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Introduction

The human consumption of energy has increased over the past decades, and has mainly been covered by burning fossil fuels at an increasing rate, which has led to an increase in CO₂ levels in the atmosphere.^{1,2} Despite an abundance of available renewable energy from sun and wind, these energy sources are intermittent and fluctuate over time and geography. Thus, energy storage is required to compensate for the variability in renewable energy fluxes, and hydrogen is a promising energy carrier with the highest gravimetric energy density among all known compounds ($\rho_m = 120 \text{ MJ kg}^{-1}$).³ However, compressed hydrogen gas has a low volumetric energy density ($\rho_V = 8.5 \text{ MJ L}^{-1}$).

Hydrogenation properties of lithium and sodium hydride – *closo*-borate, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, composites[†]

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The hydrogen absorption properties of metal *closo*-borate/metal hydride composites, $M_2B_{10}H_{10}$ –8MH and $M_2B_{12}H_{12}$ –10MH, M = Li or Na, are studied under high hydrogen pressures to understand the formation mechanism of metal borohydrides. The hydrogen storage properties of the composites have been investigated by *in situ* synchrotron radiation powder X-ray diffraction at $p(H_2)$ = 400 bar and by *ex situ* hydrogen absorption measurements at $p(H_2)$ = 526 to 998 bar. The *in situ* experiments reveal the formation of crystalline intermediates before metal borohydrides (MBH₄) are formed. On the contrary, the $M_2B_{12}H_{12}$ –10MH (M = Li and Na) systems show no formation of the metal borohydride at *T* = 400 °C and $p(H_2)$ = 537 to 970 bar. ¹¹B MAS NMR of the $M_2B_{10}H_{10}$ –8MH composites reveal that the molar ratio of LiBH₄ or NaBH₄ and the remaining B species is 1:0.63 and 1:0.21, respectively. Solution and solid-state ¹¹B NMR spectra reveal new intermediates with a B:H ratio close to 1:1. Our results indicate that the $M_2B_{10}H_{10}$ (M = Li, Na) salts display a higher reactivity towards hydrogen in the presence of metal hydrides compared to the corresponding [$B_{12}H_{12}$ ² composites, which represents an important step towards understanding the factors that determine the stability and reversibility of high hydrogen capacity metal borohydrides for hydrogen storage.

The volumetric density can be improved by storing hydrogen in a solid, for example in reversible metal hydrides.³⁻⁵ Metal borohydrides have been proposed as solid-state hydrogen storage media due to their high hydrogen content and potential reversibility.⁶⁻⁹ The challenge of using metal borohydrides as hydrogen carriers is that they often possess high hydrogen release temperatures, coupled with harsh conditions needed for hydrogenation.¹⁰⁻¹⁴ These issues have generated interest in the synthesis and investigation of hydrogen storage properties of bi- and tri-metallic main group/transition metal borohydrides with tunable hydrogen desorption temperatures.15-21 Another approach has been to stabilize unstable borohydrides *e.g.* $Fe(BH_4)_2$ and $Co(BH_4)_2$, using ammonia.²² Reactive hydride composites have also been used to thermodynamically destabilize metal borohydrides by altering the decomposition mechanism, e.g. LiBH₄-MgH₂, or by changing the morphology of the sample, e.g. NaBH₄-KBH₄, where the solid is transformed into a liquid.^{23,24} Finally, several materials have been studied as catalysts for hydrogen uptake and release, e.g., transition metals and their halides and oxides.²⁵⁻²⁷ However, to the best of our knowledge, an efficient catalyst for breaking and forming B-H bonds has not yet been discovered.

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Polyhydro-closo-polyborates (also known as closo-borates), $B_n H_n^{2-}$ (*n* = 6–12), are anions comprised of boron atoms with solely terminal hydrogen in closed polyhedral clusters. These compounds can be prepared through a variety of solid-state and solution synthetic approaches.²⁸ Higher *closo*-borates, such as dodecahydro-*closo*-dodecaborates $([B_{12}H_{12}]^{2-}$ salts) and decahydro-closo-decaborates ([B10H10]2- salts) are often assumed to be intermediates in the mechanism for hydrogen release and uptake in metal borohydrides, $M(BH_4)_x$, and their relatively high stability may retard the reversibility of these reactions.²⁸⁻³¹ The formation of higher *closo*-borates during decomposition of metal borohydrides may occur in a reaction between the metal borohydride and transient diborane (B_2H_6) . The formation of either Li₂B₁₀H₁₀ or Li₂B₁₂H₁₂, depending on temperature, has clearly been observed by mechano-chemical treatment of LiBH₄ in a diborane atmosphere.³² The formation of Li₂B₁₂H₁₂ is also observed for the reactive hydride composite, LiBH₄-MgH₂-Al, which shows decreasing reversible hydrogen content commensurate with increasing amounts of Li2B12H12 during cycling of hydrogen release and uptake.30 In a similar manner, magnesium borohydride, Mg(BH₄)₂, decomposes under vacuum at $T \approx 200$ °C and forms arachno-Mg(B₃H₈)₂, which can absorb hydrogen at more moderate conditions, *e.g.*, $p(H_2) = 120$ bar and T = 250 °C, in contrast to the *closo*-borates.³³

Hydrogen release and absorption reactions in boron-based hydrides remain not fully understood. Density functional theory (DFT) calculations have been used to predict reaction enthalpies for multiple chemical reactions that reversibly store hydrogen and to identify promising reactions with large storage capacities and relevant thermodynamic properties.^{34,35} Experiments have revealed that LiBH₄ decomposes into LiH and B, with Li₂B₁₂H₁₂ as an intermediate phase. Theoretical work has suggested formation of $(\text{LiBH}_4)_n$, $n \leq 12$, nanoclusters, which decompose into mixed Li_nB_n clusters via a series of intermediate clusters of $Li_n B_n H_m$, $(m \le 4n)$.³⁶ A variety of other intermediates have also been suggested, with the $[B_{12}H_{12}]^{2-}$ as the most stable, which is considered to hamper hydrogen uptake reactions.^{37,38} Experimental determination of structure and composition of intermediates is often hampered by poor crystallinity and difficulties in preparation of phase-pure samples.

