Mechanochemical reactions and hydrogen storage capacities in MBH₄–SiS₂ systems (M=Li or Na)

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The hydrogen storage properties, and phase compositions of mechanochemically prepared mixtures of xMBH4-SiS2 (x = 2–8), where M = Li or Na, were investigated using gas sorption analysis, powder X-ray diffraction, and infrared and solid-state NMR spectroscopic methods. The 2LiBH4:1SiS2 system forms an amorphous product that releases ca. 4.3 wt % of H2 below 385 °C with a Tonset of 88 °C without detectable diborane emission. The dehydrogenated sample reversibly absorbs 1.5 wt % of H2 at 385 °C under 160 bar pressure. The H2 release from materials with varying LiBH4:SiS2 ratios peaks at 8.2 wt % for the 6LiBH4:1SiS2 composition, with a reversible hydrogen storage capacity of 2.4 wt %. The H2 desorption capacities of the Li-containing systems surpass those of Na-containing systems. Solid-state NMR studies indicate that products of mechanochemical reactions in the LiBH4SiS2 system consist of one-dimensional chains of edge-sharing SiS4/2 tetrahedra in which the non-bridging S-ends are terminated with Li+, which are further coordinated to the [BH4]− anions. A variety of possible polymorphs in the LiSiS-(BH4) composition space have been identified using first principles and thermodynamic modeling that supports the likelihood of formation of such novel complexes.

Keywords
Mechanochemistry, Hydrogen storage, Solid-state NMR

Disciplines
Materials Chemistry | Materials Science and Engineering

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Mechanochemical reactions and hydrogen storage capacities in MBH₄-SiS₂ systems (M=Li or Na)

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Abstract

The hydrogen storage properties, and phase compositions of mechanochemically prepared mixtures of xMBH₄-SiS₂ (x = 2–8), where M = Li or Na, were investigated using gas sorption analysis, powder X-ray diffraction, and infrared and solid-state NMR spectroscopic methods. The 2LiBH₄:1SiS₂ system forms an amorphous product that releases ca. 4.3 wt. % of H₂ below 385°C with a T_onset of 88°C without detectable diborane emission. The dehydrogenated sample reversibly absorbs 1.5 wt. % of H₂ at 385°C under 160 bar pressure. The H₂ release from materials with varying LiBH₄:SiS₂ ratios peaks at 8.2 wt. % for the 6LiBH₄:1SiS₂ composition, with a reversible hydrogen storage capacity of 2.4 wt. %. The H₂ desorption capacities of the Li-containing systems surpass those of Na-containing systems. Solid-state NMR studies indicate that products of mechanochemical reactions in the LiBH₄-SiS₂ system consist of one-dimensional chains of edge-sharing SiS₄/² tetrahedra in which the non-bridging S-ends are terminated with Li⁺, which are further coordinated to the [BH₄]⁻ anions. A variety of possible polymorphs in the Li-Si-S-(BH₄) composition space have been identified using first principles and thermodynamic modeling that supports the likelihood of formation of such novel complexes.

Keywords: Mechanochemistry, Hydrogen Storage, Solid-State NMR
1. Introduction

Borohydride complexes of alkali and alkaline-earth metals have been systematically investigated as potential materials for solid-state hydrogen ($\text{H}_2$) storage because of their large gravimetric $\text{H}_2$ contents, e.g., 18 wt. % for LiBH$_4$, 10.6 wt. % for NaBH$_4$ and 14.8 wt. % for Mg(BH$_4$)$_2$. However, other equally important performance parameters such as reversibility, decomposition temperature ($T_d$) and $\text{H}_2$ sorption kinetics, still require considerable improvement, and these remain subjects of continuing research. Applications of LiBH$_4$ ($T_d = \sim 400 ^\circ \text{C}$ [1]) and its aforementioned analogues for $\text{H}_2$ storage purposes are hindered primarily by the high thermal stability of pristine metal borohydrides and their limited reversibility [2-4]. Multiple strategies to modify their thermodynamic parameters and $\text{H}_2$ sorption kinetics, and to enhance reversibility under practical conditions have been considered. A variety of dopants, including metals, metal halides, and metal oxides, have been suggested as catalysts to improve $\text{H}_2$ storage performance of LiBH$_4$-based systems. For example, mixing LiBH$_4$ with SiO$_2$ reduces the onset temperature of $\text{H}_2$ desorption by $\sim 150 ^\circ \text{C}$, from $500 ^\circ \text{C}$ to around $350 ^\circ \text{C}$ [5]. Likewise, nearly 6 wt. % $\text{H}_2$ is released at 200°C from a LiBH$_4$ - 2Fe$_2$O$_3$ mixture [6]. Unfortunately, destabilization of LiBH$_4$ by metal oxides results from irreversible redox reactions, rendering rehydrogenation under moderate conditions impractical [7]. Doping with metal halides considerably decreases the dehydrogenation temperatures [8,9], down to as low as $\sim 100 ^\circ \text{C}$ for TiF$_3$, TiCl$_3$ and ZnF$_2$ [10-12]. Further, nanoconfinement of LiBH$_4$ in porous carbon combined with catalysis by NbF$_5$ or Ni shows significant improvements in $\text{H}_2$ ab/desorption [13, 14]. Doping with metals such as Mg, Al, Ni, Ti, V, Cr and Sc [15-18], on the other hand, does not substantially improve the dehydrogenation properties of LiBH$_4$, which still requires temperatures higher than $400 ^\circ \text{C}$ for fast hydrogen desorption.

