneous diborane release from Al(BH₄)₃ and Ti(BH₄)₃ below room temperature may be responsible for the very aggressive decomposition reactions. The stabilization of Ti(BH₄)₃ was recently reported through its confinement within a metal–organic-framework (MOF UiO-66), allowing it to be stored at room temperature for months without decomposition.²¹⁰

### 6.3 Thermolysis of bi- and trimetallic borohydrides

The thermal decomposition of the metal borohydrides has been shown to occur via a wide range of pathways, often in several steps, which may involve simultaneous and, in some cases, coupled chemical reactions. The following focus is on general trends deduced from published literature regarding both the reaction pathways and thermal stability of bi- and trimetallic borohydrides. Their decomposition mechanism is so far defined by one of two schemes:

(i) Stable metal borohydrides that form the bi- and trimetallic borohydride. Here, the bi- and trimetallic borohydride will separate during thermolysis, either splitting into the individual, stable, borohydrides, or possibly melting in an eutectic composition.

For example: MₓM’ₓ(BH₄)₂, (M = Li or Na, M’ = K, Rb, Cs) are formed from stable metal borohydrides. During heating, the bimetallic compounds phase separate and may form an eutectic melt as described in Section 6.4. MₓM’ₓ(BH₄)₂, (M = Li, Na, K, Rb or Cs, M’ = Mg, Ca or Sr) are formed from stable metal borohydrides. They are observed to decompose via the formation of mono-metal alkali metal borohydrides MBH₄ and alkaline earth metal borohydrides, which decompose individually at higher temperatures.¹,¹⁶⁴,¹⁶⁵

(ii) A combination of stable and unstable borohydrides that form the bi- and trimetallic borohydride. In this case, the unstable borohydride is often stabilized by its incorporation into a bi- and trimetallic borohydride, resulting in decomposition at higher than normal temperature. However, the decomposition mechanism is unchanged and the remaining stable metal borohydride will stay intact.

For example: MₓM’ₓ(BH₄)₂, (M = Li, Na, K, Rb or Cs, M’ = Al, Y, Sc, Mn, Zn or Cd), may decompose via the formation of mono-metallic alkali metal borohydrides MBH₄ but the remaining part may decompose directly to a metal, hydrogen and diborane.⁷⁰,¹⁴⁶,¹⁵⁹ All the Cd-based borohydrides show low thermal stability. Their decomposition temperatures exhibit the following trend: β-Cd(BH₄)₂, ~75 °C < KCd(BH₄)₃, ~80 °C < KCd(BH₄)₃, ~85 °C, i.e. the higher the content of KBH₄ the higher the thermal stability.¹⁴⁶

### 6.4 Eutectic melting of bi- and trimetallic borohydrides

Two or more metal borohydrides may be combined as discussed previously in Section 6.3, forming compounds with new compositions and/or structures, e.g. a new bimetallic compound MM’(BH₄)₂. In some cases a eutectic melting mixture may form, which has been observed in a few cases involving alkali- and alkaline earth-metal borohydrides.⁴⁵ For example, LiBH₄–MBH₄ systems reveal eutectic melting, M = K, and several new bimetallic compounds for M = Rb or Cs with increasingly complex phase diagrams.⁴⁷,¹⁵⁶ The formation of an eutectic mixture was observed to cause hydrogen release at lower temperatures during thermolysis, which could be a kinetic effect. However, structural reorganization upon melting may, in principle, result in weakening or strengthening of chemical bonds, which may influence decomposition, i.e. a thermodynamic effect. These effects may also influence hydrogen uptake properties. An overview of investigated eutectic mixtures is provided in Table 18.

**Lithium borohydride–sodium borohydride.** The LiBH₄–NaBH₄ system shows almost full solubility, i.e. a solid solution, LiₓNa₁₋ₓBH₄, in the temperature range ~110–220 °C with compositions 0.0 < x < 0.9. The lowest melting point is observed for Li₀.₇₀Na₄₀.₃₀BH₄ at Tmp ~ 216 °C.¹⁶¹,³⁶⁷

**Lithium borohydride–potassium borohydride.** The LiBH₄–KBH₄ phase diagram reveals a very deep eutectic melting point of Tmp = 105 °C (Fig. 21a).⁴⁷ Interestingly, a binary stoichiometric compound, LiK(BH₄)₂, is formed mechanochemically, not thermally, but separates to the monometallic borohydrides at T > 95 °C. In contrast, the sodium borohydride–potassium borohydride system forms a solid solution upon thermal treatment at ~200 < T < 450 °C. The reason that LiK(BH₄)₂ formation is facilitated by compression (mechanochemistry) and NaₓK₁₋ₓ(BH₄)₂ formation is facilitated by thermal expansion (heating) is due to the volume (V/Z) of the bimetallic compound and solid solution in comparison to their reactants. Compression can form the bimetallic borohydride LiK(BH₄)₂ owing to a smaller volume than the reactants, whereas thermal treatment can be used to form a bimetallic borohydride with a larger volume than its reactants, in this case a solid solution, NaₓK₁₋ₓ(BH₄)₂.⁴⁷,⁹³

**Lithium borohydride–magnesium borohydride.** The decomposition of the eutectic melting LiBH₄–Mg(BH₄)₂ system initiates above Tmp ~ 180 °C. At 270 °C, a 0.5LiBH₄–0.5Mg(BH₄)₂ composite releases 7.0 wt% of hydrogen.⁴⁵,⁶⁸ The eutectic system therefore releases hydrogen at significantly lower temperature than the individual lithium and magnesium borohydrides, which occur at ~400 and ~280 °C, respectively.

**Lithium borohydride–calcium borohydride.** The system LiBH₄–Ca(BH₄)₂ has been investigated for several compositions using
DSC, *in situ* SR-PXD, etc.\(^{369,371}\) Interestingly, this composite undergoes eutectic melting with a minimum temperature of \(T_{\text{mp}} \geq 200^\circ\text{C}\) in a relatively wide composition range \(0.6 \leq x \leq 0.8\).\(^{369,371}\)

**Sodium borohydride–potassium borohydride.** The NaBH\(_4\)–KBH\(_4\) phase diagram (Fig. 21b) reveals full solubility in the entire compositional range \(0 < x < 1\) for Na\(_{1-x}\)K\(_x\)BH\(_4\) above \(200^\circ\text{C}\). The melting point of the solid solution is reduced slightly compared to the individual reactants with a minimum at \(T_{\text{mp}} \approx 460^\circ\text{C}\) for Na\(_{0.68}\)K\(_{0.32}\)BH\(_4\).\(^{93}\)

**Sodium borohydride–magnesium borohydride.** The system, \(x\text{NaBH}_4+(1-x)\text{Mg(BH}_4)_2\), \(x = 0.4–0.5\), shows melting/frothing between \(205–220^\circ\text{C}\).\(^{370}\) However, the sample does not become a transparent melt. In contrast, no eutectic is observed for NaBH\(_4\)–Ca(BH\(_4\))\(_2\).\(^{370}\)

### 6.5 Trends in thermal decomposition for metal borohydrides

Upon heating, stable mono-metallic borohydrides tend to melt and then start to decompose at slightly higher temperatures, see Fig. 22. On the other hand, the less stable molecular metal borohydrides tend to sublime, rather than melt, and decompose in the gas phase. The decomposition products from the group of stable mono-metallic borohydrides appear to change color, morphology, volume *etc.* largely related to the degree of decomposition achieved in each system.\(^{45}\) Metallic decomposition products are not observed by visual inspection, X-ray diffraction or nuclear magnetic resonance, suggesting that after heating to modest temperatures the products likely remain as metal borohydrides, or form higher metal boranes, metal hydrides, or metal borides. \(^{11}\)\(^B\) NMR is particularly useful in identifying decomposition products if they are non-crystalline, where diffraction is less useful. The \(^{11}\)\(^B\) spectra can be used to differentiate between many different metal borohydrides with different cations, due to their varied interactions with the boron nucleus (Fig. 23). Trends in the NMR chemical shifts of borohydrides have been investigated recently.\(^{372}\) Other spectroscopic methods such as IR and Raman are also useful in characterising crystalline and non-crystalline metal borohydrides, where different bonding environments display characteristic vibrations (Fig. 24).

Progress in the spectroscopic understanding of alkali and alkaline earth metal borohydrides, \(M(\text{BH}_4)_n\) \((M = \text{Li, Na, K, Rb, Cs, Be, Mg, Ca})\) and reactive hydride composites has been recently reviewed.\(^{373–375}\)

An empirical correlation between the thermal stability, \(T_{\text{dec}}\) of metal borohydrides and Pauling electronegativity was first suggested to exist in 1955\(^{391}\) and has been further investigated theoretically and experimentally by several research groups.\(^{6,392,393}\) The more stable metal borohydrides tend to follow a linear correlation between the electronegativities and decomposition temperature. This approximation, however, is less pronounced for compounds with higher electronegativities. A comparison of a linear and exponential correlation is shown in the inset in Fig. 22b. The decomposition temperatures, \(T_{\text{dec}}\) reported in Fig. 22b are measured by *in situ* SR-PXD or thermal analysis (TGA/DSC) in inert atmosphere, often \(p(\text{Ar}) = 1\) bar. In the case of the bimetallic borohydrides, the values for the Pauling

### Table 18 Eutectic melting metal borohydride compositions, melting temperatures for the two individual compounds \(T_{\text{mp1}}\) and \(T_{\text{mp2}}\), melting temperature for the eutectic composition \(T_{\text{mp}}\), temperature for major hydrogen release, \(T_{\text{dec}}\) and morphology of the melt by visual inspection.\(^{45}\)

<table>
<thead>
<tr>
<th>Eutectic mixture</th>
<th>(T_{\text{mp1}}) (°C)</th>
<th>(T_{\text{mp2}}) (°C)</th>
<th>(T_{\text{mp}}) (°C)</th>
<th>(T_{\text{dec}}) (°C)</th>
<th>Eutectic morphology</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62LiBH(_4)–0.38NaBH(_4)</td>
<td>280</td>
<td>510</td>
<td>215</td>
<td>300</td>
<td>Transparent liquid</td>
<td>366 and 367</td>
</tr>
<tr>
<td>0.725LiBH(_4)–0.275KBH(_4)</td>
<td>280</td>
<td>605</td>
<td>105</td>
<td>420</td>
<td>Transparent liquid</td>
<td>47</td>
</tr>
<tr>
<td>0.55LiBH(_4)–0.45Mg(BH(_4))(_2)</td>
<td>280</td>
<td>280</td>
<td>180</td>
<td>250</td>
<td>Froth</td>
<td>368</td>
</tr>
<tr>
<td>0.7LiBH(_4)–0.3Ca[BH(_4)](_2)</td>
<td>280</td>
<td>370</td>
<td>200</td>
<td>350</td>
<td>Froth</td>
<td>369</td>
</tr>
<tr>
<td>0.68NaBH(_4)–0.32KBH(_4)</td>
<td>510</td>
<td>605</td>
<td>460</td>
<td>465</td>
<td>Dark liquid</td>
<td>93 and 366</td>
</tr>
<tr>
<td>0.45NaBH(_4) + 0.55Mg[BH(_4)](_2)</td>
<td>510</td>
<td>280</td>
<td>205</td>
<td>360</td>
<td>Froth</td>
<td>370</td>
</tr>
</tbody>
</table>

Fig. 21 (a) Binary phase diagram for the LiBH\(_4\)–KBH\(_4\) system.\(^{47}\) (b) Binary phase diagram for the NaBH\(_4\)–KBH\(_4\) system. Adapted with permission from ref. 93. Copyright 2015 American Chemical Society.
electronegativities, \( \chi_p \), are taken from the more electronegative elements, \( i.e. \) Sc, Y, Zn, Cd and Al. This approach is justified by the stronger coordination between the more electronegative metal and BH\(_4\), causing the formation of discrete metal boro-
hydride anions (see the discussion in Section 3.8).