Recently, $M_2B_{12}H_{12}$ -10MH composites were hydrogenated at $p(H_2) = 1000$ bar and 500 °C for 72 hours forming the corresponding metal borohydrides, MBH₄, M = Li, Na or K.³⁹ This has prompted the present hydrogenation study of *closo*-polyborate-containing composites, $M_2B_{10}H_{10}$ -8MH and $M_2B_{12}H_{12}$ -10MH, M = Li or Na, using less harsh conditions in custom-made hydrogenation equipment designed to monitor the hydrogen uptake.⁴⁰ In doing so, the reaction pathway and kinetic issues associated with the hydrogenation of *closo*-borate containing samples can be assessed. It is expected that this information will provide insights into the "boron-sink" *closo*-borates in borohydride-based hydrogen storage systems. The mechanism for hydrogen uptake is investigated using *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD), *ex situ* powder X-ray diffraction (PXD), Fourier transform infrared spectroscopy

(FT-IR), as well as solution and solid-state ¹¹B NMR and ²³Na magic-angle spinning (MAS) NMR.

Experimental

Sample preparation

Lithium hydride, LiH (Sigma-Aldrich, 95%), and sodium hydride, NaH (Sigma-Aldrich, 95%), were used as supplied. Anhydrous Li₂B₁₀H₁₀ and Na₂B₁₀H₁₀ were synthesized from decaborane (B10H14, Katchem), dimethyl sulfide, liquid ammonia and the respective hydroxides MOH, using a method described elsewhere.41 Li₂B₁₂H₁₂·4H₂O and Na₂B₁₂H₁₂·xH₂O (Katchem) were heated to 245 °C under dynamic vacuum for 12 hours to remove coordinated water. The *closo*-borates $M_2B_{10}H_{10}$ or $M_2B_{12}H_{12}$ were mixed with metal hydrides MH, M = Li or Na, in the molar ratio 1:8 or 1:10, respectively, to form a composite with a M:B ratio of 1:1. The mixtures were then manually ground for 3 minutes. These samples are denoted Li2B10-A, Li2B12-A, Na2B10-A and Na2B12-A. Other samples were prepared with either 3 minutes of manual grinding (Li₂B₁₂-As and Na₂B₁₂-As) or 15 minutes of ball-milling (ball to powder ratio of 25:1) (Li₂B₁₀-Ab, Na₂B₁₀-Ab, Li₂B₁₀-Ab and Na₂B₁₂-Ab). All handling of the chemicals was performed in an argon-filled glovebox with $p(O_2, H_2O) < 1$ ppm.

The *closo*-borate-hydride composites (Li₂B₁₀-A, Li₂B₁₂-A, Na₂B₁₀-A and Na₂B₁₂-A) were hydrogenated in custom-made equipment by loading the mixed powders (80–200 mg) into a steel container, which is closed with a filter and placed in a specialized sample cell.⁴² High pressures (HP) are generated using a metal hydride hydrogen compressor, *i.e.* heating a commercial AB₅ hydrogen storage alloy with the composition MmNi_{4.35}Co_{0.8}Al_{0.05} where Mm is a mixture of rare earth metals, primarily La and Ce. The pressure generated at room temperature, $p(H_2) \sim 400$ bar, was increased to 526–547 bar during heating to either ~ 300 or ~ 400 °C ($\Delta T/\Delta t = 5$ °C min⁻¹) and was then kept isothermal for 24 hours. The high-pressure hydrogen pressures of 970 to 998 bar in a stainless steel reactor. An overview of the hydrogen-treated samples is given in Table 1.

Characterization

In-house powder X-ray diffraction (PXD). In-house powder X-ray diffraction patterns were measured on a Rigaku Smart Lab diffractometer using a Cu source and conversion beam mirror (Cu K_{a1} radiation, $\lambda = 1.540593$ Å). Data were collected in the 2θ range 5° to 50° at 3° min⁻¹ using a Rigaku D/tex detector. Samples were placed in 0.5 mm boron silicate capillaries and sealed with grease under argon in a glovebox.

Fourier transform infrared spectroscopy (FT-IR). All samples were characterized by FT-IR using a NICOLET 360 FT-IR from Thermo Electron Corporation. Data were measured in the range 4000–400 cm⁻¹ and 32 scans, with a spectral resolution of 4 cm⁻¹, were collected per sample and averaged. The samples were briefly exposed to air (\sim 10 s) prior to measurement.

Synchrotron radiation powder X-ray diffraction. In situ synchrotron radiation powder X-ray diffraction (SR-PXD)

Table 1 Overview of the hydrogenated samples. The total pressure allows calculation of hydrogen H₂ uptake ($\Delta m/m$). Unidentified compounds are denoted, 1, 2, 3, or 4

