New Li Ion Conductors and Solid State Hydrogen Storage Materials: LiM(BH₄)₃Cl, M = La, Gd

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Supporting Information

ABSTRACT: Multiple reaction mixtures with different composition ratios of MCl₃−LiBH₄ (M = La, Gd) were studied by mechano-chemical synthesis, yielding two new bimetallic borohydride chlorides, LiM(BH₄)₃Cl (M = La, Gd). The Gd-containing phase was obtained only after annealing the ball-milled mixture. Additionally, a solvent extracted sample of Gd(BH₄)₃ was studied to gain insight into the transformation from Gd(BH₄)₃ to LiGd(BH₄)₃Cl. The novel compounds were investigated using in situ synchrotron radiation powder X-ray diffraction, thermal analysis combined with mass spectroscopy, Sieverts measurements, Fourier transform infrared spectroscopy, and electrochemical impedance spectroscopy. The two new compounds, LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl, have high lithium ion conductivities of 2.3×10⁻⁴ and 3.5×10⁻⁴ S·cm⁻¹ (T = 20 °C) and high hydrogen densities of ρ_m = 5.36 and 4.95 wt % H₂, and both compounds crystallize in the cubic crystal system (space group I-43m) with unit cell parameter a = 11.7955(1) Å and a = 11.5627(1) Å, respectively. The structures contain isolated tetranuclear anionic clusters [M₄Cl₄(BH₄)₁₂]⁴⁻ with distorted cubane M₄Cl₄ cores M = La or Gd. Each lanthanide atom coordinates three chloride ions and three borohydride groups, thus completing the coordination environment to an octahedron. The Li⁺ ions are disordered on 2/3 of the 12d Wycko ff site, which agrees well with the very high lithium ion conductivities. The conductivity is purely ionic, as electronic conductivities were measured to only 1.4×10⁻⁸ and 9×10⁻⁸ S·cm⁻¹ at T = 20 °C for LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl, respectively. In situ synchrotron radiation powder X-ray diffraction (SR-PXD) reveals that the decomposition products at 300 °C consist of LaB₆/LaH₂ or GdB₄/GdH₂ and LiCl. The size of the rare-earth metal atom is shown to be crucial for the formation and stability of the borohydride phases in MCl₃−LiBH₄ systems.

INTRODUCTION

Storage of renewable energy is essential to create a new sustainable energy economy.¹ Renewable energy can be stored directly as electricity in, e.g., a Li-battery or indirectly as hydrogen in a solid state metal hydride.² Batteries are rechargeable but have limited energy storage capacity. Indeed, this calls for continued intense research within the energy storage materials scientific community. This paper describes new materials that are fast Li-ion conductors and also carry significant amounts of hydrogen.

Metal borohydrides currently receive increasing interest due to their high hydrogen densities. Unfortunately, many of the known borohydrides exhibit poor thermodynamic and kinetic properties, which hamper their utilization in technological applications.³–⁶ Therefore, significant focus has been on synthesis and characterization of novel bimetal borohydrides due to the somewhat tunable decomposition temperatures of these compounds.⁷–¹⁰ Recently, the first two binary alkali/lanthanide borohydride chlorides, NaY(BH₄)₂Cl₂,¹¹ and LiCe-(BH₄)₃Cl₄,¹²,¹³ have been described with fascinating crystal

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structures: NaY(BH₄)ₓClₓ has a polymeric pseudo-orthorhombic crystal structure and LiCe(BH₄)ₓClₓ contains tetraneutral anionic clusters of [CeₓClₓ(BH₄)ₜₓ]⁺ with a distorted cubane CeₓClₓ core known from organic crystals. Several other binary alkali/lanthanide borohydrides have also been discovered, including LiSc(BH₄)₄, NaSc(BH₄)₄, KSc(BH₄)₄, and KY(BH₄)ₓ. Recent studies of these compounds reveal structures built from isolated complex anions, such as [Sc(BH₄)₄]⁻ in MSc(BH₄)₄ (M = Li, Na, or K) and [Y(BH₄)₄]⁻ in KY(BH₄)₄. Several of these mixed-metal borohydrides exhibit improved thermodynamic properties; e.g., LiSc(BH₄)₄ and LiCe(BH₄)₃Cl are found to decompose in the temperature ranges 140–260 °C and 230–250 °C, respectively. These are significantly lower temperatures as compared to the corresponding alkali borohydrides, LiBH₄ and NaBH₄ which decompose at approximately 380 and 400 °C, respectively.¹⁹