The less electronegative metal is often an alkali metal with a dominantly ionic interaction. The validity of this assumption is illustrated by the decomposition of K\(_2\)Cd(BH\(_4\))\(_4\) to K\(_2\)Cd(BH\(_4\))\(_2\) and \( \text{Cd(BH}_4\text{)}_2 \). The latter immediately decomposes to \( \text{Cd, H}_2 \) and \( \text{B}_2\text{H}_6\). Upon further heating, K\(_2\)Cd(BH\(_4\))\(_4\) decomposes to KBH\(_4\) and \( \text{Cd(BH}_4\text{)}_2 \), where the latter again immediately decomposes to \( \text{Cd, H}_2 \) and \( \text{B}_2\text{H}_6\).146 This example illustrates that the more electronegative cation is controlling the stability. Furthermore, metal borohydrides containing complex anions, such as \( \text{[Sc(BH}_4\text{)}_4]^- \), \( \text{[Zn}_2\text{(BH}_4\text{)}_3]^- \) and \( \text{[Zn(BH}_4\text{)}_3]^- \) in the compounds MSc(BH\(_4\))\(_4\), MZn\(_2\)(BH\(_4\))\(_3\) and MZn(BH\(_4\))\(_3\) reveal only minor variations in the decomposition temperature with changes in alkali metal.70,166,380 This indicates that the decomposition temperature is specific for these complex anions rather than determined by the overall composition of the compound. This underlines the strong correlation between the decomposition temperature and the electronegativity of the complex-forming metal and the key role of the complex M–BH\(_4\) anions in the structural stability of bimetallic borohydrides.

6.6 The released gas from metal borohydrides, stability of diborane

Materials containing complex ions were overlooked as hydrogen carriers for possible hydrogen storage applications until the late nineties due to their relatively high stability and the fact

---

**Fig. 22** (a) Experimentally determined melting points for metal borohydrides as a function of the electronegativity of the metal. (b) Experimentally observed decomposition temperatures, \( T_{\text{dec}} \), for metal borohydrides M(BH\(_4\))\(_n\) and M\(_x\)M\(_y\)(BH\(_4\))\(_z\) plotted as a function of the electronegativity of the metal, M\(_0\). The \( T_{\text{dec}} \) values refer to the temperature for the maximum gas release and are measured by TGA/DSC or in situ SR-PXD at \( p(\text{He}) \) or \( p(\text{Ar}) = 1 \text{ bar} \). The inset in Fig. 22b reveal a comparison of linear and exponential correlation between observed decomposition temperatures, \( T_{\text{dec}} \), as a function of the electronegativity of the metal.

**Fig. 23** Experimentally determined \(^{11}\text{B}\) NMR chemical shifts of relevant metal borohydride and borane compounds. Bimetallic compounds are presented at the electronegativity of the most electronegative cation.158,166,197,275,342,376–389
that hydrogen uptake only occurs under extreme conditions. A paradigm shift was initiated by the discovery that titanium catalyzed NaAlH4 releases and uptakes hydrogen at moderate conditions,394 which initiated the research activities in hydrogen storage systems containing complex ions.

The boron, aluminium and nitrogen based complex hydrides, e.g. LiBH4, LiAlH4 or LiNH2, contain the complexes, BH4−, AlH4− or NH2−. These complexes form stable crystalline solids with many alkali or alkaline earth metals, which act as counter ions in the solid state. Reversible nitrogen-based complex hydride systems were discovered by Ping Chen et al. in 2002 and metal borohydrides were also found to be reversible, albeit under harsh conditions, e.g. LiBH4 in 1980.329,395 A drawback for these light element complex hydrides, e.g. LiBH4, LiAlH4 or LiNH2, appears to be that their neutral counterparts (AH3) are neutral molecules, BH3 or NH3, or metastable solids, AlH3. In fact, BH3 is in equilibrium with its dimer, B2H6, where the partial pressure of BH3 is roughly 2 × 10−6 of the pressure of B2H6 at room temperature.396 However, at higher temperature the BH3 partial pressure is higher, i.e. 104 times higher at 200 °C than RT, possibly promoting hydrogen release via polymerization reactions. Ammonia, NH3, is a reactive gas at room temperature that liquefies below −33.3 °C at p(NH3) = 1 bar. Ammonia is an industrially useful and energy dense compound (18.6 MJ kg−1), but may be converted to N2 and H2 at high temperature, with catalysts, with a Na/NaNH2 cracking system or by the omnipresent NaOH in NaNH2 as shown recently.397,398 Alane, AlH3, is a polymeric solid built from octahedra of AlH6.399,400 Alane is thermodynamically unstable at room temperature, but is stabilized in the bulk form by surface aluminium oxide layers.401,402

There are many indications that these ‘molecules’ (AH3) play a crucial role in the mechanism for hydrogen release and uptake in complex hydrides, e.g. LiBH4, LiAlH4 or LiNH2. This is exemplified by the fact that the light element complex hydrides can be prepared by a reaction between the ‘molecule’ and ionic hydrides (mentioned in Section 2.5).95,403 On the other hand, an ionic hydride, e.g. LiH or NaH may also be observed in the dehydrogenated state:

\[
AH_3 + LiH \leftrightarrow LiAH_4 \quad (6.15)
\]

Lithium borohydride, LiBH4 releases hydrogen at \( T > 400 \text{ °C} \), but was also found to emit diborane at the impurity level.339 This contrasts with, for example, Mn(BH4)2, which releases significant amounts of diborane at \( T \sim 160 \text{ °C} \).58 Thus, metal borohydrides have a tendency to release increasing amounts of diborane when they have lower decomposition temperatures.97,404 The extreme case is for LiZn2(BH4)2 that decomposes at \( T \sim 100 \text{ °C} \) and presumably releases a 1:1 mixture of hydrogen and diborane due to a reduction of Zn2+ to Zn.70 A similar type of metal ion reduction is also observed for the decomposition of Cd(BH4)2.146 Varying mixtures of hydrogen and diborane in the released gas suggests that more than one reaction mechanism is involved. Therefore, the composition of the released gas may depend on physical conditions, such as temperature and hydrogen partial pressure, which may favour a particular competing reaction.

Diborane can react with an ionic hydride and form a metal borohydride via a solid–gas addition reaction as shown for lithium borohydride at \( T > \sim 120 \text{ °C} \), reaction scheme (6.16). At slightly higher temperatures, 150 < \( T < 200 \text{ °C} \), diborane can further react with lithium borohydride and form metal closo-boranes (MxBnHn), according to reaction schemes (6.17) and (6.18).95,252,405

\[
\begin{align*}
2\text{LiH(s)} + \text{B}_2\text{H}_6(g) & \rightarrow 2\text{LiBH}_4(s) \quad (6.16) \\
2\text{LiBH}_4 + 4\text{B}_2\text{H}_6 & \rightarrow \text{Li}_3\text{B}_{10}\text{H}_{16} + 11\text{H}_2 \\
2\text{LiBH}_4 + 5\text{B}_2\text{H}_6 & \rightarrow \text{Li}_3\text{B}_{12}\text{H}_{12} + 13\text{H}_2 
\end{align*}
\]

Boron chemistry is extremely diverse and all neutral boranes, \( \text{B}_n\text{H}_m \), can be prepared, directly or indirectly, from diborane with...
the product mainly depending on the temperature and partial pressure of the reactants.406 Thus, the borane molecule, BH3, may play an active role for hydrogen release and uptake in metal borohydrides. These arguments may suggest that hydrogen release from metal borohydrides occurs via the partial reduction of borane, BH3, via the formation of higher boranes, or complete reduction forming metal borides or amorphous boron. Low total gas pressure may lead to a relatively high partial pressures of diborane, which appears to facilitate the formation of the rather stable metal closo-boranes.461 High partial pressures of hydrogen appear to facilitate the full reduction of BH3 and the formation of metal borides.

6.7 Additives to improve reaction kinetics

The hydrogen release temperatures of the stable metal borohydrides are usually considered too high for practical applications and catalysis has been widely investigated in an attempt to overcome kinetic barriers and reduce the activation energy for hydrogen release and uptake. The more stable metal borohydrides are of particular interest because they appear to have the potential to release pure hydrogen with no trace of diborane. Small amounts of additives have been sought to act as catalysts and promote both hydrogen release and absorption in metal borohydrides. Additives may also promote the formation of metal borides rather than metal closo-boranes, i.e. selective formation of a dehydrogenated state that facilitates absorption of hydrogen at more moderate conditions. The present Section 6.7 focuses on smaller quantities of additives investigated for possible catalytic properties and Section 6.8 treats larger amounts of additives that may purposefully react with the metal borohydride to form a reactive hydride composite.

Additive effects for aluminum and magnesium based hydrides.

A significant proportion of the research conducted on metal borohydride additives also tends to explore analogies with other hydrides, such as magnesium hydride, MgH2, and sodium tetrahydrido aluminate, denoted sodium alanate, NaAlH4.407–410 Catalytic nanoparticles have enabled breakthroughs in low-temperature hydrogen release and uptake in sodium alanate, NaAlH4.394,411,412 Several metals, such as titanium, scandium or cerium, have been shown to promote both hydrogen release and uptake, undertaking a bifunctional catalytic role.413 Typically, a transition metal chloride is added to NaAlH4, which then irreversibly reacts, forming inert NaCl and catalytically active Al or Ti-Al nanoparticles, possibly with the catalytically active metal on the surface of NaAlH4.412,413

Hydrogen release and uptake in magnesium hydride, MgH2, has been shown to be promoted by other principles. Alloysing effects with other metals such as Al, Cu, or Pd and the formation of Mg12Al12, Mg2Cu/Mg2Cu2, or Mg6Pd have been shown to influence hydrogen release and uptake.414–417 Other hydrides may also form and possibly act as an intermediate for hydrogen exchange, e.g. formation of Mg2Ni and Mg2NiH4 in MgH2-Ni samples418–420 or Mg2FeH6 in MgH2-Fe samples.421–425 Another mechanism is suggested for the Mg-Nb2O5 system where MgH2 tends to reduce niobium oxide forming a Mg17Nb12O3 solid solution, which possibly facilitates both hydrogen splitting at the surface as well as hydrogen diffusion through the very inert and dense MgO layer. Because of the high hardness of Nb2O5 and other additives these materials have a beneficial effect on the ball-milling process leading to the formation of smaller Mg particles and crystallites, which, in turn, improves kinetics due to surface area or grain boundary area enhancements.426–429

A significant variety of other additives have been investigated in the MgH2 system, including metals, intermetallics, oxides, hydrides and halides.430–432

Additives for metal borohydrides. The above mentioned examples have been used as inspiration in the exploration of a wide range of additives for hydrogen release and uptake in metal borohydrides. Trends in additive effects may appear when they are grouped into elements, and compounds such as hydrides, borides, oxides and halides. Mainly lithium and magnesium borohydrides have been examined systematically.

Elemental metallic additives. A range of transition metals have been considered as additives in MBH4 systems, e.g. Sc, Ti, V, Cr. Nanoscale transition metal particles are very important in organic chemistry with a long history, involving the chemical transformation of boron compounds, e.g. palladium nanoparticles for catalyzed Suzuki-Miyaura cross-coupling reactions, forming new C–C bonds. Homo-coupling reactions can also occur, which form new C–B bonds.17 For mono-metallic nanoparticles, the activity follows a sequence of Pd > Cu > Ru > Pt.17

The adsorption of BH4· on the more noble metal surfaces has also been investigated and reveals a weaker interaction with Ag and Au when compared to other noble metals, Pd, Rh, Ru, Pt, Ir and Os. This important result is related to the hydrolysis of borohydrides,433 which is further discussed in Section 6.9. Metal borohydrides may melt prior to the release of hydrogen, which also increases their reactivity. Gold powder was used as an X-ray standard in a sample of LiBH4, but a reaction took place at T > Tmp(LiBH4) ~ 290 °C and a lithium gold alloy formed.9 A range of metals (Mg, Al, Ti, V, Cr, Sc) have been mixed with LiBH4 in stoichiometric proportions with reported decreases of ~50 °C in its decomposition temperature.434 However, with high doping levels the entire reaction pathway can be shifted, as in the case of reactive hydride composites, forming alternate reaction products with different reaction thermodynamics.