Contrary to pure LiBH$_4$, which decomposes to lithium boride and hydrogen in the melt, many of the doped materials lose boron in the form of diborane, B$_2$H$_6$, during decomposition, leading to degradation [19]. Thermal decomposition of alkali metal borohydrides in the presence of nonmetals,
e.g., elemental sulfur, involve highly exothermic reactions below 200°C and is often accompanied by the release of gases, including hydrogen [20]. With the exception of NaBH₄, however, reactions of LiBH₄ and KBH₄ with S₈ produce H₂S or B₂H₆ as the main gaseous products.

In another approach, metal cation engineering allows indirect manipulations of the B–H interactions in BH₄, which has a favorable effect on the dehydrogenation–hydrogenation properties of borohydrides. In a systematic study, Nakamori et al. reported that desorption temperatures of metal borohydrides decrease with the increasing Pauling’s electronegativity of metal cations [21]. Following this observation, a series of mixed-metal borohydrides such as LiK(BH₄)₂, LiSc(BH₄)₄, NaSc(BH₄)₄, LiZn₂(BH₄)₅, Al₃Li₄(BH₄)₁₃ were synthesized and investigated [22-27]. Some of the studied materials show substantially reduced desorption temperatures when compared with the pristine LiBH₄.

Here we report a study of MBH₄-SiS₂ systems (M = Li or Na) as potential hydrogen storage media. A systematic variation in the composition and detailed analyses using X-ray diffraction, infrared spectroscopy, and an array of solid-state (SS)NMR experiments reveal the formation of previously unknown amorphous LiₓSiS₂(BH₄)ₓ materials that incorporate unusual complex cations and anions. Compared to pristine LiBH₄, these novel materials show much lower desorption temperatures, improved kinetics, and reversibility, offering new opportunities for the development of viable solid-state hydrogen storage systems.

2. Materials and methods

2.1. Mechanochemical synthesis. Sample preparation and other manipulations were carried out in an argon-filled glove box with oxygen and moisture levels maintained below 1 ppm. The precursors, LiBH₄ (> 95 wt. % purity,) and NaBH₄ (> 96 wt. % purity) were used as-purchased from Sigma-Aldrich, while silicon disulfide, SiS₂, was prepared in house from the elements. In a typical synthesis, a mixture of Si and S (total mass ~5 g with ~30 wt. % excess S over the exact SiS₂ stoichiometry), is loaded into a 60-ml tungsten carbide (WC) vial along with ~ 2 ml of heptane. The mixture is ball-
milled for 1 h using 44 g of WC balls (4 balls, 11 g each) in a SPEX 8000M mill. Milling of Si and S not only ensures homogenous distribution of the reactants, but also provides an efficient surface contact to facilitate further thermal reaction. Following the milling, heptane is removed by evaporation under vacuum, and the dried milled powder pressed into pellets, which are subsequently heated at 390°C for 7 days in quartz-lined steel container sealed under argon. After cooling to room temperature (RT), the pellets are reground, pressed into pellets, and heated again to 300°C under dynamic vacuum for 2 h. The latter step removes excess sulfur, which condenses on the colder parts of the quartz tube. The as-prepared SiS₂ typically contains less than 3 wt.% of the unreacted Si, as determined from quantitative analysis of powder X-ray diffraction data.

The mixtures of LiBH₄ (or NaBH₄) and SiS₂ at selected stoichiometries were prepared by milling in a 50-ml hardened-steel vial using 20 g of steel balls (2 large balls weighing 8 g each and 4 small balls weighing 1 g each) in a SPEX 8000M mill for 3 hours. To avoid iron contamination in samples for future SSNMR measurements, the ball milling was also performed in a 50-ml silicon nitride (Si₃N₄) vial using 14 g of Si₃N₄ balls (4 balls weighing 3.5 g each) for 9 hours (in 2LiBH₄-SiS₂ mixture) and 18 hours (in 6LiBH₄-SiS₂ mixture). The duration of milling necessary to complete reactions was determined by analysis of the X-ray powder diffraction patterns of samples ball-milled for different times; the increased LiBH₄:SiS₂ ratios require longer milling times to complete the reactions. The resulting products obtained in both types of vials were identical.

2.2. Hydrogen desorption/absorption: The hydrogen content and kinetics of de/absorption were measured using the PCTPro-2000 gas-sorption system: a fully automated Sieverts-type instrument that enables experiments in the temperature and pressure range of 25–400°C and 0–200 bar, respectively. Approximately 0.2 g of pelletized sample was loaded in an autoclave inside a glove box. The autoclave was then transferred to the gas-sorption system and evacuated. This was followed by volume calibration of the sample space using He gas at RT. In a typical temperature programmed desorption (TPD) experiment, a sample was heated from RT to 385°C at 1°C/min leading to gas release from the sample. After saturation was reached, as indicated by evening out of pressure, the
sample was cooled to RT, and removed for further characterization. In most cases, samples were quickly (usually 5–10 min) cooled to RT using forced air in order to quench the phase(s) at the equilibration temperature. For H₂ absorption experiments, samples were heated from RT to 385°C at 1°C/min under H₂ pressure of ca. 160 bar, followed by equilibration for 10 h and cooling under residual H₂ pressure to RT at 1°C/min. The autoclave was then evacuated and the sample removed for analysis, unless additional cycling experiments were performed. The released gas(es) were quantitatively analyzed using the RGAPro-2500 residual gas analyzer, connected to the PCT autoclave.