Name	Ratio $M_2B_{10/12}H_{10/12}$: MH, M = Li or Na	Synthesis, hydrogenation of sample	$T [^{\circ}C]$	p(H ₂) _{start} [bar]	<i>p</i> (H ₂) _{end} [bar]	$\Delta m/m$ [wt% H ₂]	Time [h]	Products
Li ₂ B ₁₀ -B	1:8	Li ₂ B ₁₀ -A	307	526	516	2.9	24	$LiBH_4 + LiH + 1$
Li ₂ B ₁₀ -C	1:8	Li ₂ B ₁₀ -Ab	400	998	773 ^a	_	48	$LiBH_4 + LiH$
Li ₂ B ₁₂ -B	1:10	Li ₂ B ₁₂ -A	402	547	540	2.2	24	$Li_2B_{12}H_{12} + LiH$
Li ₂ B ₁₂ -C	1:10	Li ₂ B ₁₂ -Ab	400	970	955	_	48	$Li_{2}B_{12}H_{12} + LiH$
Li ₂ B ₁₂ -D	1:10	Li ₂ B ₁₂ -As	400	970	955	_	48	$Li_2B_{12}H_{12} + LiH$
Na_2B_{10} -B	1:8	Na ₂ B ₁₀ -A	289	534	527	3.2	24	$NaBH_4 + NaH + 2$
Na_2B_{10} -C	1:8	Na ₂ B ₁₀ -Ab	400	998	773 ^a	_	48	$NaBH_4 + NaH$
Na_2B_{12} -B	1:10	Na ₂ B ₁₂ -A	401	536	533	1.5	24	$Na_2B_{12}H_{12} + NaH + 3 + 4$
Na_2B_{12} -C	1:10	Na ₂ B ₁₂ -Ab	400	970	955	_	48	$Na_2B_{12}H_{12} + NaH$
Na_2B_{12} -D	1:10	Na ₂ B ₁₂ -As	400	970	955	_	48	$Na_2B_{12}H_{12} + NaH$

measurements were conducted at beam line P02.1 at the synchrotron facility PETRA III, DESY, Germany, with a high photon energy of 60 keV, $\lambda = 0.20775$ Å. The data were collected using a fast area detector from Perkin Elmer (XRD1621) and an X-ray exposure time of 10 seconds per diffraction pattern. The high photon energy is required to penetrate the thick-walled sapphire capillaries (o.d. = 3.0 mm, i.d. = 0.8 mm) that are necessary when working at high pressure ($p(H_2) > 200$ bar). For the high pressure measurement, a modified high pressure cell is used as described previously.⁴⁰ The *in situ* hydrogenation was performed by increasing the hydrogen pressure to 407-440 bar at room temperature (RT), followed by heating to 300 °C for the M₂B₁₀H₁₀-8MH composites and 400 °C for the M₂B₁₂H₁₂-10MH composites with a heating and cooling rate of $\Delta T / \Delta t = 10 \ ^{\circ}\text{C min}^{-1}$. The in situ HP SR-PXD experiment for Li₂B₁₀H₁₀-8LiH was conducted for ~12 hours, whereas the experiments for $Na_2B_{10}H_{10}$ -8NaH and Na₂B₁₂H₁₂-10NaH were conducted for \sim 4 hours.

NMR spectroscopy. The solid-state ¹¹B and ²³Na MAS NMR spectra were acquired on a Bruker AVANCE-700 spectrometer (16.4 T) using a triple-tuned ¹H-X-Y 4 mm MAS probe and a spinning speed of $\nu_{\rm R}$ = 15.0 kHz. The ¹¹B NMR experiments employed a 0.5 µs excitation pulse ($\gamma B_1/2\pi = 62$ kHz), ¹H SPINAL-64 decoupling ($\gamma B_2/2\pi = 100$ kHz) and a relaxation delay of 10 s. The ²³Na spectra were acquired with a 0.5 µs excitation pulse ($\gamma B_1/2\pi = 60$ kHz) and a 10 s relaxation delay. The solution ¹¹B NMR spectra were obtained on a Varian Direct Drive VNMRS-600 spectrometer (14.1 T) using a 4 mm CP/MAS probe for solids, no sample spinning, and ¹H decoupling ($\gamma B_2/2\pi = 50$ kHz). All samples were packed in airtight end-capped zirconia rotors in an argon-filled glovebox. Solutions for ¹¹B NMR measurements were prepared by dissolving 20-40 mg of sample in dry tetrahydrofuran (THF). ¹¹B and ²³Na chemical shifts are relative to neat F₃B-O(CH₂CH₃) and a 0.1 M aqueous solution of NaCl, respectively.

Results and discussion

Hydrogenation of metal decahydro-*closo*-decaborate M₂B₁₀H₁₀-8MH compositions

Sample Li₂B₁₀H₁₀-8LiH. The Li₂B₁₀-A sample was heated to 307 °C ($\Delta T/\Delta t = 5$ °C min⁻¹) and kept isothermal for 24 hours at

 $p(H_2)_{\text{start}} = 526$ bar, Fig. S1 (ESI[†]). The hydrogen pressure decreased slowly, 0.054 wt% per h, for the first 6 hours, then \sim 5× faster (0.262 wt% per h) for 8 hours, and again slower for the remaining 8 hours, suggesting that there was an incubation period before hydrogen absorption could proceed rapidly or that several reactions take place. The pressure decrease corresponds to a total uptake of 2.9 wt% H₂, which is about $4 \times$ less than the theoretical hydrogen uptake, *i.e.* 11.3 wt%, which would correspond to full conversion of the sample to LiBH₄. PXD of the post-hydrogenation sample, Li₂B₁₀-B (Fig. 1), reveals that the reactants, Li2B10H10 and LiH, are almost completely consumed during the formation of LiBH₄ and 1. PXD of Li_2B_{10} -A treated at 400 °C, $p(\text{H}_2) = 998$ bar H_2 for 48 h $(Li_2B_{10}-C)$ (Fig. S2, ESI[†]) also reveals the formation of LiBH₄ and intermediate 1. However, additional Bragg reflections appear at low Bragg angles (2θ) , which are assigned to impurities from the reaction vessel. Compound 1 has not previously been reported and may be an intermediate in the formation of LiBH₄ with a lithium/boron ratio in between Li₂B₁₀H₁₀ and $LiBH_4$, *i.e.*, 0.2 < Li/B < 1. Observed Bragg diffraction data,



Fig. 1 Normalized powder X-ray diffraction patterns of $\text{Li}_2\text{B}_{10}\text{H}_{10}$ -8LiH after manually grinding (Li_2B_{10} -A) and after hydrogenation (Li_2B_{10} -B) at T = 307 °C and $p(\text{H}_2) = 526$ bar for 24 hours ($\lambda = 1.540593$ Å). Symbols: o-LiBH₄, \bullet Li₂B₁₀H₁₀, \blacktriangle LiH, and compound **1**. The dotted pattern is that of pure LiBH₄, overlaid for comparison.