Elemental non-metallic additives. The addition of excess quantities of amorphous boron to LiBH4 was found to enhance the decomposition process by leading to an alternative reaction mechanism, which reduces the decomposition temperature by ΔT ~ 150 °C and the activation energy by ΔEA ~ 55 kJ mol−1.435,436 Pendolino et al. propose a reaction of the intermediate Li3B2H12 and B to cause this change in desorption behaviour, by surplus B facilitating faster formation and growth of the solid intermediate by forming a polymer chain or layers with the boron of B12H12·.436

Carbon. Carbon has been investigated as an additive to promote hydrogen exchange in metal borohydrides, both theoretically and experimentally. Theoretical modelling suggests that increased curvature of the carbon surface decreases the ‘hydrogen removal energy’, i.e. C2 is expected to have a stronger effect in comparison to graphene and graphite.437 Density functional theory (DFT) was used to evaluate a wide range of chemical reactions suggesting the formation of bimetallic carbides, e.g. LiBC in a
reaction between LiBH₄ and carbon, which releases 11.95 wt% H₂ with a moderate reaction enthalpy (ΔU₀ = 45.1 kJ mol⁻¹ H₂).⁴³⁸ In a similar manner, the formation of Li₂C₂ was observed in mixtures of LiBH₄ with carbon nanotubes, which could be rehydrogenated back to LiH.⁴⁴⁹ Another example is the reaction between LiBH₄, ScH₃ and C, which is suggested to form ScBₓC and LiH in the decomposed state with a relatively low enthalpy change of ΔU₀ ~ 52 kJ mol⁻¹ H₂.⁴⁴⁸ The ‘carbon-effect’ on metal borohydrides is further discussed in Section 6.10 in regard to nanoco confinement.

**Sulphur.** The reactions between metal borohydrides and elemental sulfur have been investigated in situ during thermal treatment and were found to be highly exothermic (up to 700 J g⁻¹). These reactions are exceptionally rapid and result in the sudden release of substantial quantities of hydrogen gas and should be handled with caution. The metal borohydrides react with molten S at 140, 190 and 180 °C, respectively for LiBH₄–S, NaBH₄–S and KBH₄–S. Remarkably, NaBH₄–S release pure hydrogen, whereas LiBH₄–S and KBH₄–S systems also release some H₂ or B₂H₆ gases.⁴⁴⁰ The drawback may be the very complex metal sulphur chemistry that results in the formation of multiple complex compounds and intermediates, as observed for the NaAlH₄–S system.⁴⁴¹ The reaction between metal borohydrides and sulphur could have implications for their use as solid state electrolytes in Li–S battery applications.

**Metal hydrides as additives.** Different types of hydrides have also been considered in order to promote hydrogen exchange in metal borohydrides.⁴³⁴,⁴³⁸,⁴⁴² Many of these systems alter the decomposition pathway, resulting in altered thermodynamics and are discussed in the following section on reactive hydride composites.

**Metal oxides as additives.** A variety of metal oxides have also been considered to enhance the hydrogen exchange properties of metal borohydrides. This was initiated by the study of glass powders having an effect on lithium borohydride, i.e. LiBH₄–SiO₂, which enabled hydrogen release at lower temperatures than observed for pure LiBH₄.⁴² However, in situ diffraction shows an irreversible reaction between SiO₂ and molten LiBH₄ at T > 370 °C and the formation of orthosilicate, Li₃SiO₄, for small amounts of additive (< 10 mol% SiO₂, i.e. excess of lithium) and lithium metal silicate (Li₂SiO₃) for larger amounts of additive.⁹ The fate of boron remain unclear but the formation of lithium borates may occur.

A minor change in hydrogen release profile for γ-Mg[BH₄]₂ with 0.02 mol% TiO₂ and MoO₃ is observed, i.e. the DSC events appeared broader and were shifted to slightly lower temperatures (ca. 20 °C), as compared to the pure γ-Mg[BH₄]₂.⁴⁴³ A large decrease in the dehydrogenation temperature was found for stoichiometric ratios of LiBH₄ with TiO₂ (down to 150 °C), but was due to a redox reaction forming Li₂TiO₃.⁴⁴⁴ Several transition metal oxides have also been explored, which have some tendency for release of diborane due to reduction of the metal by BH₄⁻, accompanied by the irreversible formation of borates or ternary metal oxides.⁴⁴⁵,⁴⁴⁶

**Metal fluorides as additives.** Nickel fluoride, NiF₂, tends to react with γ-Mg[BH₄]₂ and form Ni₃B and possibly Mg[B₃H₈]₂, which absorbs hydrogen at moderate conditions to form β-Mg[BH₄]₂.⁴⁴⁷ Similarly, the reaction between LiBH₄ and TiF₃ results in an exothermic reaction to form LiF and TiB₂.⁴⁴⁸ Borofluorides, NaBF₄ and KBF₄, are described in Section 4 and enable fluoride substitution in metal borohydrides to possibly promote the formation of closo-boranes during thermolysis. In general, fluorides tend to ‘destabilise’ the metal borohydride often by promoting irreversible chemical reactions that tend to form stable metal fluorides, closo-boranes and possibly diborane gas. Halides of Al, Ti, Zr and Hf may form volatile molecular borohydrides, which then sublime and decompose in the gas phase.

**Heavier halides: chlorides, bromides and iodides, as additives.** Heavier halides of metals with relatively low electronegativity (i.e. alkali- and alkali earth metals) may lead to anion substitution in the metal borohydride, as discussed in Section 4. Anion substitution tends to stabilize the hydrogenated state, and provide hydrogen release at slightly higher temperatures, tendency to facilitate the hydrogenation of the sample. Titanium trichloride has a well-documented catalytic effect on the hydrogen release and uptake from NaAlH₄.⁴³⁹,⁴¹³ and appears to decrease the decomposition temperature of LiBH₄.⁴⁴⁹ A color change from light red/purple to gray/black of a LiBH₄–TiCl₃ (2 mol%) sample when kept a few hours at RT in an argon-filled glove box indicates that a chemical reaction takes place. This chemical reaction can be suppressed when the sample is kept at low temperatures, e.g. T ~ 35 °C and in situ SR-PXD reveals the formation of LiCl initiated at RT.⁷ Thus, the reaction between LiBH₄ and TiCl₃ results in the formation of Ti[B(H₄)]₃, which decomposes at room temperature by an unknown mechanism.¹¹⁰ One of the most effective additives was suggested to be LiBH₄–0.2MgCl₂–0.1TiCl₃, which released about 5 wt% H₂ at T > 60 °C and absorbed ~ 4.5 wt% H₂ at T = 600 °C, p(H₂) = 70 bar.⁴⁵⁰ The addition of TiCl₃ also changes the hydrogen exchange properties for other metal borohydrides, e.g. Mg[BH₄]₂.⁴⁵¹

**Metal borides as additives.** Metal borides are known as inert materials with high melting points that have also been under consideration as additives. Titanium boride, TiB₂, appears to have a limited effect on the decomposition pathway of the LiBH₄–1.5Al system, but seems to facilitate the formation of intermediate compounds (i.e. Li–Al–B solid solutions) at lower temperatures compared to samples without an additive.² Similarily, zirconium boride, ZrB₂, appears to stabilize the hydrogen storage capacity for reactive hydride composites, e.g. LiBH₄–MgH₂, discussed in the following section, possibly by facilitating nucleation and growth of layered magnesium diboride.⁴⁵³

**Assessment of additive effects by comparative studies.** A series of nickel-based materials, Ni powder (30 nm), Ni₄B, NiF₂ and NiCl₂ (2 mol%), have been added to γ-Mg[BH₄]₂ and the hydrogen storage properties were evaluated.⁴⁴⁷ EXAFS spectra indicate that NiCl₂ and NiF₂ react with γ-Mg[BH₄]₂ and transform to amorphous nickel boride. The γ-Mg[BH₄]₂–NiF₂ sample releases 6.5 wt% gas and the other three samples release 2.7 wt% at moderate conditions, 220 < T < 264 °C, 10 < t < 60 h, under static vacuum. Different side-reactions in the fluoride-containing sample may be responsible for the larger gas release. Spectroscopy suggests the formation of Mg[B₃H₈]₂ in the decomposed sample due to the relatively low thermolysis temperature. The four
samples absorb 1–2 wt% H2 at 210 < T < 262 °C, 10 < t < 48 h, and 100 < p[H2] < 155 bar.447

A series of cobalt-based materials Co2B, CoF3, CoCl2 and Co3O4 (2 mol%), have been added to γ-Mg(BH4)2 in a similar manner to the nickel additives.454 Three full cycles of hydrogen release and uptake were conducted and the first cycle, at T ~ 286 °C, 2.6 < p(H2) < 4 bar, 10 < t < 40 h, releases 3.1–4.4 wt% H2, which is very similar to that of pure γ-Mg(BH4)2, 4.1–4.2 wt% H2. Hydrogen absorption was conducted at 280–290 °C at 110 < p(H2) < 125 bar. The third cycle releases 1.4–2.0 wt% H2 and the kinetics for hydrogen release and uptake is similar to pure γ-Mg(BH4)2.454

**General discussion of the effect of additives on metal borohydrides.** Overall, no real catalyst for B–H bond breaking or formation has been identified. The investigated additives may be divided into either reactive or inert additives. Reactive additives may react reversibly with metal borohydrides and typically enhance the mass loss from the system in the first hydrogen release cycle. Reactive additives may contain a metal with a relatively high oxidation state and/or electronegativity, which may be reduced during release of diborane and hydrogen. Reactive anions may react irreversibly with the metal borohydride and form metal borates or more stable boranes, e.g. closo-borane. Inert additives may be metals or metal borides. However, the latter may have a beneficial effect and facilitate the crystallization of metal borides in the decomposed state. Small amounts of transition metal compounds like VCl3, ZrCl4 or Zr-isopropoxide added prior to the ball-milling process of reactive hydride composites (discussed in Section 6.8), e.g. 2LiBH4–MgH2 have beneficial kinetic effects. The additives may transform to transition metal boride nanoparticles during thermolysis or aggressive ball-milling, which could facilitate the formation of metal borides in the dehydrogenated state and thereby hydrogen absorption.455

In most cases, only the first dehydrogenation is investigated, which hampers the distinction between irreversible chemical reactions and possible catalytic effects. Chemical reactions often show a significant enhancement of the first hydrogen release reaction, which may occur with faster kinetics and therefore also at apparently lower temperatures. A disadvantage for the use of volumetric or Sievert’s methods for measuring the gas release is that measured changes in pressure is converted to an equivalent amount of hydrogen, which is incorrect if gases other than hydrogen are released. A chemical reaction between a reactive additive and a metal borohydride may often be identified by a mass loss, which scales with the amount of additive. Irreversible chemical reactions will lead to significant losses of the hydrogen storage capacity in the first cycle, illustrating the importance of conducting experimental evaluations over several cycles of hydrogen release and uptake.

The available knowledge on the exact mechanism for hydrogen release/uptake remains limited partly owing to difficulties in determining the decomposition products from metal borohydrides, which are often non-crystalline. In several cases, more than one reaction mechanism for hydrogen exchange is proposed, which may change as a function of the physical conditions, e.g. p, T, as discussed in Section 6.2. Thus, the rate determining step in the mechanism remain unknown, which also hampers the design of a catalyst.

Another largely overlooked problem is the fact that many metal borohydrides melt before or during hydrogen release. Fusion eliminates the grain structure and reduces the surface area of multicomponent samples. The partly molten state of the metal borohydride – additive system usually has a relatively high viscosity, thus a gas release leads to bubbling, foaming and possible phase segregation, which further limits reversibility and the use of catalysts.