The complex borohydride ion may resemble the halide ions in the solid state, which might facilitate anion substitution in metal borohydrides. The halide stabilized lithium borohydrides LiBH₄–LiX (X = Cl, Br, or I) form solid solutions, Li(BH₄)ₓ–Xₙ which tend to stabilize the hexagonal polymorph to room temperature.²⁰–²³ The hexagonal halide stabilized polymorphs LiBH₄–LiX (X = Cl, Br, or I) form solid solutions, Li(BH₄)ₓ–Xₙ, which tend to stabilize the hexagonal polymorph to room temperature (RT), which increase to approximately 10⁻¹ S·cm⁻¹ at room temperature (RT), which increase to approximately 10⁻² S·cm⁻¹ at 150 °C.²⁴–²⁶ The crystal structure of LiCe(BH₄)₃Cl concords with the observed high Li ion conductivity of 1.0 × 10⁻² S·cm⁻¹ at 20 °C as the tetraneutral anionic clusters of [CeₓClₓ(BH₄)ₜₓ]⁺ are charge balanced by disordered Li⁺ ions occupying 2/3 of the available positions in the crystal lattice, allowing them to move within the structure.¹⁹ These materials are considered as possible electrolytes for solid state lithium batteries.²⁷

LaCl₃–LiBH₄ and GdCl₃–LiBH₄ systems have both been studied previously and reveal improved thermodynamic and kinetic properties, i.e., decompositions with evolution of mainly hydrogen gas in the temperature range 230–300 °C.²⁸–³⁰ Production of LiBH₄ from LaCl₃ has been reported for the mixture of LaCl₃–LiBH₄.²⁸ However, no structural information is currently available. Ball-milling (BM) the mixture GdCl₃–LiBH₄ produces LiCl and Gd(BH₄)₃, which is isostructural to Y(BH₄)₃.³¹ However, upon heating to 200 °C, an unknown compound is formed.²⁹ This has prompted the present study, where we report on the synthesis, characterization, and thermal decomposition of two new lithium borohydride chloride materials, LiₓM(BH₄)ₓClₙ (M = La or Gd), using in situ synchrotron radiation powder X-ray diffraction (SR-PXD), simultaneous thermal analysis and mass spectroscopy (DTA-TGA-MS and DSC), Sieverts measurements, Fourier transform infrared spectroscopy (FTIR), and electrochemical impedance spectroscopy (EIS).

## Experimental Section

**Synthesis.** The different samples prepared for this study are summarized in Table 1. The title compounds, LiₓLa(BH₄)ₓClₓ and LiₓGd(BH₄)ₓClₓ, were prepared from mixtures of LaCl₃–LiBH₄ and GdCl₃–LiBH₄ in the molar ratio 1:3 (s1 and s2). The samples were ball-milled (BM) in repeated sequences for 120 min applying 2 min BM and 2 min pauses using a Fritsch Pulverisette 4 planetary mill under inert conditions (argon atmosphere) in 80 mL tungsten carbide containers with tungsten carbide balls (d. o. d. 10 mm). The sample to ball mass ratio was approximately 1:35. Speeds of the main disk and the planetary disks were 200 and 560 rpm, respectively.

A solvent-extracted sample of Gd(BH₄)₃ (s3) was obtained from s2 using solvent-based extraction techniques.³² Samples s4 and s5 for conductivity measurements were obtained mechano-chemically as described above. Afterward, sample s4 was annealed at 200 °C for 30 min at p(H₂) = 10 bar to increase the weight fraction of LiₓLa(BH₄)ₓClₓ. Sample s5 was then annealed at 220 °C for 45 min at p(H₂) = 10 bar to produce the new compound, LiₓGd(BH₄)ₓClₓ. Annealing was in both cases performed in a homemade autoclave connected to a gas supply system. All preparation and manipulation of the samples were performed in a glovebox with a circulation purifier maintained under an argon atmosphere with less than 1 ppm of O₂ and H₂O. The chemicals used were lanthanum chloride, LaCl₃ (Sigma-Aldrich 99.9%), gadolinium chloride, GdCl₃ (Sigma-Aldrich 99.9%), and lithium borohydride, LiBH₄ (Sigma-Aldrich, 95%). All chemicals were used as received.

**Laboratory Structural Characterization.** All samples were initially investigated using laboratory powder X-ray diffraction (PXD) to identify the reaction products and estimate the crystallinity of the samples. PXD measurements were performed in Debye–Scherer transmission geometry using a Stoe diffractometer equipped with a curved Ge(111) monochromator (Cu Kα₁ radiation, λ = 1.54060 Å) and a curved position-sensitive detector. Data were collected at room temperature (RT) in the 2θ-range 4 and 127°. Phase analysis of samples used for Li ion conductivity measurements and samples from the Sieverts measurements were performed using a Rigaku Smart Lab configured with a Cu source and a parallel beam multilayer mirror (Cu Kα₁ radiation, λ = 1.540593 Å, Cu Kα₂ radiation, λ = 1.544414 Å). Data were measured in the 2θ-range 5 to 70° at 2°/min. All air-sensitive samples were mounted in a glovebox in 0.5 mm glass capillaries sealed with glue.