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Fig. 2 In situ high pressure synchrotron powder X-ray diffraction patterns of the hydrogenation of Li₂B₁₀H₁₀-8LiH heated from RT to 300 °C, at $p(H_2) = 407$ bar ($\Delta T/\Delta t = 10$ °C min⁻¹, $\lambda = 0.20720$ Å). The sample was kept isothermal at T = 300 °C for ~10 hours. The dashed line indicates the temperature profile. Symbols: \blacksquare o-LiBH₄, \boxtimes h-LiBH₄, \spadesuit Li₂B₁₀H₁₀, \blacktriangle LiH, and compound **1**.

d-spacings and relative intensities, from **1** are listed in Table S1 (ESI[†]), which can be indexed with an orthorhombic unit cell, a = 6.0754(2), b = 6.2494(2), c = 21.019(5) Å, V = 778.0(3) Å³.

The hydrogenation of $\text{Li}_2\text{B}_{10}\text{H}_{10}$ –8LiH was further studied by in situ SR-PXD at high hydrogen pressure, $p(\text{H}_2) = 407$ bar, and isothermal conditions, T = 300 °C (Fig. 2). The PXD signatures of the reactants, $\text{Li}_2\text{B}_{10}\text{H}_{10}$ and LiH, were observed at RT, after ~6 hours the unidentified compound **1** emerged in accordance with *ex situ* PXD (Fig. 1 and Table S1, ESI†), and reflections from $\text{Li}_2\text{B}_{10}\text{H}_{10}$ completely disappeared after ~9 hours. This agrees with the induction period observed in Fig. S1 (ESI†). As Bragg reflections from $\text{Li}_2\text{B}_{10}\text{H}_{10}$ disappear, the reflections from **1** become more pronounced. After ~11 hours the sample is cooled and crystallization of h-LiBH₄ (h-hexagonal) is observed ($T_{\text{melt}} = 280$ °C), which transforms into the ambient o-LiBH₄ polymorph (o-orthorhombic).^{12,43} This indicates that **1** may be an intermediate in the formation of LiBH₄.

The ¹¹B MAS NMR spectrum of Li₂B₁₀-B is dominated by the narrow centerband resonance at -41.1 ppm from LiBH₄ (Fig. 3a). In addition, a somewhat broader centerband is observed at -23 ppm, which is ascribed to boron in compound 1, since the resonance does not match with the chemical shift reported for Li₂B₁₀H₁₀ at -28.8 ppm.⁴⁴ All spinning sidebands for the central and satellite transitions are observed for LiBH₄ whereas only a part of the spinning sideband manifold from the satellite transitions is observed for compound 1. Thus, the total intensity for the ¹¹B central and satellite transitions for LiBH₄ is obtained as the sum of intensities for the centerband and all spinning sidebands, whereas the central-transition intensity for compound 1 is obtained from the intensities for the centerband and first-order spinning sidebands after an intensity correction to these peaks from the contribution from



Fig. 3 ¹¹B MAS NMR spectra (16.45 T, $\nu_R = 15.0$ kHz) of the hydrogenated samples (a) Li₂B₁₀-B and (b) Na₂B₁₀-B. The centerbands for LiBH₄ and NaBH₄ are cut-off at 1/2 and 1/50 of their total heights in (a) and (b), respectively. The asterisk indicates the second-order quadrupole line-shape from a minor impurity of BO₃ species (identified for both samples), most likely produced prior to the NMR experiments, whereas the open circle in (a) identifies a centerband at -15.1 ppm (0.7% of the boron in the sample) from a small amount of Li₂B₁₂H₁₂ in the sample.

the satellite transitions. The central-transition intensity for LiBH₄ is obtained as 4/10 of the total intensity, which holds for a spin 3/2 nucleus, and comparison of this value with the central transition intensity for 1 reveals that the molar ratio for boron in $LiBH_4$ and 1 is 1:0.63, which corresponds to an uptake of 2.8 wt% H₂, matching well with the observed hydrogenation, 2.9 wt% H2.44 This indicates that the absorbed hydrogen only goes toward producing LiBH₄ as the B:H ratio in the unknown compound 1 is 1:1, consistent with a higher borate, which is also reflected in its characteristic IR mode and ¹¹B chemical shift. Thus, ¹¹B MAS NMR reveals that all Li₂B₁₀H₁₀ (-0.9 ppm and -28.8 ppm) is consumed during hydrogenation and that LiBH₄ and 1 are the only reaction products, besides a minor amount of a BO₃ species (~ 20 ppm), corresponding to 3.5% of the boron in the sample. Solution-state ¹¹B NMR spectra of Li₂B₁₀-B dissolved in THF obtained without and with ¹H decoupling (Fig. S4, ESI[†]) allow identification of resonances at -14.0 ppm (${}^{1}J_{BH}$ = 142 Hz), -15.6 ppm (${}^{1}J_{BH}$ = 120 Hz), -16.0 ppm (${}^{1}J_{BH}$ = 120 Hz), -16.7 ppm (${}^{1}J_{BH}$ = 120 Hz), $-18.0 \text{ ppm} (^{1}J_{BH} = 150 \text{ Hz}) \text{ and } -20.7 \text{ ppm} (^{1}J_{BH} = 142 \text{ Hz}) \text{ in}$ addition to the main peak at -41.8 ppm from the $[BH_4]^-$ units.