**6.8 Reactive hydride composites**

Larger amounts of additives may lead to stoichiometric reactions among the components in a system, denoted Reactive Hydride Composites (RHC). P. Chen (China) was first to apply this approach to nitrogen containing systems like Mg(NH2)2–2LiH.456 Later the approach was extended to borohydride containing systems by J. J. Vajo (USA), Y. W. Cho (South Korea) and R. Bormann (Germany).37,39,42 Several systems combining metal borohydrides and magnesium hydride have been studied intensively during the past decade, e.g. LiBH4–MgH2, NaBH4–MgH2 and Ca[BH4]2–MgH2.43,457 A chemical reaction takes place between two or more components during decomposition, which lowers the overall reaction enthalpy (Fig. 25). This concept is analogous to Medima principles applied to d-block metals and the well-known Hess law from chemistry. The gravimetric hydrogen storage capacity is then the weighted average of the individual hydrogen storage capacity of the components of the RHC system.8 In the following, selected RHC systems are discussed in more detail and Table 19 provides an overview of the thermodynamic data.

**Lithium borohydride–magnesium hydride, 2LiBH4–MgH2.** The reactive hydride composite lithium borohydride–magnesium

---

Fig. 25 Schematic illustration of the concept of reactive hydride composites illustrated for 2LiBH4–MgH2.
hydride releases and absorbs hydrogen under less harsh conditions (p, T, t) compared to the individual components. This is due to an exothermic formation of MgB2 during the endothermic dehydrogenation reaction of the 2LiBH4–MgH2 system, i.e. a chemical reaction between LiBH4 and Mg, which leads to hydrogen release, the formation of LiH and a reduction of the total reaction enthalpy, see reaction scheme (6.19). In addition, hydrogen uptake from MgB2–2LiH occurs at more moderate conditions than for the decomposition products from pure LiBH4, i.e. amorphous boron, lithium boride and/or higher boranes like Li2B12H12.37

This is caused by the open layered structure of MgB2 as well as the non-covalent bonding between Mg and B in MgB2.466 The full reversibility of the 2LiBH4–MgH2 system is reported to only be obtained when the decomposition occurs in a hydrogen back pressure of p(H2) = 1–5 bar, which facilitates the formation of MgB2 by suppressing the individual decomposition of LiBH4 and MgH2.39,467,468

The phase diagram has recently been investigated for the 2LiBH4–MgH2 system from a comprehensive pressure–composition-isotherm study.460 It was shown that there is a single equilibrium pressure plateau below 413 °C represented by reaction (6.19a), but there are two plateaus above 413 °C represented by reaction (6.19b). A similar phenomena exists for NaMgH2.F440

2LiBH4 + MgH2 $\leftrightarrow$ 2LiH + MgB2 + 4H2  (6.19a)

2LiBH4 + MgH2 $\leftrightarrow$ 2LiH + Mg + H2 $\leftrightarrow$ 2LiH + MgB2 + 4H2  (6.19b)

A calculation of the decomposition enthalpy change yields $\Delta H_{dec} \approx$ 40–46 kJ mol$^{-1}$ H2, corresponding to $\tau$(1 bar) $\approx$ 169 °C.39,41,469 A similar reaction occurs for a magnesium-rich system, e.g. 0.5LiBH4–MgH2 that decomposes to MgB2 in p(H2) > 1 bar.470,471 In contrast, the system LiBH4–MgH2 (0.3:1) and (2:1) decompose through different reactions in dynamic vacuum forming $\alpha$- and $\beta$-alloys of Mg,Li$_{1-x}$, x $\approx$ 0.82 and 0.70, respectively.470,472 Hydrogen absorption also occurs at rather low pressures and temperatures $p$(H2) < 50 bar and T < 300 °C. These conditions are substantially more favourable than those for LiBH4 and are considered a breakthrough in utilizing borohydrides for reversible hydrogen storage.

The kinetics for hydrogen release and uptake reactions can be significantly enhanced by the addition of suitable additives, e.g. small amounts of transition metal compounds like VCl$_4$, ZrCl$_4$ or Zr-isopropoxide. Initially, the additives have a beneficial effect on the ball-milling process through the reduction of grain and particle sizes and thereby reducing hydrogen diffusion pathways.455 Further investigations using extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES) and anomalous small angle scattering (ASAXS) measurements indicate the formation of the respective transition metal boride nanoparticles during aggressive ball-milling or subsequent thermolysis.453,455,473

The transition metal compounds with the best enhancement of reaction kinetics for RHC systems form transition metal borides with small directional and interplanar misfits to MgB2 by 0.1 and 2.8%. Thus, these transition metal borides may act as favorable heterogeneous nucleation sites for the formation of the MgB2 during decomposition.453,455 Therefore, hydrogen absorption kinetics are significantly faster when compared to RHC without additives. Nanoscale MgH2 synthesized via an organometallic method and used as a starting component appears to suppress the formation of closo-boranes, e.g. [B$_2$H$_{12}$]$^-$ 474

**Sodium borohydride–magnesium hydride, 2NaBH4–MgH2.** Sodium borohydride readily forms by the hydrogenation of a 2NaH–MgB2 composite, see reaction (6.20).57 The composite 2NaH–MgB2 has a calculated gravimetric hydrogen capacity of $\rho_m = 7.8$ wt% H2, and reaction enthalpy of $\Delta H = 62$ kJ mol$^{-1}$ H2, corresponding to a decomposition temperature of $\tau$(1 bar) = 350 °C.459 Hydrogenation of the 2NaH–MgB2 composite also occurs at low pressure i.e. $p$(H2) = 25 bar (t = 63 h) at 400 °C where 6.2 wt% H2 is absorbed.473 Hydrogenation starts at T $\approx$ 250 °C but appears to become more complex at lower hydrogen pressures, proceeding via an unknown compound and NaMgH2.475

2NaBH4 + MgH2 $\leftrightarrow$ 2NaH + MgB2 + 4H2  (6.20)

The decomposition pathway of 2NaBH4–MgH2, RHC system appears to be a two-step reaction similar to 2LiBH4–MgH2, see reaction scheme (6.19b). However, the reactivity appears to be lower and some NaBH4 often remains in the sample after the reaction with Mg to form MgB2.476

**Calcium borohydride–magnesium hydride, Ca(BH4)$_2$–MgH2.** The calculated gravimetric hydrogen capacity for the Ca(BH4)$_2$–MgH2 system is $\rho_m = 8.3$ wt% H2 and it shows a complex reaction pathway with a number of intermediates, e.g. formation of CaBH4.
Ca,Mg,H$_{14}$ and other Ca–B–H compounds.\textsuperscript{338,477–479} The idealized hydrogenation reaction takes place as illustrated in reaction scheme (6.21), which can take place at $p$(H$_2$) = 140 bar and $T$ = 250 °C,

$$\text{CaH}_2 + \text{MgB}_2 + 4\text{H}_2 \rightarrow \text{Ca}[	ext{BH}_4]_2 + \text{MgH}_2 \quad (6.21)$$

Until now, only partial reversibility has been obtained, however, transition metal-based additives facilitate the formation of MgB$_2$ in the Ca[B(H$_4$)$_2$]+MgH$_2$ system in a similar way to the LiBH$_4$–MgH$_2$ system.\textsuperscript{250,463}

**Lithium borohydride–aluminium, 2LiBH$_4$–Al.** Access to the hydrogen content of LiBH$_4$ may be facilitated by the addition of a reactive metal, e.g. the 2LiBH$_4$–Al system. The 2LiBH$_4$–Al composite is more prone to rehydrogenation when compared to LiBH$_4$, e.g. at $T = 400$ °C and $p$(H$_2$) = 100 bar.\textsuperscript{371,480–483} In fact, the 2LiBH$_4$–Al, 2NaBH$_4$–Al and CaBH$_4$–Al systems can all be hydrogenated under 100 bar at 350–400 °C, but better kinetics are obtained under 600 bar.\textsuperscript{464} However, cycling of hydrogen release and uptake in 2LiBH$_4$–Al has shown that the system suffers from a significant degradation in hydrogen storage capacity.\textsuperscript{452,484,485} The composite 2LiBH$_4$–Al has been suggested to release hydrogen in two steps at $T < 500$ °C represented by reaction schemes: \textsuperscript{473,480–483}

$$2\text{LiBH}_4(\text{l}) + \text{Al(s)} \rightarrow \text{AlB}_2(\text{s}) + 2\text{LiH(s)} + 3\text{H}_2(\text{g}) \quad (6.22)$$
$$\text{LiH(s)} + \text{Al(s)} \rightarrow \text{LiAl(s)} + 0.5\text{H}_2(\text{g}) \quad (6.23)$$

The enthalpy change for reaction (6.22) is calculated as $\Delta H = -59.3$ kJ mol$^{-1}$ H$_2$,\textsuperscript{486} which corresponds to $T$(1 bar) = 166 °C.\textsuperscript{483} Reactions (6.22) and (6.23) illustrate that the full H$_2$ capacity of LiBH$_4$ ($\rho_{m,n} = 18.3$ wt% H$_2$) can be utilized for the composite of LiBH$_4$–1.5Al. However, the addition of Al lowers the gravimetric H$_2$ capacity of this composite to only $\rho_{m,n} = 6.5$ wt% H$_2$.

The decomposition of LiBH$_4$–Al results in the formation of LiAl, AlB$_2$ and Li$_2$B$_12$H$_{12}$ via several reactions and intermediate compounds. Apparently, there is significant formation of Li$_2$B$_12$H$_{12}$ rather than a diborane release or amorphous boron production.\textsuperscript{452} The hydrogen storage capacity reduces significantly over ten cycles of hydrogen release and uptake for the reactive composite LiBH$_4$–1.5Al, see Fig. 26.\textsuperscript{452}

**Lithium borohydride–sodium alanate composite, LiBH$_4$–NaAlH$_4$.** Other metal hydrides have also been explored as possible Al sources, e.g. the system, 2LiBH$_4$–NaAlH$_4$, $\rho_{m,n} = 11.9$ wt% H$_2$.\textsuperscript{484} However, the samples prepared by ball milling reveal diffraction from both LiAlH$_4$ and NaBH$_4$, due to a metathesis reaction (6.24).\textsuperscript{487}

$$\text{LiBH}_4(\text{s}) + \text{NaAlH}_4(\text{s}) \rightarrow \text{LiAlH}_4(\text{s}) + \text{NaBH}_4(\text{s}) \quad (6.24)$$

Several (coupled) chemical reactions are involved in hydrogen release and uptake. NaBH$_4$ decomposes at a much lower temperature than normal, at $\sim 340$ °C, after which some Na vapour is also released due to dynamic vacuum, leaving a LiAl alloy and amorphous boron in the solid state. Sodium borohydride, NaAlH$_4$, only partly decomposes to B and NaH at $T = 400$ °C under $p$(H$_2$) $\sim$ 1 bar. The formation of AlB$_2$ is observed at $T = 450$ °C along with AlB$_3$ or Al$_{1-x}$Li$_x$B$_2$, which stabilizes boron in the solid state. The LiBH$_4$–NaAlH$_4$ system is partially reversible and LiBH$_4$ was rehydrogenated under moderate conditions, $T = 400$ °C and $p$(H$_2$) = 110 bar. During hydrogenation, the diffraction intensity from LiAl decreases at $T \sim 200$ °C and the formation of LiH and Al is observed, while the consumption of AlB$_2$ occurs at $T \sim 280$ °C. Crystalline h-LiBH$_4$ forms upon cooling at $T \sim 260$ °C. Apparently, the loss of sodium vapour prevents the formation of sodium alanate.\textsuperscript{484}

The lithium borohydride–magnesium hydride–aluminium system LiBH$_4$–MgH$_2$–Al. Several reactive hydride composites (RHC) may also be combined to form more complex systems, e.g. the LiBH$_4$–MgH$_2$ and LiBH$_4$–Al RHC systems are combined to form LiBH$_4$–MgH$_2$–Al,\textsuperscript{465} which has an even lower decomposition temperature via another mechanism and results in the formation of Mg$_{1-x}$Al$_x$ as shown in the idealized reaction scheme: \textsuperscript{465}

$$2\text{LiBH}_4(\text{s}) + x\text{MgH}_2(s) + (1 - x)\text{Al(s)} \rightarrow 2\text{LiH(s)} + \text{Mg}_{1-x}\text{Al}_x(s) + (4 + x)\text{H}_2(\text{g}) \quad (6.25)$$