2.3. X-ray diffraction: Phase analysis of the reactions products was carried out by powder X-ray diffraction (XRD) analysis at room temperature on a PANalytical powder diffractometer using Cu Kα₁ radiation with a 0.02° 2θ step, in the range of Bragg angles 2θ from 10° to 80°. The measurements were carried out using a sample holder covered by the polyimide (Kapton) film to protect the sample from air during the measurement. The presence of the film visibly adds amorphous-like background in the XRD patterns at 13° < 2θ < 20°.

2.4. Infrared spectroscopy: Fourier transform infrared spectroscopy (FT-IR) data were collected on a Bruker Tensor 37 spectrometer and covered the spectral range from 4500 cm⁻¹ to 400 cm⁻¹ with a maximum resolution of 0.5 cm⁻¹. The investigated sample was mixed with KBr and pressed into a transparent pellet for collection of the IR spectra. To avoid the interaction of the sample with the air, all measurements were performed under the nitrogen gas flow.

2.5. Solid-state NMR: SSNMR experiments were carried out on a Varian/Agilent NMR spectrometer operated at 9.4 T, equipped with 3.2-mm and 5-mm double-resonance magic-angle spinning (MAS) probes. ¹¹B and ²⁹Si experiments were performed under MAS, using direct polarization (DPMAS) or cross-polarization (CPMAS). The samples were packed in MAS zirconia rotors in a glovebox under an argon atmosphere and sealed with double O-ring caps to avoid possible oxygen and moisture contamination. The experimental parameters are given in the relevant figure captions, using the following symbols: ν_R denotes the MAS rate; ν_{RF(X)}, the magnitude of the RF magnetic field applied
to X spins; $\tau_{CP}$, the cross-polarization time; and $\tau_{RD}$, the recycle delay. The $^{11}$B and $^{29}$Si shifts are reported using the $\delta$ scale and are referenced, respectively, to diethyl ether-boron trifluoride complex ($\text{BF}_3\cdot\text{OEt}_2$) and tetramethyldisilane (TMS) at 0 ppm, based on the measurement of sodium-3-(trimethylsilyl)propanesulfonate (DSS) as a secondary external reference.[28]

**Computational methods:** Density functional theory (DFT) calculations of the total energies and phonon spectra were performed using the Vienna Ab initio Software Package (VASP). [29-32] Standard projector-augmented wave (PAW) pseudopotentials [33,34] were used with the PW91 [35] generalized gradient approximation (GGA) for exchange and correlation. A plane wave cutoff of 600 eV was used with a self-consistent field (SCF) convergence of $10^{-6}$ eV. Sampling of the Brillouin zone was performed with Monkhorst-Pack grids with a minimum of $2\times2\times2$ k-space points per unit cell for insulating structures, and $14\times14\times14$ k-space points for metallic structures. The vibrational modes of the structures were calculated in the harmonic approximation using the method of frozen phonons or the response function methods available in the VASP code. Finite temperature thermodynamic parameters were calculated from the vibrational modes using standard techniques. Structural candidates for borohydrides in the Li-S-Si-B-H system were generated using the prototype electrostatic ground states (PEGS) method described in Ref. [36], which requires placing the rigid structural units consisting of tetrahedral [BH$_4$]$^-$ anions in a simulation cell with hard-spheres representing Li, Si, and S atoms. The nominal charges were Li$^+$, Si$^{+4}$, and S$^{-2}$. A simulated-annealing Monte Carlo routine minimizes the total electrostatic energy of the simulation cell using a combination of structural changes including atom translations, anion rotations, and swapping of objects, as well as full freedom to change the unit cell volume and shape. All PEGS structures were subsequently relaxed via DFT to obtain accurate total energies and thermodynamic properties. Cell symmetries were searched after DFT-relaxation of the PEGS prototypes using the FINDSYM code from the ISOTROPY software package [37].

The partial phase diagram indicating the relative stabilities of the structural candidates for structures in the Li-S-Si-B-H system was established using the Multiple-gas Canonical Linear Programming
(MGCLP) method described in detail in Ref. [38]. Free energy minimization in the canonical ensemble is a convenient approach to treat multiple gas phases, as opposed to the grand canonical linear programming method (GCLP) [39], where the reference reservoir is hydrogen gas. In the MGCLP method, the concentration of multiple gases is determined self-consistently.

3. Results and discussion

3.1. Synthesis and gas sorption analysis

<table>
<thead>
<tr>
<th>System, ratio LiBH$_4$:SiS$_2$</th>
<th>Theor.$^a$ H$_2$ wt.%</th>
<th>1$^\text{st}$ desorption</th>
<th>2$^\text{nd}$ desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>wt. % H$_2$</td>
<td>T$_{\text{onset}}$ $^\circ$C</td>
</tr>
<tr>
<td>2:1</td>
<td>5.9</td>
<td>4.3</td>
<td>88</td>
</tr>
<tr>
<td>4:1</td>
<td>8.9</td>
<td>7.1</td>
<td>113</td>
</tr>
<tr>
<td>5:1</td>
<td>9.9</td>
<td>7.5</td>
<td>116</td>
</tr>
<tr>
<td>6:1</td>
<td>10.7</td>
<td>8.2</td>
<td>92</td>
</tr>
<tr>
<td>8:1</td>
<td>11.9</td>
<td>6.2</td>
<td>96</td>
</tr>
<tr>
<td>LiBH$_4$ (ball-milled for 3h)</td>
<td>18.2</td>
<td>2.9</td>
<td>276</td>
</tr>
</tbody>
</table>

$^a$ theoretical total hydrogen content in the system.