All resonances in the -14.0 to -20.7 ppm region show doublets in the ¹H-coupled spectra, demonstrating that they originate from boron sites which are directly bonded to one H atom. The resonance and ¹J_{BH} coupling at -15.6 ppm is in agreement with the ¹¹B NMR data reported for $[B_{12}H_{12}]^{2-,45}$ matching the impurity of Li₂B₁₂H₁₂ in the solid-state ¹¹B NMR spectrum (Fig. 3a). The remaining resonances, and, in particular, the peak at -20.7 ppm, may originate from the unknown compound **1** and thereby suggest that this phase contains boron sites directly bonded to a single H atom. Moreover, comparison of the ¹¹B chemical shifts with those reported for relevant borate species (Table S4, ESI†) strongly suggests that compound **1** contains *closo*-borate units.

The formation of LiBH₄ is also confirmed by FT-IR (Fig. S3, ESI[†]). The IR spectrum of Li₂B₁₀-A has a single large B–H stretching mode at 2500 cm⁻¹ with minor modes at lower wavenumbers consistent with metal *closo*-borates.^{46,47} For Li₂B₁₀-B, the B–H stretching mode at 2500 cm⁻¹ has almost disappeared while B–H stretching modes appear around 2300 cm⁻¹, which correspond to those of LiBH₄.^{48,49}

This work suggests that **1** has a lithium-boron ratio in between $\text{Li}_2\text{B}_{10}\text{H}_{10}$ and LiBH_4 , *i.e.* 0.2 < Li/B < 1, and a hydrogen-boron ratio close to **1**:1. A hydrogen uptake of 2.9 wt% H₂ was measured, which corresponds to a sample composition of 10Li-10B-23.6H. After hydrogenation, the sample contains LiBH_4 and LiH and, therefore, also some metal borates richer in boron and hydrogen than lithium. However, the spectroscopy and diffraction data do not unambiguously identify any such compounds.

Sample Na₂B₁₀H₁₀-8NaH. Hydrogenation of Na₂B₁₀-A was conducted at T = 289 °C and $p(H_2) = 534$ bar and kept isothermal for 24 hours, Fig. S5 (ESI†). The hydrogen pressure was steady for the first 3 hours at $p(H_2) = 534$ bar, then decreased, at 0.248 wt% per h, over the next 12 h, and then more slowly at 0.091 wt% per h during the remaining 8 hours (Fig. S5, ESI†). This reveals an induction period of 3 h prior to absorption of 3.2 wt% H₂, which is approximately half of the theoretical maximum, *i.e.* 6.23 wt%, which would correspond to full conversion to NaBH₄.

PXD of Na₂B₁₀-B reveals Bragg reflections from NaBH₄ along with an unidentified compound, denoted **2**, and some unreacted NaH (Fig. 4). PXD of the high-pressure sample, Na₂B₁₀-C, reveals that NaBH₄ is the major crystalline product, along with **2** (Fig. S6, ESI†). The new compound **2** has reflections at low Bragg angles $2\theta < 7^{\circ}$ (d > 13 Å) (Table S2, ESI†), which can be indexed with a relatively large monoclinic unit cell, a = 12.7068(5), b = 23.3384(7), c = 16.8802(8) Å, $\beta = 105.456(4)^{\circ}$, V = 4824.9(5) Å³.

The formation of NaBH₄ is further confirmed by IR spectroscopy (Fig. S7, ESI†). The two B–H stretching bands at ~2500 cm⁻¹ from Na₂B₁₀H₁₀ in Na₂B₁₀-A are replaced by a single broad band at ~2400 cm⁻¹ in Na₂B₁₀-B, indicating that a different B–H containing cluster is formed, possibly a *closo-*, *arachno-*, or *nido*-borate, which could potentially be ascribed to the unidentified compound **2**. Finally, the two stretching modes between 2350–2250 cm⁻¹ are assigned to NaBH₄.



Fig. 4 Normalized powder X-ray diffraction patterns of Na₂B₁₀H₁₀–8NaH after manually grinding (Na₂B₁₀-A) and after hydrogenation (Na₂B₁₀-B) at T = 289 °C and $p(H_2) = 534$ bar for 24 hours ($\lambda = 1.54056$ Å). Symbols: NaBH₄, \bigcirc NaH, \triangle LT-Na₂B₁₀H₁₀, and compound **2**. The dotted pattern is that of pure NaBH₄, overlaid for comparison.

The hydrogenation of the composite Na₂B₁₀H₁₀–8NaH was investigated by HP *in situ* SR-PXD and the diffraction data is presented in Fig. 5. Initially, Bragg reflections from the reactants, Na₂B₁₀H₁₀ and NaH, are observed followed by the wellknown α - to β -Na₂B₁₀H₁₀ polymorphic transition at $T \sim 130$ °C.⁵⁰ After 20 min at T = 302 °C and $p(H_2) \sim 440$ bar (t = 60 min), Bragg reflections from 2 are observed, whereas NaBH₄ is observed after approximately 220 minutes at T = 250 °C during cooling. This reaction time agrees well with the ~ 4 hours induction time observed in *ex situ* hydrogen absorption in Fig. S5 (ESI†). Thus, 2 may represent an intermediate in the formation of NaBH₄ from the Na₂B₁₀H₁₀–8NaH composite.

The ¹¹B MAS NMR spectrum of Na₂B₁₀-B (Fig. 3b) reveals at least two different boron environments, with the dominating resonance at -41.9 ppm originating from NaBH₄.⁵¹ The second broad resonance is centered at -28 ppm and includes a sharp low-intensity component at -30 ppm. The main component of the resonance at -28 ppm is ascribed to 2 while the sharp resonance at -30 ppm is ascribed to a small amount of the Na₂B₁₀H₁₀ starting material.⁴⁴ The molar ratio for boron in NaBH₄ and 2 of 1:0.21 and is derived from the intensities of the central and satellite transitions for NaBH₄ and the central transition for the -28 ppm resonance.