The hydrogen storage capacity of the LiBH$_4$–MgH$_2$–Al system decreases upon continuous hydrogen cycling (see Table 20). Boron in the hydrogenated sample 4LiBH$_4$–MgH$_2$–Al exists as Li$_2$B$_12$H$_{12}$ (19.1 mol%) and LiBH$_4$ (80.9 mol%) after three cycles of hydrogen release and uptake, when dehydrogenated in low hydrogen pressure, $p$(H$_2$) = 0.15 bar. However, the ratio Li$_2$B$_12$H$_{12}$–LiBH$_4$ is only 8.7:91.3 mol% when the sample is dehydrogenated at $p$(H$_2$) = 5.0 bar. For the sample 4LiBH$_4$–MgH$_2$–5Al only 2.4 mol% $p$(H$_2$) = 110 bar. During hydrogenation, the diffraction intensity from LiAl decreases at $T \sim 200$ °C and the formation of LiH and Al is observed, while the consumption of AlB$_2$ occurs at $T \sim 280$ °C. Crystalline h-LiBH$_4$ forms upon cooling at $T \sim 260$ °C. Apparently, the loss of sodium vapour prevents the formation of sodium alanate.\textsuperscript{484}

**Table 20** Molar composition of LiBH$_4$–MgH$_2$–Al (4:1:1) and LiBH$_4$–MgH$_2$–Al (4:1:5) after three hydrogen release and uptake cycles applying different hydrogen backpressure during desorption\textsuperscript{465}

<table>
<thead>
<tr>
<th>Sample</th>
<th>$p$(H$_2$) (bar)</th>
<th>Li$_2$B$<em>12$H$</em>{12}$ (mol%)</th>
<th>LiBH$_4$ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH$_4$–MgH$_2$–Al (4:1:1)</td>
<td>0.15</td>
<td>19.1</td>
<td>80.9</td>
</tr>
<tr>
<td>LiBH$_4$–MgH$_2$–Al (4:1:1)</td>
<td>5.0</td>
<td>8.7</td>
<td>91.3</td>
</tr>
<tr>
<td>LiBH$_4$–MgH$_2$–Al (4:1:5)</td>
<td>0.15</td>
<td>8.0</td>
<td>92.0</td>
</tr>
<tr>
<td>LiBH$_4$–MgH$_2$–Al (4:1:5)</td>
<td>5.0</td>
<td>2.4</td>
<td>97.6</td>
</tr>
</tbody>
</table>
Li₂B₁₂H₁₂ and 97.6 mol% LiBH₄ is formed using the higher dehydrogenation partial pressure of hydrogen, \(p(H₂) = 5.0\) bar. These results show that both sample composition and hydrogen partial pressure, e.g. \(p(H₂) > 1\) bar, during thermalysis is crucial to suppress the formation of more stable closo-boranes, Li₂B₁₂H₁₂, and thereby preserve the hydrogen storage capacity.

Manganese borohydride-metal hydrides. Mn(BH₄)₂ is an interesting candidate for hydrogen storage, owing to its high stability at room temperature, low decomposition temperature of 130–180 °C, high theoretical hydrogen capacity of 9.5 wt% H₂ and the high abundance of manganese in the lithosphere. A drawback for the utilization of Mn(BH₄)₂ is that the gas released during decomposition contains high levels of diborane. This mechanism for decomposition remains not fully understood, in particular the possible side reactions that produce diborane. Thus, the hydrogen storage capacity is expected to decrease due to the loss of boron from the system during continued hydrogen release and uptake in manganese borohydride. In the reactive hydride composites, Mn(BH₄)₂–MHₓ (M = Li, Na, Mg, Ca), the formation of the more stable M[BH₄]ₓ for M = Li, Na and Ca suppresses the release of diborane and provides a higher hydrogen content in the released gas during the decomposition (Fig. 27).

Bimetallic transition metal hydrides. Reactive hydride composites including Mg₂NiH₄, Mg₂FeH₆ etc. have also been explored to promote hydrogen release and uptake in metal borohydrides. The first example was discovered by J. J. Vajo (US, 2010), LiBH₄–Mg₂NiH₄, which reversibly stores hydrogen at moderate conditions, \(\Delta H = 15.4 \pm 2\) kJ mol⁻¹ H₂ and \(\Delta S = 62.2 \pm 3\) J K⁻¹ mol⁻¹ H₂. This is due to the formation of a bimetallic boride in the decomposed state, see reaction (6.26), which also absorbs hydrogen at moderate conditions.

4LiBH₄ + 5Mg₂NiH₄ → 2MgNi₂.5B₂ + 4LiH + 8MgH₂ + 8H₂  \(\text{(6.26)}\)

This result suggests that there could be other similar systems because there are numerous complex transition metal hydride anions including [FeH₆]³⁺, [CoH₄]³⁻, and [NiH₄]⁴⁻. The magnesium iron hydride–lithium borohydride system also stores hydrogen reversibly but forms a monometallic boride, FeB, in the decomposed state.

2Mg₂FeH₆ + 2LiBH₄ → 2LiH + 4MgH₂ + 2FeB + 5H₂  \(\text{(6.27)}\)

The enthalpy change for this system is slightly larger, \(\Delta H = 72 \pm 4\) kJ mol⁻¹ H₂ and \(\Delta S = 147 \pm 7\) J K⁻¹ mol⁻¹ H₂, and occurs in the temperature range 310–400 °C. Yttrium hydride. The reactive hydride composite, 4LiBH₄–YH₃ releases ~7 wt% H₂ at \(T \sim 350\) °C following reaction scheme (6.28), which corresponds to a calculated hydrogen content of \(\rho_m = 8.5\) wt% H₂.

4LiBH₄ + YH₃ → 4LiH + YB₄ + 7.5H₂  \(\text{(6.28)}\)

This reaction is reversible at relatively mild rehydrogenation conditions, e.g. \(T = 350\) °C and \(p(H₂) = 90\) bar. Also, a hydrogen pressure of e.g. \(p(H₂) = 90\) bar facilitates the formation of metal borides during decomposition.

Rare earth metal hydrides are also used as additives, in 6LiBH₄–MHₓ compositions (M = La, Ce), which provide hydrogen release after LiBH₄ melting, but below its normal dehydrogenation temperature. PCT measurements performed on 6LiBH₄–CeH₂ provide thermodynamic data for the decomposition reaction \(\Delta H_{dec} = 58 \pm 3\) kJ mol⁻¹ H₂ and \(\Delta S_{dec} = 113 \pm 4\) J K⁻¹ mol⁻¹ H₂ corresponding to \(T(1\) bar) = 240 ± 32 °C. The change in thermodynamics suggests the formation of a reactive hydride composite.

Summary. The concept to lower both the total reaction enthalpy and thus the hydrogen release temperatures of hydride-borohydride mixtures (RHC) is currently working. In some cases, quite astonishing properties are found, such as enhanced absorption kinetics, in spite of a lowered driving force for absorption, however, the progress reached so far is limited. The sorption temperatures are still too high for many technical applications. Less stable borohydrides, decomposing at lower temperatures, show not only the release of hydrogen but also diborane, as mentioned above. To reach a significant breakthrough hydrides and/or reactive additives have to be found that react (reversibly) with the borohydrides at much lower temperatures and thereby capture the boron and prevent the release of diborane or the production of higher boranes.

6.9 Hydrolysis – decomposition by reaction with water

In an alternative process to thermal decomposition, hydrogen can also be released from hydrides in a reaction with water, denoted hydrolysis. An advantage is that half of the released hydrogen originates from the water and increases the hydrogen capacity of the system. Sodium borohydride can be stabilized in basic solution with a typical composition of 20% NaBH₄ and 1% NaOH (solubility of NaBH₄ is 55 g per 100 mL at 20 °C). The hydrolysis reaction is controlled by a catalyst, e.g. a late transition metal, such as Ru. The catalytic effect of Pt for the generation of H₂ from BH₄⁻ hydrolysis was discovered in the early 1960s and this reaction has been extensively investigated on a variety of high-surface area catalysts such as Pt–C.
DFT calculations indicate that the hydrolysis reaction takes place for BH4− co-adsorbed with H2O on a surface.433

The low concentration of NaBH4 reduces the storage capacity of the system to 4 wt% H2. The product obtained from hydrolysis is sodium metaborate NaBO2 and hydrogen, see reaction (6.29). The concentration of the reactants should be kept sufficiently low in order to prevent precipitation of NaBO2, which may block the catalytic active sites (the solubility of NaBO2 in water is 26 g per 100 mL at 20 °C).501

\[ \text{NaBH}_4(aq) + 2\text{H}_2\text{O}(l) \rightarrow 4\text{H}_2(g) + \text{NaBO}_2(s) \] (6.29)

A significant drawback of the hydrolysis approach is that the dehydrogenated product is typically a stable oxide, e.g. sodium metaborate NaBO2, with a heat of formation of \( \Delta H_f = -1058 \text{ kJ mol}^{-1} \). The heat of formation for NaBH4, \( \Delta H_f = -191 \text{ kJ mol}^{-1} \) is significantly less negative, illustrating that a large amount of energy is required for the preparation of NaBH4 from NaBO2, e.g. from a reaction using molten magnesium. Thus, hydrolysis often provides hydrogen at RT, but is considered difficult to reverse because off-board regeneration is needed.30

6.10 Nanoconfinement

Nanoparticles may have significantly different properties compared to bulk materials due to (i) increased surface area, (ii) nanoscale diffusion distances, (iii) increased numbers of atoms in the grain boundaries and (iv) intimate contact between different reacting solids, or a melt.502,503 These nanoscale properties facilitate the release and uptake of hydrogen and enhance reaction kinetics. Thermodynamic properties may also be improved and theoretical studies predict that the increased surface area to bulk volume destabilizes MgH2 nanoparticles and thereby reduces the reaction enthalpy.523,503–506 However, thermodynamic improvements are suggested to occur only for MgH2 nanoparticles with sizes less than \( \sim 5 \text{ nm} \), while kinetic enhancement also occurs for larger nanoparticles below \( \sim 50 \text{ nm} \).123,506–508 The most widely used technique for the preparation of hydride nanoparticles is probably mechanochemical treatment, i.e. ball milling. In this top-down approach the size of the bulk material is reduced mechanically, in some cases to \( <100 \text{ nm} \). However, the samples are often contaminated with trace material from the vial and balls,52 and are challenging to characterize.509 Furthermore, nanosized particles may grow into larger particles upon continuous hydrogen release and uptake reactions. Nano materials may be directly synthesized and stabilized in a nanoporous scaffold, denoted nanoconfinement, which is discussed below.

Nanoconfinement. The topic for this section is the utilization of nanoporous materials as scaffolds for the preparation and confinement of nanosized metal borohydrides. This bottom-up approach limits the particle size of the borohydride to the pore size of the scaffold material, which allows direct production of smaller particles than mechanically obtainable. Furthermore, particle growth and agglomeration may be hindered by the compartmentalization of nanoparticles within the scaffold material and may also limit the mobility of the decomposition products and keep them in intimate close contact. Thereby, nanoconfinement may improve hydrogen absorption properties of metal hydrides. Phase segregation of decomposition products upon bulk dehydrogenation can limit hydrogen uptake reactions, which can be circumvented with nanoconfinement. A large amount of heat may also be exchanged during hydrogen release and uptake in metal hydrides and heat transport may be a kinetic limiting factor. Metal hydride powders have low thermal conductivities of \( \sim 0.1 \text{ W m}^{-1} \text{ K}^{-1} \) in contrast to carbon based support materials, which can have high thermal conductivities, e.g. 12–75 \( \text{ W m}^{-1} \text{ K}^{-1} \) for graphite.510 Nanoconfined chemistry is receiving increasing general interest and is becoming an important tool within several research areas.502,514–515 The aim of the following is to highlight selected results obtained by the nanoconfinement of metal borohydrides.