$^b$ arrows “↑” and “↓” represent the increase or decrease of the amount of the identified phase in a mixture upon increasing the LiBH$_4$ content.

$^c$ the presence, though likely, was not detectable due to limited sensitivity of XRD analysis.

The hydrogen storage properties of the ball-milled LiBH$_4$-SiS$_2$ mixtures taken in different molar ratios of components are summarized in Table 1. The TPD of as-milled products for the 2:1 mixture shows H$_2$ desorption at a significant rate starting at 88°C, releasing ~4.3 wt. % of H$_2$ at 385°C (Fig. 1a), corresponding to about 73 % of the total H$_2$ available in the nominal composition. The amount of released hydrogen increases with the increasing LiBH$_4$ content in the mixture and reaches a maximum H$_2$ desorption of ca. 8.2 wt. % (~80 % of theoretical capacity) in the 6:1 mixture (Fig. 1c). Upon further increase of the LiBH$_4$ concentration to an 8:1 molar ratio, a net decrease in the amount of released H$_2$ was observed (Table 1). This is due to the presence of excess LiBH$_4$ in the mixture.
that does not release H₂ under the test conditions, and hence acts as a dead weight in the sample. All samples with various mixing ratios show a significant decrease in the decomposition temperature compared to pristine LiBH₄, and the RGA of the released gases show pure H₂ in the entire temperature range for all mixtures with no discernable diborane emission.

Although several earlier investigations reported improved H₂ sorption properties of LiBH₄ in reactive hydride composites, meaningful comparisons of different composites is difficult [40, 41]. For example, the 4LiBH₄:5Mg₂NiH₄ system yields close to stoichiometric amount of H₂ (~5.2 wt. %) upon heating to 400°C. However, this system contains less than 15 % of LiBH₄ by weight compared to approximately 60 wt. % of LiBH₄ in the 6LiBH₄:1SiS₂ system. Despite the much higher LiBH₄ to additive mass ratio in 6LiBH₄:1SiS₂, it releases nearly 80 % of the total H₂ around 400°C with T_{onset} = 92°C, which is much lower than T_{onset}=250°C of the 4LiBH₄:5Mg₂NiH₄ and other systems with similar additives [42-46]. Another example is 3LiBH₄:1AlCl₃ system which, when mechanochemically processed in a similar fashion, releases only about 50 % of the total hydrogen at 400°C with even lower T_{onset} of ~50°C [47].
The reversible H₂ holding capacities in 2:1 and 6:1 LiBH₄:SiS₂ mixtures were studied by cycling the dehydrogenated materials. As indicated earlier, the regeneration was performed at 385 °C under 160 bar H₂, followed by hydrogen desorption from rehydrogenated samples. The product from the 2:1 mixture shows net H₂ release of ~1.5 wt. % starting at ~230 °C (Fig. 1b, Table 1), corresponding to ~35 % of the initial H₂ release in the material. Similar dehydrogenation profiles were observed for the 2nd, 3rd, and 4th cycles. In the 6:1 mixture, after the 1st rehydrogenation of products from the desorption of the as-milled sample, ca. 2.4 wt. % of H₂ was released starting at 199°C. This corresponds to nearly 30 % of the reversible capacity for this composition (Fig. 1d, Table 1).

According to the TPD experiments on the NaBH₄-SiS₂ system, the 2:1 ball-milled mixture shows the highest H₂ release among all of the compositions investigated. Hydrogen (>99.7 % purity) release starts at 124°C and reaches ca. 3.3 wt. % at 385°C (see Table S1 and Fig. S1a). This equates to about 69 wt. % of all initially available H₂. Approximately 30 % (~0.9 wt. % of H₂) of the initial H₂ capacity is recoverable after hydrogenation of the decomposed products, with the desorption onset at 270°C. Further, the ball-milled 5:1 and 6:1 molar mixtures release 2.1 and 2.4 wt. % of H₂ with Tonset = 134°C and 159°C, respectively. Again, the drop in the net capacity compared to the 2:1 mixture is explained by the higher amounts of unreacted NaBH₄ in the decomposed mixtures.

### 3.2. XRD Analysis

The XRD patterns of as-synthesized products with various LiBH₄/SiS₂ ratios are shown in Fig. 2. The ball-milled 2:1 mixture was X-ray amorphous with no traces of starting materials present. When the molar ratio of LiBH₄ to SiS₂ was increased to 4:1, SiS₂ was completely consumed and/or
amorphized, while the Bragg peaks assigned to LiBH₄ could still be detected in the diffraction pattern of the reaction mixture. These signals were slightly but clearly shifted towards higher Bragg angles, but featured relative intensities characteristic of pristine LiBH₄ (Fig. S2). The observed shift can be explained by the partial substitution of larger [BH₄]⁻ (2.03 Å) [48] with the smaller S²⁻ anions (1.84 Å) [49] in the LiBH₄ structure, leading to a decrease in the lattice parameters. For the mixtures showing the most interesting dehydrogenation behaviors (i.e., prepared with molar ratios 2:1 and 6:1), subtle changes in the local atomic coordination in LiBH₄ resulting from the mechanochemical transformations were further analyzed using the FT-IR (see supporting information, Fig. S3) and SSNMR (*vide infra*).