The ²³Na MAS NMR spectrum of the Na₂B₁₀-B sample (Fig. 6a) is dominated by resonances from NaBH₄ (-7.9 ppm) and NaH (18.2 ppm).⁵² Spectral integration, considering the centerband intensities only, reveals that NaBH₄ and NaH are present in a 1:0.16 molar ratio. The vertical expansion of the spectrum (Fig. 6a) shows at least four additional resonances, *i.e.*, a second-order quadrupolar lineshape with singularities at 12.2 and 11.1 ppm, a broadened resonance at 2.7 ppm, a shoulder to the NaBH₄ centerband at -2.8 ppm and a resonance at -17.9 ppm. These additional resonances constitute 8.3% of the total intensity in the centerband region and thereby represent smaller amounts of other Na containing compounds, possibly 2.

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Fig. 5 In situ high pressure synchrotron powder X-ray diffraction patterns of the hydrogenation of $Na_2B_{10}H_{10}$ –8NaH heated from RT to 302 °C, at $p(H_2) = 440$ bar ($\Delta T/\Delta t = 10$ °C min⁻¹, $\lambda = 0.20720$ Å). The sample was kept isothermal at T = 302 °C for ~3 hours. The dashed line indicates the temperature profile. Symbols: \Box NaBH₄, \bigcirc NaH, \triangle LT-Na₂B₁₀H₁₀, \bigstar HT-Na₂B₁₀H₁₀, and compound **2**.

Solution ¹¹B NMR spectra of Na₂B₁₀-B dissolved in THF and obtained with and without ¹H decoupling (Fig. 7) show resonances at -1.7 ppm (¹*J*_{BH} = 134 Hz), -17.5 ppm (¹*J*_{BH} = 125 Hz), -20.7 ppm (¹*J*_{BH} = 125 Hz), -21.3 ppm (¹*J*_{BH} = 125 Hz) and -29.9 ppm (¹*J*_{BH} = 119 Hz), all corresponding to boron bonded to one H atom, and a main peak at -41.8 ppm from the [BH₄]⁻ units. The peaks at -1.7 ppm and -29.9 ppm exhibit a 1:4 intensity ratio and are ascribed to the two distinct B sites in [B₁₀H₁₀]²⁻, in accordance with ¹¹B NMR data from literature.⁵³ Thus, the resonances at -17.5 ppm, -20.7 ppm, and -21.3 ppm are assigned to 2 and is in accord with data reported for [B₁₁H₁₁]²⁻ (Table S4, ESI[†]), which is a *closo*-borate with terminal hydrogens only, *i.e.*, B–H units producing doublets in liquid state NMR spectra.

Thus, the measured hydrogen uptake of 3.2 wt% H_2 corresponds to a sample composition of 10Na-10B-29.3H, and Na NMR reveals a sample composition of NaBH₄-NaH 1:0.16 and that Na₂B₁₁H₁₁ (denoted 2) accounts for <8.3% of the sodium in the sample. Boron NMR reveals a ratio between NaBH₄-Na₂B₁₁H₁₁ of 1:0.21. The products besides NaBH₄ and Na₂B₁₁H₁₁ are difficult to determine and may be a mixture of different borates.

Hydrogenation of metal dodecahydro-closo-dodecaborate $M_2B_{12}H_{12}$ -10MH compositions

Sample Li₂**B**₁₂**H**₁₂**-10LiH.** PXD of the physical mixture Li₂B₁₂-A is shown in Fig. 8. Li₂B₁₂-A was heated to T = 402 °C and kept isothermal for 24 hours at $p(H_2)_{\text{start}} = 546$ bar. The total pressure decrease corresponds to a H₂ uptake of 2.19 wt% H₂. However, PXD of Li₂B₁₂-B reveals no changes in the composite except for weak reflections from Li₂O. Experiments



Fig. 6 ²³Na MAS NMR spectra (16.45 T, $\nu_{\rm R}$ = 15.0 kHz) of the hydrogenated samples (a) Na₂B₁₀-B and (b) Na₂B₁₂-B. The spectra illustrate the spectral region for the central transitions and they are shown on normalized as well as expanded intensity scales.

conducted on $\text{Li}_2\text{B}_{12}\text{H}_{12}$ -10LiH samples at high pressure, $p(\text{H}_2) = 970$ bar and T = 400 °C for 48 h (Li₂B₁₂-C and Li₂B₁₂-D), confirmed that no LiBH₄ or other compounds were produced under the conditions used in this study (Fig. S9, ESI†). Hence, the pressure decrease observed in Fig. S8 (ESI†) is possibly due to a slight hydrogen gas leak.

This finding is further supported by the ¹¹B MAS NMR spectrum of Li_2B_{12} -B (Fig. S10a, ESI[†]) that almost exclusively shows a single resonance peak at -15.2 ppm, in agreement with the reported chemical shift for $Li_2B_{12}H_{12}$.⁴⁴

Sample Na₂B₁₂H₁₂–10NaH. The physical mixture of Na₂B₁₂H₁₂–10NaH (Na₂B₁₂-A) was heated to T = 401 °C and kept isothermal for 24 hours at $p(H_2) = 537$ bar (Fig. S11, ESI†). PXD of Na₂B₁₂-B (Fig. 9) reveals no formation of NaBH₄; however, another unidentified compound is observed, denoted **3**. The total pressure decrease corresponds to a H₂ uptake of 1.5 wt% H₂ (Fig. S11, ESI†). Experiments conducted on Na₂B₁₂H₁₂–10NaH samples at higher pressure, $p(H_2) = 970$ bar and T = 400 °C for 48 h (Na₂B₁₂-C and Na₂B₁₂-D), confirmed that no NaBH₄ was produced (Fig. S12, ESI†); however, both samples show formation of **3**. The ballmilled sample, Na₂B₁₂-C, shows less remaining Na₂B₁₂H₁₂



Fig. 7 Solution 11 B NMR spectra (14.1 T) of Na₂B₁₀-B dissolved in THF obtained (a) without and (b) with 1 H decoupling.