Nanoconfinement of lithium borohydride, LiBH4. Lithium borohydride can be melt infiltrated in ordered mesoporous SiO2 scaffolds (\( D_{\text{max}} \sim 5–10 \text{ nm} \)), e.g. at \( T \sim 295 \text{ °C} \), and high hydrogen pressure, e.g. \( p(\text{H}_2) = 100 \text{ bar} \), can suppress a reaction with the scaffold, which would otherwise produce lithium silicates, \( \text{Li}_2\text{SiO}_3 \) or \( \text{Li}_3\text{SiO}_4 \).516

Lithium borohydride has a higher stability than nanoconfined in carbon materials and absorbs hydrogen at significantly more mild conditions when compared to bulk LiBH4. Lithium borohydride, solvent infiltrated in mesoporous carbon scaffolds (\( D_{\text{max}} \sim 4 \text{ nm} \)), releases hydrogen at \( T \sim 300 \text{ °C} \). About 70% of the initial hydrogen content is released during the third hydrogen release cycle for LiBH4, confined in microporous activated carbon (\( D_{\text{avg}} < 2 \text{ nm} \)), when hydrogen absorption is conducted at \( p(\text{H}_2) = 100 \text{ bar}, T = 400 \text{ °C} \) for two hours. A lower stability of the hydrogen storage capacity is observed for scaffolds with larger pores, e.g. carbon aerogel, \( D_{\text{avg}} = 25 \text{ nm} \), where LiBH4 only releases 40% of the initial hydrogen content in the third release cycle. However, the observed increase in hydrogen release and uptake rates with decreasing pore size may be a kinetic effect, which may also contribute to the apparently higher cyclic stability. The hydrogen storage capacity appears to be stabilized and preserved to a higher degree for nanoconfined systems in comparison to bulk systems. This effect may be associated with a different hydrogen exchange mechanism due to the nanoconfinement of reactants and decomposition products, i.e. \( \text{Li}_3\text{B}_2\text{H}_6, \text{Li}_2\text{B}_6\text{B}_12, \text{ or LiB}_n \).516–519 However, systematic investigation into the effect of varying pore sizes suggests that diborane release and the formation of closo-boranes may be reduced using carbon scaffolds with smaller pores.520

Nanoconfinement of sodium borohydride, NaBH4. Sodium borohydride has a high decomposition temperature, \( T_{\text{dec}} > 500 \text{ °C} \), with an onset at \( \sim 470 \text{ °C} \), which may be reduced to 250 °C upon nanoconfinement in porous carbon. Here, 43% of the hydrogen content is reversible under mild conditions \( p(\text{H}_2) = 60 \text{ bar}, T = 325 \text{ °C} \) for five hours.521 Encapsulation of NaBH4 nanoparticles by a Ni layer, forming a core shell nanostructure, provides effective nanoconfinement of the molten NaBH4 core and the dehydrogenation products. These nanostructures have high stability and were cycled 5 times with hydrogen release (\( p(\text{H}_2) = 1 \text{ mbar} \)) and uptake (\( p(\text{H}_2) = 40 \text{ bar} \)) at
Borohydride system, 0.725LiBH4–0.275KBH4, which has a low melting temperature, $T = 350 \degree C$, demonstrating a hydrogen capacity of 5 wt% where ca. 80% of the H2 capacity was exchanged within 1 h.524

**Nanofinement of magnesium borohydride, Mg(BH4)2.** The synthesis of Mg(BH4)2/carbon nanocomposites from MgH2 nanoparticles supported on carbon aerogel in a B2H6/H2 atmosphere has been conducted.523 The nanocomposite exhibits a lower kinetic barrier and a lower peak hydrogen release temperature, $T = 160 \degree C$, when compared to bulk Mg(BH4)2. Furthermore, hydrogen uptake occurs at mild conditions, $T = 200 \degree C$ and $p(H_2) = 80–150$ bar.523 Magnesium borohydride has also been infiltrated into ordered mesoporous carbon (CMK-3) functionalized by Ni nanoparticles (5 wt%).524 The hydrogen release temperature was significantly decreased with onset at $T = 75 \degree C$ and peak release at $T = 155 \degree C$, compared to $270 \degree C$ and $>350 \degree C$, respectively, for pure Mg(BH4)2. Hydrogen release also occurs with faster kinetics in the nanoconfined system.524

**Lithium-potassium borohydride, LiBH4–KBH4.** Eutectic melting, reactive hydride composites and nanofinement all have the potential to improve the reversible hydrogen storage capacity in metal borohydrides. The combined effect of all three methods has been explored in an attempt to improve the lithium-potassium borohydride system, 0.725LiBH4–0.275KBH4, which has a low melting temperature $T_m = 105 \degree C$.48 The bulk eutectic mixture and the RHC with magnesium, LiBH4–KBH4–Mg and LiBH4–KBH4–MgH2, have been melt-infiltrated into a nanoporous carbon scaffold. The decomposition of 0.725LiBH4–0.275KBH4 (and the RHC) initiates simultaneously with melting at 105 $\degree C$, but remains slow until higher temperatures are reached $T > 300 \degree C$. Eutectic melting appears to improve the kinetics of the hydrogen de- and absorption, while nanoconfinement lowers the main hydrogen release temperature in the first cycle by up to 200 $\degree C$.48

**Lithium–magnesium borohydride, LiBH4–Mg(BH4)2.** The decomposition of nanofinned lithium–magnesium borohydride, Li11BD4–Mg11BD3, was investigated by thermal analysis and small-angle neutron scattering.525 The dehydrogenation temperature was decreased by up to 60 $\degree C$ in the nanofinned system and occurred without the formation of diborate, B2D6, or closo-boranes, which evolve from the bulk mixture.525

**Lithium–calcium borohydride, LiBH4–Ca(BH4)2.** Eutectic melting LiBH4–Ca(BH4)2 has been nanofinned in different types of carbon scaffolds with surface areas 500 to 2600 m2 g–1 and pore sizes 5–50 nm. In general, the nanofinned systems provide faster kinetics and higher stability over several cycles of hydrogen release and uptake, which also occurs at more mild conditions.369,526–528 Nanoconfined LiBH4–Ca(BH4)2 in CO2-activated scaffolds release up to 80 or 73% of the calculated hydrogen content in the second and third hydrogen release cycle, respectively. They can potentially reach hydrogen storage densities in the range ~10–12 wt% H2 for scaffolds with large pore volumes, 3.1 mL g–1, and large surface areas, 2660 ± 208 m2 g–1.527

**Reactive hydride composites, 2LiBH4–MgH2.** The first nanofinned reactive hydride composite (RHC) 2LiBH4–MgH2 was infiltrated in a nanoporous RF-CA scaffold ($D_{325} \approx 21$ nm) in an attempt to combine the beneficial effect from nanofinement and RHC.529 The onset temperature for hydrogen release is reduced by 90 $\degree C$ and the nanofinned sample desorbed 3.9 wt% H2 at 390 $\degree C$, $p(H_2) = 2$ bar after 20 h, in accordance with the calculated hydrogen content for the sample of 3.9 wt% H2. The hydrogen absorption was performed under relatively mild conditions and the fourth desorption released 3.0 wt% H2, i.e. 92 and 74% of the capacity is preserved over three and four cycles, respectively.529 Similar results were obtained with other methods for infiltration and other scaffold materials.592,530,531 However, improved capacity as been achieved for 2LiBH4–MgH2 encapsulated within graphene, where an impressive reversible capacity of 8.9 wt% H2 is reported after 25 cycles at 350 $\degree C$.532

Functionalization of nanoporous scaffolds may further improve kinetics during hydrogen release and uptake. The stability during cycling was explored for TiCl3,533 TiCl4,534 and ZrCl4.535 Several other composites based on lithium borohydride have also been successfully nanoconfined, e.g. 2LiBH4–NaAlH4,536 LiBH4–Mg2NiH4537 and LiBH4–NaBH4.538

7. New properties and future perspectives of metal borohydrides

Metal borohydrides have diverse compositions with overwhelmingly rich structural chemistry, which has led to new perspectives for the future utilization of this fascinating class of new materials. Furthermore, a wide range of approaches for tailoring the composition and structure of metal borohydrides was discussed in previous sections, along with the effect of additives, reactive hydride composites and nanoconfinement etc., in Section 6. This section provides the state-of-the-art for new perspectives on the utilization of metal borohydrides for practical applications, in addition to those involving their extreme energy densities. This chapter reveals multiple novel properties for metal borohydrides, e.g. optical, magnetic, ion or semi conductivity.

7.1 Porous metal borohydrides for gas adsorption

The extreme structural flexibility found for metal borohydrides is highlighted by magnesium borohydride, as described in detail in Section 3.1. The γ polymorph has 33% ‘empty space’ and a 3D network of interpenetrated channels with pore sizes in the range 5.8–8.8 Å, being the first complex metal hydride with large permanent porosity.3 Furthermore, it is the first complex metal hydride capable of reversibly adsorbing hydrogen, nitrogen and other small molecules such as CH2Cl2. The adsorption of dichloromethane, CH2Cl2 is reversible and fast (within minutes), occurring near room temperature with negligible unit cell expansion, forming $\gamma$-Mg(BH4)2-0.18CH2Cl2. Here, the only host-guest contacts are the dihydrogen bonds B–H–C of 1.9 and 2.0 Å. There are neither substantial guest–guest interactions nor coordination of the guest to the metal atom ($\gamma$-Mg–H–C 3.5 Å, Mg–Cl 4 Å). The host–guest interactions illustrate the selectivity of the anionic borohydride groups being capable of binding positively charged moieties. Neutral molecules such as nitrogen (N2) and hydrogen (H2) also adsorb in the $\gamma$-Mg(BH4)2 framework at elevated pressure and low temperature. In situ SR-PXD data revealed storage capacities of $\gamma$-Mg(BH4)2: 0.63N2 at $p(N_2) = 30.6$ bar and $\gamma$-Mg(BH4)2: 0.80H2 at $p(H_2) = 105$ bar at...
This journal is © The Royal Society of Chemistry 2017 Chem. Soc. Rev., 2017, 46, 1565--1634 | 1617

−193 °C. The latter corresponds to a total of 17.4 wt% H₂, including the hydrogen in the framework. Nitrogen or hydrogen molecules are grouped into diffuse rods within the structure, centered around (1/8, 1/8, 1/8) and extended along the cube diagonal (x, x, x), which indicates van der Waals interactions occur between gas molecules and BH₄ groups. The desorption isobars (p(H₂) = 105 bar, p(N₂) = 30.6 bar) indicate that the gas molecules are leaving the framework at relatively high temperatures; desorption of hydrogen starts at −143 °C, with ~50% H₂ remaining inside the pores at −73 °C. This suggests the potential for efficient hydrogen storage in related materials at moderate temperatures. The isosteric heats of adsorption, Q_st, of nitrogen and hydrogen in γ-Mg(BH₄)₂ were determined to be: Q_st(N₂) ≈ 15 kJ mol⁻¹ and Q_st(H₂) ≈ 6 kJ mol⁻¹ (average value), with Q_st > 7 kJ mol⁻¹ at a loading of 15 mg H₂ g⁻¹.³ The latter value is among the highest values measured for MOFs and other porous solids.²³³

The structural similarity between metal borohydride frameworks and covalently bonded metal organic frameworks (MOFs) is illustrated by the significant degree of directionality in the interaction between a metal and the complex borohydride anion. In particular, the same framework topology is observed for both γ-Mg(BH₄)₂ and the zinc imidazolate framework ZIF-72,²³⁴,²⁴⁰ and several metal borohydrides have interpenetrated framework structures similar to MOFs, e.g. MZn₂(BH₄)₃ (M = Li and Na) and Li₂Mg₂Zn₁₂(BH₄)₁₅ (M = Mg, Mn). Although, there are other borohydrides that mimic the tetrahedral framework of cristobalite, such as δ-Mg(BH₄)₁₂, or α- and β-Cd(BH₄)₂. γ-Mg(BH₄)₂ shares gas adsorption properties with MOFs and also shares an ‘amorphous’ to ‘crystalline’ phase transition at elevated pressures. However, metal borohydride frameworks give rise to specific guest–host interactions with hydridic atoms of the BH₄⁻ anion, which do not occur in MOFs.