![XRD patterns of LiBH₄-SiS₂ mixtures](image)

**Fig. 2.** The XRD patterns of LiBH₄-SiS₂ mixtures ball-milled with different molar ratios. (The asterisks * represent positions of Bragg reflections of impurities from the SiS₂ precursor).

To provide insight into the chemical transformations occurring during the thermal treatment, the 6:1 mixture was heated to 180°C, 260°C, 300°C and 385°C and kept at these temperatures for 24 h. The products were further analyzed by XRD. Heating of the ball-milled sample to 180°C leads to a release of ~2.4 wt. % of hydrogen (Fig. S4). The XRD analysis shows the beginning of the formation of Li₂S, while the material with a structure similar to LiBH₄, obtained after milling, still remains in the heated mixture (Fig. S5). Heating the sample to higher temperatures (260°C, 300°C and 385°C), leads to the formation of Li₂S as the only crystalline product of the decomposition reaction (Fig. S5).
The amount of released hydrogen increases with the temperature (Fig. S4). The high amount of released hydrogen upon heating the sample to 265°C, 300°C and 385°C shows that these temperatures are sufficient for complete decomposition of the mixture. As no crystalline intermediate products were observed, it is likely that the Si- and B-containing species remain X-ray amorphous. Furthermore, investigations of the decomposed and rehydrogenated mixtures show no significant change in their XRD patterns, suggesting that H₂ may cycle in this system through one or more amorphous phase(s); hence, SSNMR was extensively employed to study the desorption products.

In contrast to the LiBH₄-SiS₂ system, the ball-milled mixtures of NaBH₄-SiS₂ prepared in all examined molar ratios (Table S1) show unreacted NaBH₄ in the XRD, while SiS₂ either reacts with some of NaBH₄ to yield an amorphous product or itself amorphizes upon milling. The XRD of the desorbed product shows Bragg peaks of NaBH₄, which does not decompose below 385°C (Fig. S6). Besides residual NaBH₄, Na₂S was also observed in all of the products after TPD. Since Na-based materials release only a small fraction of hydrogen compared to the Li-containing materials, our main effort was concentrated on the study of the LiBH₄-SiS₂ mixtures.

3.3. Solid-state NMR Experiments.

A series of ²⁹Si and ¹¹B SSNMR experiments were carried out on the samples produced from 2:1 and 6:1 mixtures (Fig. 3a-c) to monitor the transformations of the samples during the dehydrogenation and subsequent rehydrogenation processes.

3.3.1. As-milled samples. The ¹¹B DPMAS spectra of the 2:1 and 6:1 ball-milled mixtures show only one signal at -42 ppm, assigned to [BH₄]⁻ anions (Fig. 3a). The ²⁹Si DPMAS spectra of those samples in Fig. 3c show a broad signal at +30 ppm and a relatively sharp signal at +6 ppm. An additional signal was observed around -4 ppm in the ²⁹Si {¹H} CPMAS spectra (Fig. 3d). The +30 ppm signal could not be assigned to any known species that contain Li, B, Si, and/or S in any combination, or corresponding hydrides. The +6 ppm and -4 ppm signals were assigned to E⁰ and E¹ sites in corner sharing only and one edge sharing configurations shown in Fig. 3b, respectively, based on the study...
by Eckert et al. [50]. The resonance attributable SiS$_2$ with edge shared E$^2$, which would be expected at -22 ppm, was not observed. The authors of Ref. [50] also noted that the resonance frequency of Si in the SiS$_4$ tetrahedra is not sensitive to nuclei in the second or further coordination sphere; thus two assignments are possible for X in Fig. 3b: i) the corner S is shared with the adjacent SiS$_4$ unit, and/or ii) the corner S is terminated with Li (S····Li$^+$) [51]. In the latter case, most likely the BH$_4^-$ anions are coordinated to the Li$^+$ cation. The pronounced E$^1$ signal in the $^{29}$Si{$^1$H} CPMAS spectra (Fig. 3d) suggests that the E$^1$ site has more $-$S····Li$^+$ (BH$_4$)$_n^-$ structures than the E$^0$ site. The buildup of $^{29}$Si magnetization during the cross-polarization, which is governed by the strength of heteronuclear dipolar coupling and thus can be used to estimate the $^1$H--$^{29}$Si distance [52], was measured as a function of contact time (spectra are not shown). The interatomic distance between Si and the nearest $^1$H is roughly estimated to be around 4 Å for all Si sites.