Fig. 8 Normalized powder X-ray diffraction patterns of Li₂B₁₂H₁₂-10LiH after manually grinding (Li₂B₁₂-A) and after hydrogenation (Li₂B₁₂-B) at T = 402 °C and $p(H_2) = 546$ bar for 24 hours ($\lambda = 1.54056$ Å). Symbols: \bigcirc LT-Li₂B₁₂H₁₂, \blacktriangle LiH, and \divideontimes Li₂O.

compared to the hand-ground sample, Na_2B_{12} -D, probably due to a smaller particle size and hence a higher reactivity.

The change in structures is investigated by IR spectroscopy (Fig. S13, ESI[†]). The B–H stretching bands at ~2478 cm⁻¹ from Na₂B₁₂H₁₂ in Na₂B₁₂-A are shifted slightly to a lower value of 2462 cm⁻¹ in Na₂B₁₂-B, which may be ascribed to 3 along with a new bending mode at ~1650 cm⁻¹.

The formation of 3 is studied by HP *in situ* SR-PXD (Fig. 10). Initially, Bragg reflections from $Na_2B_{12}H_{12}$ and NaH are present,



Fig. 9 Normalized powder X-ray diffraction patterns of Na₂B₁₂H₁₂–10NaH after manually grinding (Na₂B₁₂-A) and after hydrogenation (Na₂B₁₂-B) at *T* = 401 °C and *p*(H₂) = 537 bar for 24 hours (λ = 1.54056 Å). Symbols: \Diamond LT-Na₂B₁₂H₁₂, \bigcirc NaH, and compound **3**.



Fig. 10 *In situ* high pressure synchrotron powder X-ray diffraction patterns of the hydrogenation of Na₂B₁₂H₁₂-10NaH heated from RT to 407 °C, at $p(H_2) = 417$ bar ($\Delta T/\Delta t = 10$ °C min⁻¹, $\lambda = 0.20720$ Å). The sample was kept isothermal at T = 407 °C for ~3 hours. The dashed line indicates the temperature profile. Symbols: \diamond LT-Na₂B₁₂H₁₂, \blacklozenge HT-Na₂B₁₂H₁₂, \bigcirc NaH, compound **3**, and compound **4**.

and, during heating, the polymorphic transition of α - to β -Na₂B₁₂H₁₂ is observed at ~275 °C.⁵⁴ In addition, an unidentified compound denoted **4** is observed. No changes in the diffraction pattern are observed at the isothermal temperature, but Bragg reflections from compound **4** disappear at $T \sim 210$ °C during cooling. At the same time, Bragg reflections from compound **3** appear, which indicates a phase transition of **4** into **3**. Reflections from compounds **3** and **4** are listed in Table S3 (ESI[†]) with the *d*-spacing and relative intensities. Indexing suggests an orthorhombic unit cell for **3**: *a* = 6.9114(6), *b* = 12.877(2), *c* = 14.296(1) Å, *V* = 1272.2(5) Å³, and an orthorhombic unit cell for **4**: *a* = 6.3383(2), *b* = 10.5223(8), *c* = 14.8283(7) Å and *V* = 987.4(2) Å³.

The ¹¹B MAS NMR spectrum of Na₂B₁₂-B (Fig. S10b, ESI†), exhibits a narrow resonance (full width at half maximum (FWHM) = 0.7 ppm) at -15.7 ppm, in accordance with the ¹¹B chemical shift reported for Na₂B₁₂H₁₂, which may suggest that 3 has boron coordination similar to that of Na₂B₁₂H₁₂.⁴⁴ PXD clearly shows the formation of a new crystalline product after hydrogenation at high temperature, whereas NMR results only indicate the presence of $[B_{12}H_{12}]^{2-}$ -containing compounds. A previous study has shown that annealing Li₂B₁₂H₁₂ under hydrogen pressure can result in the formation of additional Bragg diffraction peaks, indicating that other compounds may form at high temperature.⁵⁵ Compound 3 appears to consist of $[B_{12}H_{12}]^{2-}$ anions as suggested by NMR.

The ²³Na MAS NMR spectrum of Na₂B₁₂-B (Fig. 6b) is dominated by a resonance at 18.2 ppm from NaH. In addition, minor peaks are observed at 32.1 ppm, 11.9 ppm, 2.3 ppm, -11.4 ppm, -28.8 ppm and -38 ppm. A ²³Na MAS NMR spectrum of Na₂B₁₂H₁₂ reveals that the resonance at -11.4 ppm originates from this compound. Moreover, the peaks at -28.8 ppm and -38 ppm are most likely the low-frequency part (singularity and edge) of a second-order quadrupolar lineshape. However, the resonances at 32.1 ppm, 11.9 ppm, 2.3 ppm, -28.8 ppm, and -38 ppm are not assigned and thus they may include contributions from the unidentified compound **3**. Spectral integration shows that the four resonances correspond to 10.7% of the total ²³Na centerband intensity.

The Na₂B₁₂-B sample absorbed 1.5 wt% H₂, which corresponds to a sample composition of 12Na–12B–28.4H. Solid state ¹¹B MAS NMR show that **3** has similar chemical environment as $[B_{12}H_{12}]^{2-}$ and diffraction reveal that **4** transforms to **3** upon cooling.