7.2 Metal borohydrides as ion conductors

Hydrides of intermetallic compounds such as LaNi₅H₆ have been widely used as electrodes in rechargeable batteries, replacing toxic metal Cd in the Ni–Cd pair. Following the report on the conversion reaction of the redox couple MgH₂/Li₅BH₃, many other complex metal hydrides have been studied as battery electrodes.⁷,₂³⁴,²⁴³ The use of borohydrides in batteries is very recent, and is actually limited to solid-state electrolytes (Fig. 28). This is despite several reactions having been proposed theoretically by ab initio calculations for conversion electrodes in Li-batteries, including a promising reaction, based on Mg(BH₄)₂, that results in an enormous theoretical charge capacity of 3969 mA h g⁻¹.⁵⁴⁴ The numerous advantages of metal borohydrides as battery materials include their high weight (high charge density), apparent material compatibility with Li and Na electrodes, thermal and electrochemical stability, and easy manufacturing of the electrolyte/electrode interface and thus of the whole battery.

Fast Li-ion conduction in a borohydride was first discovered in the high temperature polymorph h-LiBH₄,²⁵⁴ where conductivities exceeding 2 × 10⁻³ S cm⁻¹ above 110 °C (the polymorphic transition temperature) were reported. Since then, several other solid-state metal-borohydride and borohydride-based mixed-anion electrolytes have been developed that exhibit fast Li- and Na-ion conduction.²⁹

**Lithium borohydride halides as Li-ion conductors.** Above the polymorphic transition temperature of 110 °C, the Li ion conductivity of the HT-polymorph h-LiBH₄ is three orders of magnitude higher than that of the RT-orthorhombic polymorph, o-LiBH₄. It was shown that anion substitution BH₄⁻ ↔ X⁻ (X = Halide) stabilizes the h-LiBH₄ polymorph down to room temperature, e.g. h-Li[BH₄]₁₋ₓ[N₂]ₓ.¹⁵⁴ The RT Li ion conductivity in the halide stabilized h-LiBH₄ reaches 2 × 10⁻³ S cm⁻¹.¹⁴³

**Alkali rare-earth spinel-like borohydride halides as Li-ion conductors.** Recently, a new series of mixed-cation mixed-anion borohydride chlorides based on rare-earths elements, Li⁺[BH₄]ₓCl, M⁺ = La, Gd, and Ce, was discovered using combined mechanochemical synthesis and heat treatment from MCl₃−LiBH₄ (1 : 3) mixtures.¹⁷⁸ This growing class of materials has a new structure type and contains isolated tetranuclear anionic clusters [M₄Cl₄(BH₄)₁₂]⁺ with a distorted cubane M₄Cl₄ core, charge-balanced by Li⁺ cations. This compound can also be understood as containing fragments of the spinel structure, i.e. LiCl₄ tetrahedra and M₄Cl₄ cubane. The Li⁺ ions are disordered and occupy 2/3 of the 12d Wyckoff sites and DFT calculations indicate that LiCe[BH₄]Cl is stabilized by larger entropy rather than smaller enthalpy. Thus, the structural model and DFT calculations agree well with the very high lithium ion conductivity measured for LiCe[BH₄]Cl, 1.03 × 10⁻⁴ S cm⁻¹ at T = 20 °C. The other members of this series of isostructural compounds, LiLa[BH₄]Cl and LiGd[BH₄]Cl, also have high Li-ion conductivities at RT and low electronic conductivities, see Table 21. This class of materials, Li⁺[BH₄]ₓCl, holds significant potential in the design of other new ion conductors, which is not yet fully explored. Cation and anion substitution may allow for the preparation of new sodium or magnesium ion conductors.
Other borohydride-based mixed-anion ion conductors. Some metal amides and imides are good ion conductors, such as lithium imide Li2NH with an excellent solid-state Li-ion conductivity at RT ($2.5 \times 10^{-4}$ S cm$^{-1}$), but with very low electrochemical stability, 0.7 V. Addition reactions between nitrogen-based compounds and metal borohydrides have therefore been studied, leading to several novel solid-state electrolytes such as Li$_2$(BH$_4$)(NH$_2$) and Li$_4$(BH$_4$)(NH$_2$)$_3$ with Li-ion conductivities of up to $2 \times 10^{-4}$ S cm$^{-1}$ at RT. The disordered anti-perovskite Na$_3$(BH$_4$)(NH$_2$)$_3$ was also recently shown to have a Na-ion conductivity of $2 \times 10^{-6}$ S cm$^{-1}$ at RT.553 and Mg-ion conductivity in tetragonal Mg(BH$_4$)$_2$(NH$_2$) reaches $1 \times 10^{-6}$ S cm$^{-1}$ at 150 °C.570

Alkali rare-earth garnet borohydrides as Li-ion conductors. The oxide-borohydride analogy is a new tool for the design of novel materials with useful properties, clearly illustrated by the recently discovery of metal borohydride-garnets. Metal borohydride-garnets were synthesized,168 based on the fact that doped lanthanide-oxide garnets Li$_3$M$_2$O$_12$ (where M denotes various metals) are excellent Li-ion conductors.554 The new metal borohydride garnet analogues, Li$_3$K$_3$Ce$_2$(BH$_4$)$_12$ and Li$_3$K$_3$La$_2$(BH$_4$)$_12$ show high room temperature Li-ion conductivity ($3 \times 10^{-7}$ and $6 \times 10^{-7}$ S cm$^{-1}$). Most importantly, these values are 5 to 6 orders of magnitude above those of undoped metal oxide garnet conductors. The effect of heterovalent cation substitution was investigated as a means of tailoring the ion conductivity. Substitution with divalent Sr$^{2+}$ and Eu$^{2+}$ showed that the Li-ion conductivity can be increased by one order of magnitude in the whole temperature range measured.168

Higher-boranes and mixed anion higher borane-borohydrides as Li- and Na-ion conductors. Higher boranes such as B$_{12}$H$_{10}^{2-}$ or B$_{12}$H$_{12}^{2-}$ form inorganic salts which, in the case of Na- and Li-based compounds, are good ionic conductors when the cations become disordered in HT-phases, and are the focus of a recent review.252 The Na-ion conductivity of Na$_3$B$_{12}$H$_{12}$ increases by 3 orders of magnitude between the phase transition from the ordered monoclinic phase to the disordered cubic phase at 256 °C, and reaches a conductivity value of close to 0.1 S cm$^{-1}$.546

The concept of anion-mixing was applied to this novel class of solid electrolytes generating Na$_3$BH$_4$B$_{12}$H$_{12}$ and (Li$_{0.5}$Na$_{0.5}$)B$_{12}$H$_{12}$, capable of conducting either Na$^+$ or both Na$^+$ and Li$^+$ ions. Unlike order–disorder governed dodeca- and decaboranes the cationic mobility is not entropically activated in Na$_3$BH$_4$B$_{12}$H$_{12}$ and (Li$_{0.5}$Na$_{0.5}$)B$_{12}$H$_{12}$, thus a HT phase transition is not required to enable fast ion conduction. Na$_3$BH$_4$B$_{12}$H$_{12}$ reaches RT conductivity values close to $10^{-3}$ S cm$^{-1}$. (Li$_{0.7}$Na$_{0.3}$)B$_{12}$H$_{12}$, on the other hand, forms only by a reversible chemical reaction at 230 °C, which is accompanied by a dramatic increase in ionic conductivity $>10^{-1}$ S cm$^{-1}$. Such high temperatures are nevertheless within reasonable limits for large-scale facilities, which operate at over 300 °C in the case of Na–S power grids, for instance.

### The paddle-wheel mechanism for ion conduction

Many potential solid-state ionic conductors can be rationally designed from salts containing dynamically disordered complex anions. In such materials, the conduction is not purely vacancy-dependent. The structure typically contains polyanions [AB$_y$PO$_4$]$_{n-}$ with covalent A-B bonds (e.g. PO$_4^{3-}$, SO$_4^{2-}$ and NO$_3^-$), where the rotational diffusion of [AB$_y$PO$_4$]$_{n-}$ promotes cationic conductivity, decreasing the associated activation energy via a so-called “paddle-wheel” mechanism. After the first reports on a possible “paddle-wheel” mechanism of the complex anion [BH$_4$]$^{-}$ in superionic metal borohydrides,557–559 it was shown by solid state NMR and quasi-elastic neutron scattering,560,561 that the high rotational mobility promotes superionicity in the respective materials (Fig. 29). There is also structural evidence for the “paddle-wheel” Ag$^{+}$ migration mechanism in Ag$_2$B$_{12}$H$_{12}$, where Ag$^{+}$ cations can only occupy particular atomic sites in the crystal structure for certain [B$_{12}$H$_{12}$$^{2-}$] anion orientations.362

#### Table 21

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit cell $a$ (Å)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\rho_m$ (wt%)</th>
<th>$\rho_f$ (kg H$_2$ m$^{-3}$)</th>
<th>$T_{dec}$ (°C)</th>
<th>Li-ion $\times 10^{-4}$ (S cm$^{-1}$)</th>
<th>Electronic $\times 10^{-8}$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiLa(BH$_4$)$_3$Cl</td>
<td>11.7955</td>
<td>1.86</td>
<td>3.36</td>
<td>96.4</td>
<td>260</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>LiCe(BH$_4$)$_3$Cl</td>
<td>11.7204</td>
<td>2.61</td>
<td>5.33</td>
<td>99.8</td>
<td>260</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>LiGd(BH$_4$)$_3$Cl</td>
<td>11.5627</td>
<td>2.16</td>
<td>4.95</td>
<td>102.6</td>
<td>260</td>
<td>3.6</td>
<td>9</td>
</tr>
</tbody>
</table>

Fig. 29: Polymorphic transition temperatures for fast anion rotational motion in selected boron-based solids.24,101,132,555,560,563–572
7.3 Metal borohydrides with optical properties

Recent reports on perovskite-type borohydrides motivated investigations into lanthanide-luminescence in perovskites and double perovskite host lattices such as CsCa(BH₄)₂ or LiCs₂Y(BH₄)₆. These systems provided the structural simplicity required in order to study light emission in metal borohydrides, but also enabled tailoring of the emitted spectrum and the efficiency of the light-emitting process in these potential solid-state borohydride phosphors. Very little is known about the Eu(II) luminescence in metal hydrides. Kunkel et al. have reported relatively low quantum yields of yellow-red emission in simple binary alkaline earth hydrides Eu₂M₄₋ₓHₓ(M = Ca, Sr, Ba) as well as in perovskite hosts based on alkali and alkaline earth metals such as KMgH₃, NaMgH₄ and LiBaSrH₄, where the emission ranges from yellow to green. While such red-shifts of the Eu(II) emission were explained on the basis of the nephelauxetic effect, in metal borohydrides the bright Eu(II) emission is centred in the blue regime, which is far more common for Eu(II). To our knowledge, the first reports on Eu(II) luminescence in a complex hydride date back only very recently, and is similar to the unsolvated homoleptic borohydrides. These compounds show little concentration quenching and a high quantum yield, rare observations for bulk Eu(II)-based phosphors.

CsPb(BH₄)₃ crystallizes in the perovskite type, and is the first borohydride to show a bandgap in the visible light regime, while metal borohydrides commonly are wide gap insulators with band gaps above 5 eV. This material was synthesized in view of the current revolution in photovoltaics, triggered by the hybrid perovskites AMX₃, where A is a bulky organic cation such as CH₃NH₃ or HC(NH₂)₂, M is a group IV metal (Pb, Sn, Ge) and X is a halogen. The substitution X ↔ BH₄ may harness alterations to the band gap of the material and hence to the light spectrum that may be harvested by the material.