Fig 3. $^{11}$B DPMAS (a), $^{29}$Si DPMAS (c), and $^{29}$Si{$^1$H} CPMAS (d) spectra of LiBH$_4$-SiS$_2$ mixtures (2:1 and 6:1) after ball milling, dehydrogenation and rehydrogenation. The local structures of Si species are shown in (b). The $^{11}$B NMR spectra were acquired using $v_R = 12.5$ kHz, $v_{RF}(^{11}$B) = 125
kHz for short pulse (corresponding to a flip angle of 15°), \( v_{RF}(^1H) = 50 \) kHz for \(^1H\) decoupling during acquisition, and \( \tau_{RD} = 1s \). The \(^{29}Si\) NMR spectra were acquired using \( v_R = 10 \) kHz, \( v_{RF}(^{29}Si) = 50 \) kHz, \( v_{RF}(^1H) = 40 \) kHz for cross polarization and for \(^1H\) decoupling, \( \tau_{CP} = 4 ms \), whereas \( \tau_{RD} = 1s \) and 900 s for CP and DPMAS, respectively. \( NS = 8000 \div 16000 \) for the CP and 80 \div 160 for the DPMAS experiments. The spectra were normalized based on the sample amount and number of acquisitions and show the absolute intensities within each column unless otherwise noted. Note that the absence of an Si₃N₄ signal (~ -43 ppm) [53] ensures that a very low contamination from the Si₃N₄ vial is present. The signals that appear upon hydrogenation are marked by asterisks. Dashed lines are eye-guides for a comparisons of signal positions.

3.3.2. Dehydrogenation. The \(^{11}B\) DPMAS spectra of both dehydrogenated samples show a broad signal between +20 and -40 ppm (Fig. 3a), assigned to four-coordinated boron sites, which, based on the \(^{11}B\{^1H\}\) CPMAS spectra shown in Fig. S7 and the discussion below, can be assigned to species described as \( B(-H)_{n}(-B)_{4-n} \) \( (n = 1, 2, 3) \). The 6:1 sample also shows the signal of the remaining BH₄ in the 6:1 sample. The presence of a small amount of elemental boron, whose \(^{11}B\) NMR signal is expected around 0 ppm, cannot be ruled out. In the \(^{29}Si\) DPMAS spectrum of the dehydrogenated 2:1 sample (Fig. 3c), the +30 ppm signal shifts slightly toward the lower frequency (+22 ppm) and its relative intensity increases, while the E⁰ signal remains nearly unchanged (the signal at -78 ppm is the spinning sideband of the +22 ppm signal). Practically no signals were observed in the corresponding \(^{29}Si\) CPMAS spectrum (Fig. 3d), which indicates that none of the Si atoms have \(^1H\) in their close proximities after the dehydrogenation. In contrast to the 2:1 sample, a drastic change was observed in the \(^{29}Si\) DPMAS spectrum of the dehydrogenated 6:1 sample; all \(^{29}Si\) signals observed in the as-milled sample disappeared, whereas a new broad signal ranging between -50 and -150 ppm and a sharp signal at -76 ppm were observed. The broad signal was also observed in the CPMAS spectrum (note that it polarized very quickly, in less than 100 \( \mu s \)), while the sharp signal was no longer detected. Thus, the broad signal is assigned to an amorphous hydrogenated silicon phase, which features small inclusion of polycrystalline silicon represented by the sharp peak (Fig. 4b) [54, 55]. The complete transformation to the H-capped elemental silicon species indicates that the silicon and the boron species comprise separated components in the 6:1 sample upon heating. Given the
similarities between the $^{11}$B NMR spectra of the 2:1 and the 6:1 samples (except for the remaining BH$_4$), the separation of boron and silicon can be assumed to occur upon dehydrogenation also in the 2:1 sample, without forming the hydrogenated silicon species. All hydrogen in this sample must be associated with boron, further substantiating our assignment of the broad $^{11}$B signal to the tetracoordinated boron species $B(-H)_n(-B)_{4-n}$ ($n = 1, 2, 3$) (see Fig. 4a). The formation of closo-boranes has been suggested in many studies; however, no results conclusively support the presence of closo-boranes in our samples.

Upon heating the 6:1 mixture from RT to 385°C, the [BH$_4$]$^-$ units progressively transform into a less protonated boron as indicated by the gradual shift of the $^{11}$B signal to higher $\delta$ in the temperature-sampled products (Fig. S8). Although the BH$_4$ signal is predominant below 260°C (Fig. S8), the transformation starts much below this temperature, with the concentration of partially dehydrogenated species becoming significant at temperatures above 260°C.

3.3.3. Rehydrogenation. In the $^{11}$B NMR spectra, the rehydrogenated 2:1 mixture shows a small but clear [BH$_4$]$^-$ signal and a shoulder of the broad signal around -30 ppm (shaded region in Fig. 3a). In the 6:1 mixture, the line width of the broad peak centered around -10 ppm is significantly reduced (shaded part in Fig. 3a) suggesting the partial rehydrogenation of $B(-H)_n(-B)_{4-n}$ species to more hydrogenated form(s). The observed change upon the rehydrogenation is explained by the reaction, $B(-H)_n(-B)_{4-n} + \alpha H \rightarrow B(-H)_{n+\alpha}(-B)_{4-n-\alpha}$. In the $^{29}$Si DP- and CPMAS spectra of the 2:1 sample, no significant changes are observed upon hydrogenation, suggesting that rehydrogenation mainly involves the boron species. In the 6:1 sample, two minor signals are resolved at -20 and -96 ppm in the CPMAS spectrum (indicated by the asterisk in Fig. 3b), assigned to polysilicon hydride and clustered Si–H, respectively [54-56].