Comparison of the investigated closo-borate composites

Comparison of the reactivity of the Li and Na closo-borate composites, Li2B10H10-8LiH and Na2B10H10-8NaH, reveals several important differences. For instance, the Na composites have faster kinetics for hydrogenation than the corresponding Li samples, e.g., Li₂B₁₀-A absorbs hydrogen slowly for the first 6 hours, then $\sim 5 \times$ faster for 8 hours and then again slower whereas Na2B10-A does not absorb hydrogen for the first 3 hours then absorbs quickly for 12 h, and then more slowly. From a kinetic point of view, the shorter induction period for the sodium system may be associated with faster nucleation and growth of intermediate compounds prior to formation of NaBH₄ as compared to similar reactions for the analogous lithium composites. This is well documented by solid-state ¹¹B NMR, which reveals sample compositions of LiBH₄-1 (1:0.63) for $Li_2B_{10}H_{10}$ -8LiH and NaBH₄-2 (1:0.21) for Na2B10H10-8NaH after 24 h. In situ HP SR-PXD experiments reveal the formation of NaBH4 after 4 hours of Na2B10B10-8NaH, whereas LiBH₄ forms after 10 hours. A major difference between composites based on M₂B₁₀H₁₀ and M₂B₁₂H₁₂ is their reactivity; those based on M2B10H10 more readily form the corresponding metal borohydride, MBH₄, and intermediate compounds. In contrast, only unidentified compounds are observed in the Na2B12H12-10NaH composite, whereas no

reaction is observed for $\text{Li}_2\text{B}_{12}\text{H}_{12}$ -10LiH under the conditions used in this study. Four different intermediate compounds have been observed during hydrogenation reactions in this investigation. However, they are different than intermediates predicted theoretically for the decomposition of LiBH₄ and to those observed experimentally.^{36,56}

In a previous study, Li₂B₁₂H₁₂-10LiH and Na₂B₁₂H₁₂-10NaH were fully converted to the respective metal borohydrides, LiBH₄ and NaBH₄, under harsher conditions, *i.e.* T = 500 °C, $p(H_2) = 1.0$ kbar for 72 h.³⁹ Milder conditions are used in this study, *i.e.* $T \sim 400$ °C, $p(H_2) \sim 998$ bar for 24 h for hydrogenation of M₂B₁₀H₁₀-8MH and $T \sim 400$ °C, $p(H_2) \sim 970$ bar for 48 h for M₂B₁₂H₁₂-10MH, which proves insufficient to form the respective metal borohydride. The M₂B₁₀H₁₀ composites are clearly more reactive and take up hydrogen at milder conditions compared to the M₂B₁₂H₁₂ composites, possibly due to the lower thermodynamic stability of the $[B_{10}H_{10}]^{2-}$ anion, which allows B–B bond breaking to occur under milder reaction conditions.

Conclusions

The composites $M_2B_{12}H_{12}$ -10MH and $M_2B_{10}H_{10}$ -8MH (M = Li and Na) have been reacted with hydrogen at elevated pressures and temperatures and studied by X-ray diffraction both PXD and in situ SR-PXD and FT-IR, ²³Na and ¹¹B NMR spectroscopy. Both the in situ and ex situ characterization results show that the M2B10H10-8MH composites react with hydrogen gas to form the respective metal borohydride, MBH₄, at $T \sim 300$ °C and $p(H_2) > 500$ bar. These conditions were deliberately selected to obtain partial hydrogenation of the samples in order to focus on the mechanism of hydrogen uptake. The relatively mild conditions used in this investigation did not allow formation of MBH₄ by hydrogenation of the $M_2B_{12}H_{12}$ -10MH composites: no hydrogen absorption was detected for Li2B12H12-10LiH, but new intermediates were observed for Na2B12H12-10NaH. Generally, the sodium-containing composites are observed to be more reactive towards hydrogen compared to the lithium analogues under similar conditions of temperature and H₂ pressure, and M₂B₁₀H₁₀-8MH are more reactive than $M_2B_{12}H_{12}$ -10MH. The high stability of the $[B_{12}H_{12}]^{2-}$ anions is associated with the pseudoaromatic bonding in dodecahydro-closo-dodecaborate cages and lack of chemically distinct and more reactive apical boron atoms within the closo-borate polyhedra that the decahydro-closo-decaborate cages contain.

The conditions for hydrogenation used in this study are clearly above the thermodynamic limit needed to form the corresponding metal borohydrides, LiBH_4 or NaBH_4 , for the composites containing $[\text{B}_{10}\text{H}_{10}]^{2-}$. Therefore, the observed differences in the length of the induction periods prior to hydrogen absorption, which occur at different rates, are assigned to kinetic constraints. Remarkably, four different intermediate compounds have been observed in this study for the hydrogenation of the composites. The formation of intermediate compounds appears to be the rate-limiting step of the reaction, with the slowest kinetics observed for the $M_2B_{12}H_{12}$ compounds. This suggest that the molecular mechanism for hydrogen absorption is different for the two *closo*-borate cages, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$.

This study not only demonstrates that lithium and sodium $M_2B_{10}H_{10}$ salts can be hydrogenated into the corresponding metal borohydrides, but it also reveals the presence of, at least, four B–H intermediates, which are different to those previously observed experimentally or suggested based on theoretical calculations. Additional investigations are needed to clarify composition, structure, and properties of these intermediate compounds. The analysis of the available solid-state and solution ¹¹B NMR data indicates that these intermediates are not salts of $[B_3H_8]^-$, $[B_{10}H_{10}]^{2-}$ or $[B_{12}H_{12}]^{2-}$ anions. We hypothesize that these could be other *closo*-polyborates, *e.g.*, $[B_9H_9]^{2-}$ or $[B_{11}H_{11}]^{2-}$ salts, or oligomers resulting from $[B_{10}H_{10}]^{2-}$ polymerization.²⁹ For example, *closo*-decaborate salts are known to form dimeric anions, such as various isomers of $[B_{20}H_{18}]^{4-}$ and $[B_{20}H_{18}]^{2-}$ anions.⁵⁷

A detailed understanding of the reactivity of these important compounds may allow further tailoring of the reaction mechanisms of hydrogen storage reactions. Further investigations should focus on identifying reaction pathways in the dehydrogenation of metal borohydrides that avoid the formation of stable $[B_{12}H_{12}]^{2-}$ anions, and favoring formation of intermediate B–H species that can be cycled under more reasonable conditions of hydrogen pressure and temperature.

Conflicts of interest

There are no conflicts to declare.

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