7.4 Metal borohydrides with magnetic properties

Most physical properties related to magnetism arise from long-range magnetic order, which is dependent on the exchange interaction between magnetic centers, and requires unpaired electrons in open-shell configurations. The interesting transition metals used to generate such ordering are prone to reduction by the borohydride group and hence not stable. Thus, magnetic/electronic correlation has hitherto not been observed in metal borohydrides. Indeed, the only transition metal with an open shell reported amongst borohydrides is Mn, with oxidation state Mn²⁺. On the other hand, and as shown throughout this review, all di- and many trivalent oxidation states of rare-earth elements form stable borohydride compounds. A series of bimetallic Gd-borohydrides was investigated with the aim of identifying paramagnetic salts and investigating their properties related to the magnetic entropy change —ΔSM, which is one of the key properties of magnetic refrigerants. Oxed to its isotropic f⁷ electronic configuration, and hence its large ground state spin multiplicity, most competitive coolers have been based on Gd³⁺, such as the benchmark material GGG (gadolinium gallium garnet Gd₃Ga₅O₁₂). Additionally, a paradigm shift is currently taking place, attempting to develop Mn²⁺-based materials for sub-Kelvin cooling. Similar to most energy-related materials, restrictions imposed on potential candidates are, in addition to weight and volume, the absence of any long-range ordering down to very low temperatures, in order to replace costly He-3. The mass of the borohydride ligand is close to that of the oxide anion, and hence much lighter than most of the organic ligands employed in MOF materials currently under investigation. The magnetic entropy change per unit mass is thus highly competitive and the recently reported K₂Gd(BH₄)₅ reaches values that lie amongst the 5 highest reported to date, and further increases in the magnetic to non-magnetic mass ratio can be expected due to cation substitution NH₄⁺ ↔ K⁺. Furthermore, many metal borohydrides, both pseudo-binary and -ternary, crystallize in packed structure types derived from ccp or hcp, which allows sensible values concerning the magnetic entropy change per unit volume. Both pseudo-binary Mn(BH₄)₂ as well as Mn-bearing double-salts are stable compounds that are paramagnetic down to at least 2 K and their magnetic refrigeration properties will be investigated in the future. The thermal conductivities of some simple metal borohydrides lie in the range of 2–5 W m⁻¹ K⁻¹ which is appropriate for the heat transfer in magnetic cooling devices.

7.5 Perspectives for design of novel metal borohydrides

Borohydrides are beginning to play a role as interesting materials in a variety of technical fields. For instance, a semiconductor compound CsPb(BH₄)₃ was recently reported, which relates well to the plombohalides also under investigation for photovoltaics, however, it is not chemically stable for a long time period. Neutron shielding applications were also proposed due to the high absorption cross section of boron (767 barn for natural isotope abundance). In this context, the energy transfer from the neutron to the material could also be exploited to develop neutron detectors (or scintillators in general) where a luminescent RE-ion emits light upon irradiation of the host, similar to what has been done with borates in the past.

The hydrolysis of metal borohydrides has been investigated since 1953 as a mechanism to quickly generate hydrogen gas from a solid-state storage medium. This research field is still evolving and current research strives for a cost reduction for using hydrolysis as a reversible energy generation and storage system. In a similar manner, metal borohydrides are also investigated as reducing agents in direct borohydride fuel cells. A redox reaction occurs between the borohydride anion itself and an oxidant to generate electricity. These fuel cells offer advantages over traditional fuel cells due to their operating temperatures, voltages, and high power densities. Further reduction reactions have also recently been investigated with the sulfurization of metal borohydrides.

Perovskite-type compounds were briefly discussed in Section 3.4 and 3.5. It was also mentioned that the homopolar dihydrogen contacts between hydridic species pertaining to adjacent BH₄⁻ ligands generate lattice instabilities. It can be assumed that such close contacts constitute a novel kind of “weak” interaction in perovskites that may be further exploited regarding the stabilization of low symmetries and the possibility of switching between polar bi-stable configurations of the
structure, thus potentially culminating in a novel type of geometric ferroelectricity. From an applied viewpoint, such a scheme would be closely related to the supramolecular ferroelectrics where ferroelectricity arises from various kinds of weak interactions. From a fundamental point of view such hydridic interactions are both highly interesting and timely, forming part of the ever growing family of intriguing weak interactions. Homoeletic metal borohydrides, but also heteroleptic ones, offer a unique opportunity of studying this hydridic interaction, which currently challenges all levels of ab initio theory.

Indeed, homo- and heteropolar interactions between protons and hydrides could potentially be meticulously implemented in order to tailor lattice distortions in hybrid organic–inorganic borohydride-based materials. Further means of taking influence on symmetry-determining parameters such as order, polarizability and dipole moments include anion-substitution of the BH4 group by amides or halides, but also within the BH4 group by the scheme \( H^+ \leftrightarrow F^- \). As such, this inorganic family of materials could be placed into the landscape of molecular and supramolecular chemistry. In this context, we could extend the focus from homoeletic metal borohydrides to the heteroleptic compounds, where the tetrahydridoboranate anion may be employed as a hydridic building block in the crystal engineering of molecular and metalorganic compounds.

All in all, this young but vast family of materials offers exotic and enticing new chemistry to materials scientists working in energy-related fields.

7.6 CO2-recycling with metal borohydrides

Our current energy system is, to a large extent, based on fossil fuels, i.e. carbon-based materials, and our energy system is not considered a ‘closed materials cycle’, because we consume these fuels by combustion on a much faster rate than they are produced by photosynthesis and geological processes. Hence, in order to close the carbon cycle, we must find a route to convert the produced CO2 into useful fuel. Some metal borohydrides have recently been investigated in this context, of CO2 capture and recycling. It has been suggested to generate hydrogen by a CO2-enhanced hydrolysis of KBH4 where the waste products of fossil fuel combustion, i.e. CO2 and H2O, can be used in a further cycle for hydrogen production for fuel cells. The proposed reaction results in the formation of a carbonate salt, water and gaseous hydrogen. The porous polymorph \( \gamma\)-Mg(BH4)2 was also found to have potential in CO2 recycling where upon CO2-reduction chemical products such as formate or methoxy-species are produced. Owing to the large specific surface area of \( \gamma\)-Mg(BH4)2, CO2 conversion occurs with unprecedented fast kinetics at 30 °C and \( p(CO_2) = 1 \) bar. Metal borohydrides with low surface area, such as KBH4, readily react with CO2 under mechanochemical conditions at room temperature, yielding mainly formylhydroborates. Whilst, solid–gas reactions in the KBH4–CO2 system at high temperature reveal the formation of methanol and methane under water-free conditions.

7.7 A possible paradigm shift for solid state hydrogen storage

The design of a possible successor for liquid fuels like diesel and gasoline faces numerous challenges. About twenty properties need to be optimized simultaneously, which span wide areas including low cost, fast energy recharging, large gravimetric and volumetric energy storage densities, low operation temperature etc. This review has illustrated numerous examples of the rational design of novel metal borohydrides with interesting properties, e.g. using borohydride–oxide analogies, and also the possibilities of post-modification of the materials, e.g. by anion substitution etc. Thus, new classes are likely to be discovered in the near future. Two decades ago, alloying metals that reacted with hydrogen to different degrees tended to provide an alloy with intermediate properties. During the past decade, reactive hydride composites were explored, which have an average hydrogen storage capacity compared to the individual components. Recently, the first stabilization of the metastable compound, NH4BH4 was discovered by a reaction with the more stable metal borohydride, Ca[BH4]2. The product, NH4Ca[BH4]3, has a different decomposition profile and may be considered as the first member of a larger series of compounds. Notice that, the series BH4, NH4, CH4 are isoelectronic and the hydrogen density of NH4BH4, \( \rho_V = 157 \text{ g H}_2 \text{ mL}^{-1} \) and \( \rho_m = 24.5 \text{ wt% H}_2 \), is even higher than liquid natural gas, \( \text{CH}_4(\text{l}) \), \( \rho_V = 137 \text{ g H}_2 \text{ mL}^{-1} \) and \( \rho_m = 24.8 \text{ wt% H}_2 \). Recently, other borane based materials have been discovered, e.g. hydrazine bisborane, \( \text{BH}_3\text{N}_2\text{H}_6 \).

8. Conclusions

Metal borohydrides have received increasing interest over the past decade with a wide range of new materials discovered. An extremely rich chemistry has been outlined including fascinating structural flexibility and a wide range of elemental compositions. Furthermore, derivatives of metal borohydrides have also been discovered, which strongly contribute to the diverse chemistry. These materials have a wide range of unexpected properties, which may lead to new applications in the future. The systematic work on crystalline metal borohydrides has provided enough results to understand the basic principles which control their crystal structures, and consequently their properties. One of the most important understandings is the description of borohydrides as ionocovalent solids comparable with many other inorganic compounds such as oxides or halides. The crystal chemistry of borohydrides may then be explained by known principles such as Pauling rules, involving the polarisation of the rather soft borohydride anion, various factors based on ionic radii etc. A consequences is that the huge crystal chemistry knowledge accumulated for oxides or halides can be applied to borohydrides in designing new compounds with desired chemical composition, atomic coordination and, in the best case, with desired properties.

This review has outlined trends across the synthetic approaches for metal borohydrides and their halide and neutral molecule complexes, classing reactions into addition, metathesis, or complex metathesis-addition mechanisms. Trends in structural chemistry have also been listed and over 100 compounds are reported for mono-, bi- and tri-metallic borohydrides. Many similarities can be found within certain classes of borohydride, for example those rich in alkali metals, or rare earth metals. The metal borohydride halides
can also be classed into those compounds that exhibit completely ordered, partly ordered, or completely disordered structures. Many new metal borohydrides have been discovered that are complexed with neutral molecules that can exhibit many interesting properties suitable for technical applications, but have also been shown to influence the decomposition pathway of the parent borohydride. A number of metal borohydrides have been shown to melt individually or in eutectic compositions, but often decompose shortly after in often multi-step pathways that are temperature and pressure dependent. The kinetics of hydrogen release and uptake have typically been poor for metal borohydrides and traditional additives have not been successful in enhancing kinetics, as they have been in many other metal–hydrogen systems. However, techniques including reactive hydride composites and nanoconfinement have offered new possibilities in improving kinetics and thermodynamics of hydrogen release and uptake. The rehydrogenation of metal borohydrides can be performed under more mild conditions by controlling the desorption by-products to restrict the quantity of higher boranes, i.e. with lower desorption temperatures or with hydrogen back-pressure. Recently, metal borohydrides have been studied for new applications, taking advantage of cation conduction in the solid-state, optical properties, porous structures for gas adsorption, and also magnetic properties.

The knowledge gained mainly during the past decade of research within metal borohydrides is presented in this review, which provides analysis of the trends in synthesis, structure and properties. An overview of the current frontiers of research and new perspectives for the future utilization of this fascinating class of new materials is also provided. A wide range of approaches for tailoring the composition and structure of metal borohydrides is also discussed, which provides new methods for tailoring properties. This is an important step towards rational design of new functional materials. This review also demonstrates that there is still plenty of room for discovering new metal borohydrides since these types of materials have extreme flexibility in composition, structure and properties.

Acknowledgements

The work was supported by the Danish National Research Foundation, Center for Materials Crystallography (DNRF93), The Innovation Fund Denmark (project HyFill-Fast), and by the Danish Research Council for Nature and Universe (Danscatt) and the Danish Council for Independent Research (HyNanoBorn, DFF – 4181-00462). MP acknowledges financial support from The Danish Council for Independent Research for DFF Mobility 1325-00072. We are grateful to the Carlsberg Foundation. This work was partly supported by the Swiss National Science Foundation and Fonds de la Recherche Scientifique – FNRS.

References