3.4. Pathway for the complex formation and its hydrogen cycling.

Based on the obtained TPD, XRD and SSNMR data, we conclude that the mechanochemical reactions in the LiBH$_4$-SiS$_2$ system lead to the formation of a mixture of multiple species whose
compositions can be broadly described as \( \text{Li}_x(\text{SiS}_2)_y(\text{BH}_4)_z \), where \( x \) and \( y \) depend upon the ratio of \( \text{LiBH}_4 \) and \( \text{SiS}_2 \) in the initial mixture. Their formation proceeds through a sequence of chemical events, which start from transformation of the edge-shared \( \text{SiS}_4 \) (E\(^2\)) [50] moieties originally present in pristine \( \text{SiS}_2 \) into a mixture of one- (E\(^1\)) and no-edge-shared (E\(^0\)) moieties upon milling. Such a transformation proceeds through creation of “dangling” Si-S bonds with negatively charged sulfur atoms, which in the presence of the \( \text{LiBH}_4 \) are terminated by positively charged Li\(^+\) ions coordinated to the \([\text{BH}_4]^-\) anions (Fig. 3b).

The newly formed complexes have improved hydrogen cycling ability compared to the pristine \( \text{LiBH}_4 \), which can be explained in terms of the nature of their components in the internal structure. The blocking of Li-coordination sites by \( \text{SiS}_2 \) in \( \text{SiS}_2-\text{LiBH}_4 \) complexes reduces the number of Li-H-B interactions in the material, which may reduce the thermal stability of the BH\(_4\) group. This assumption correlates with previous reports about the reduced thermal stability of \( \text{LiBH}_4 \)-crown ether complexes, where most of the Li coordination sites are blocked by oxygen atoms of the crown ethers [57]. Such complexes decompose at much lower temperatures than the pure \( \text{LiBH}_4 \) does [58]. It is also known that the charge compensation by Li\(^+\) cations is a key feature for the stability of the internal bonding of \([\text{BH}_4]^-\) anions [59]. In the case of \( \text{SiS}_2-\text{LiBH}_4 \) complexes, the coordination of Li to \( \text{SiS}_2 \) reduces the positive charge on Li\(^+\); i.e. partial transfer of an electron to Li leads to an improvement of dehydrogenation kinetics. The rearrangement upon dehydrogenation of the newly formed active boron-containing species into amorphous \( B(-H)_n(-B)_{4-x} \) \((n = 0, 1, 2, 3)\) moieties prevents the release of diborane [1, 60, 61]. The mixture of amorphous polyboranes is likely responsible for the observed partial reversibility of hydrogen release in the 2:1 mixture, because the \(^{29}\text{Si} \) DP and CPMAS spectra before and after the rehydrogenation showed no noticeable difference (Fig. 4a). This may also be true for the 6:1 mixture; however, a minor contribution of the newly formed amorphous Si to recyclable hydrogen capacity at this ratio is also possible. Therefore, the hydrogen cycling mechanism in the 6:1 sample includes two types of ab/desorption. The first is the hydrogenation/dehydrogenation of
polyborane moieties, similarly to the 2:1 mixture (Fig. 4a), and the second is the cycling of polysilicon hydrides on the surface of amorphous silicon, schematically shown in Fig. 4b.

![Diagram](image)

**Fig. 4.** Schematic representation of the mechanism of rehydrogenation of the a) polyborane moieties and b) polysilicon hydride on the surface of amorphous silicon. The red lines represent sites of breaking bonds and hydrogenation of atoms.

### 3.5 Theoretical Considerations

Thermodynamic calculations of the LiBH$_4$-SiS$_2$ system were performed for a variety of ratios of LiBH$_4$:SiS$_2$ in order to project thermodynamically favorable structures. Because in our experiments the compounds appear X-ray amorphous, we investigated the local structure and thermodynamics of the as-synthesized compounds using the PEGS method. Candidate structures generated with PEGS were fully relaxed using DFT and their thermodynamic properties were calculated. There is no a priori symmetry in the PEGS simulation cell; the search results in a large number of possible local geometries. Further, we based some simulations on suggested local coordination provided by the NMR data. These included corner shared, rigid SiS$_4$ tetrahedra and the presence of [BH$_4$]$^-$ anions.
While many of the candidate structures generated are relatively high in total energy, their formation is possible through energetic ball-milling.

Covering all of the composition space, we generated structures of stoichiometry $n\text{LiBH}_4+\text{SiS}_2$, with $n = 1,2,3,4,5$. For each value of $n$, both one- and two-formula unit structure candidates were generated. Candidate PEGS structures were added to a thermodynamic database of the following known compounds in the H-Li-B-Si-S system (symmetries in parenthesis): B ($R-3m$, and $P4_2/nmm$), $\text{B}_2\text{H}_6$ (gas), Li ($P4/mmm$), $\text{Li}_2\text{S}$ ($Fm-3m$), $\text{Li}_2\text{SiS}_3$ ($Cmc2_1$), LiB ($Pnma$), LiH ($Fm-3m$), $\text{LiBH}_4$ ($Pnma$, $Cc$, $P6_3mc$), $\text{Li}_2\text{S}$ ($Fm-3m$), S ($Fddd$), Si ($Fd-3m$), Si(\text{BH}_4)_2 ($P1$), SiB$_4$ ($R-3m$), Si(\text{BH}_4)_4 ($I-42m$), SiB$_6$ ($P4mm$), SiS$_2$ ($Ibam$).

The lowest-energy Li-Si-S-(BH$_4$) compound that was also calculated to be stable against decomposition had the stoichiometry $\text{Li}_2\text{SiS}_2(\text{BH}_4)_2$ or a 2:1 ratio of LiBH$_4$:SiS$_2$. The atomic arrangement (see Fig. 5a) in this compound consists of polymeric-like square planar chains of Li-S in the form of a ladder. The Li-S ladders are cross-linked with bridging Si, which are 5-coordinated with 2 S and 3 hydrogen atoms from distorted BH$_4^-$ anions. This structure, containing three nearest neighbor hydrogen atoms for each Si, is not in agreement with the SSNMR measurements indicating a Si-H distance larger than 4 Å, suggesting that higher-energy metastable polymorphs may have been synthesized in the mechanical milling process. PEGS candidates that do conform to the SSNMR measurements were generated, but were about 35 kJ/mol f.u. higher in energy than the ground state structure. The lowest-energy metastable structure is shown in Fig. 5(b): a layered structure with corner-sharing SiS$_4$ tetrahedra with the nearest Si-H distance just over 4 Å. Another 4-coordinated Si-S structure, considerably higher in energy at 160 kJ/mol f.u. above the ground state structure, is shown in Fig 5(c). This high-energy structure contains edge-sharing SiS$_4$ tetrahedra with S-Li bonds and has a Si-H distance of about 3 Å, in agreement with the SSNMR data. These results suggest that the mechanical milling may have produced amorphous structures resembling the projected higher-energy crystalline polymorphs of the $\text{Li}_2\text{SiS}_2(\text{BH}_4)_2$ compound.
Fig. 5. PEGS-generated Li$_2$SiS$_2$(BH$_4$)$_2$ structures. (a) Ground state structure with 5-coordinated Si and Li-S polymeric chains; (b) metastable layered structure containing corner-sharing SiS$_4$ tetrahedra; (c) higher energy polymorph containing edge-sharing SiS$_4$ tetrahedra.

The lowest-energy structure shown in Fig. 5a was computed to be stable against decomposition into its elements and any of the higher energy polymorphs. Its decomposition pathway is predicted by MGCLP to occur at 240 K, within the following reaction: Li$_2$SiS$_2$(BH$_4$)$_2$ → 2B + Li$_2$S + 0.5Si + 0.5SiS$_2$ + 4H$_2$, with an enthalpy of 32.5 kJ/mol H$_2$.

The simulated NMR chemical shifts based on the obtained structural models did not show agreement with our experimental results. This can be explained by the method used for the preparation of our materials. Mechanochemical synthetic methods often lead to the formation of metastable phases that are thermodynamically less stable. Therefore, compounds with structural models obtained via PEGS calculations can be possibly stabilized by other synthetic methods and conditions.

4. Conclusions

Mechanochemically prepared LiBH$_4$-SiS$_2$ systems demonstrate significant advantages in hydrogen de/absorption ability compared to the analogous systems with NaBH$_4$. The experimental results clearly show that SiS$_2$ readily reacts with LiBH$_4$ during the solid-state mechanochemical processing. Upon subsequent thermal treatment, the resulting hydride composite shows a considerable decrease in dehydrogenation onset temperature compared to pristine LiBH$_4$. Not only a significant
destabilization was achieved, but the release of diborane was suppressed to below the detection limits. Comprehensive phase and gas sorption analyses of several reactions with varying compositions revealed that the 6:1 molar mixture of LiBH₄-SiS₂ releases the highest amount of hydrogen (ca. 8.2 wt. %) upon heating to 385°C with the onset temperature close to 92°C. The hydrogen de/absorption study of this mixture showed that 2.4 wt. % of H₂ (30 % of initial release) could be recycled under easily achievable hydrogen pressures and temperature. The ball-milled 2:1 LiBH₄-SiS₂ mixture shows hydrogen release at a significant rate starting at 88°C, releasing 4.3 wt. % of hydrogen at 385°C. Nearly 35 % of this hydrogen could be cycled (1.5 wt. %).

The mechanochemical reactions in the LiBH₄-SiS₂ system lead to the formation of a mixture of multiple species whose compositions are given as Liₓ(SiS₂)ᵧ(BH₄)ᵦ, in which x and y depend upon the ratio of LiBH₄ and SiS₂ in the initial mixture. Although the structure of these complex borohydrides was not fully determined, the FT-IR and ²⁹Si SSNMR data strongly suggest the presence of amorphous Si and its hydride within the structure of complex borohydrides, which is unprecedented to the best of our knowledge. In one plausible explanation, the blocking of Li-coordination sites by SiS₂ in SiS₂-LiBH₄ complexes, which reduces the number of Li-H-B interactions, is responsible for the decrease of decomposition temperature and the purity of the released hydrogen. The possible charge compensation by Li⁺ cations could also be the key feature for the stability of the internal bonding of [BH₄]⁻ anions: coordination of Li to SiS₂ would reduce the positive charge on Li⁺, and the charge transfer to Li would lead to improvement of dehydrogenation kinetics. Meanwhile, formation of amorphous B(−H)ₙ(−Bₓ₋ₓ)ₓ (n = 0, 1, 2, 3) moieties upon dehydrogenation of the SiS₂-LiBH₄ complexes prevents the release of diborane. The thermodynamic MGCLP and structure search using PEGS calculations identified a variety of potentially stable Li₂SiS₂(BH₄)₂ phases.

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