Infrared spectra of BM samples as well as samples from the Sieverts measurements were measured using a Nicolet 380 Avatar Fourier transform infrared spectrometer (FTIR) in transmission mode. The samples were shortly exposed to air when mounted in the spectrometer.

**In Situ Time-Resolved Synchrotron Radiation Powder X-ray Diffraction.** In situ time-resolved synchrotron radiation powder X-ray diffraction data (SR-PXD) were collected at the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A glass capillary (d. o. d. 0.5 mm) containing the sample was heated from RT to between 220 and 500 °C at a rate of 2 or 5 °C/min, while SR-PXD data were collected.³³ The temperature was controlled with a Cyberstar hot air blower. The data were collected during two visits at the SNBL using a MAR345 image plate detector at a sample to detector distance of 250 mm and selected X-ray wavelengths of λ = 0.69736, 0.75338, or 0.75277.
corresponding to 8 Li ions per unit cell. The structures must be neutral, the idealized occupancy for Li is 2/3 atoms per unit cell for both compounds. However, since both Wycko R

Structural Solution of LiM(BH4)3Cl (M = La or Gd). SR-PXD data collected at ∼115 °C for LaCl3–LiBH4 (1:3, s1) and at ∼225 °C for GdCl3–LiBH4 (1:3, s2) containing the highest amount of the new compounds were selected for indexing and structure solution. The PXD patterns of both compounds have a clear resemblance to the pattern observed for LiCe(BH4)3Cl. Hence, structure refinement was performed in space group I-43m using atomic coordinates from LiCe(BH4)3Cl. The cell parameters for La and Gd compounds are a = 11.7955(1) and a = 11.5627(1) Å, respectively. Lanthanum, gadolinium, and chloride atoms are located on the 8c Wyckoff site, and boron is located on the 24g Wyckoff site. The structure contains three different hydrogen positions; i.e., one hydrogen (H1) is positioned on the 48h site, and two (H2 and H3) are found on 24g Wyckoff sites. Li atoms are positioned on the 12c Wyckoff site. The occupancy for the Li atoms is refined to ~4 atoms per unit cell for both compounds. However, since both structures must be neutral, the idealized occupancy for Li is 2/3 corresponding to 8 Li ions per unit cell. The final refinement for LiLa(BH4)3Cl (Figure 1a) resulted in the following refinement factors, Rg = 2.01%, Rp = 1.56%, Rwp = 2.03%, Rwp = 2.44% (not corrected for background) and Rg = 4.51%, Rwp = 4.83% (corrected for background), and χ2 = 107. The final refinement using the Rietveld method for LiGd(BH4)3Cl (Figure 1b) resulted in the refinement factors, Rg = 2.29%, Rp = 1.20%, Rg = 2.07%, Rwp = 2.56% (not corrected for background) and Rg = 5.60%, Rwp = 5.98% (corrected for background), and χ2 = 6290. The χ2 values are high due to the very high counting statistics accumulated by the 2D detector. The atomic coordinates for LiLa(BH4)3Cl and LiGd(BH4)3Cl are shown in Tables S1 and S2 of the Supporting Information.

Conductivity Measurements. Electrochemical Impedance Spectroscopy (EIS) measurements were performed using a BioLogic VMP3 potentiostat-galvanostat. Steel disks, covered by carbon sheets to improve the interface with our materials, were also performed using a specific developed two-electrode Swagelok cell screwed with metallic rings ensuring a perfect airtightness of the cell at temperatures up to 300 °C.

From the Nyquist plots of the complex impedance (imaginary part Z" as a function of the real part Z' with the Nyquist plots of the complex impedance (imaginary part Z" as a function of the real part Z' with the Nyquist plots of the complex impedance (imaginary part Z" as a function of the real part Z' with the Nyquist plots of the complex impedance (imaginary part Z" as a function of the real part Z') the resistance-ohmic resistances were determined, and the electronic conductivities were calculated.

Thermal Analysis and Sieverts Measurements. Samples s4 and s5 were studied by simultaneous thermogravimetric analysis (TGA), differential thermal analysis (DTA), and mass spectrometry (MS) using a Netzsch STA449C connected to a Netzsch QMS403C mass spectrometer equipped with a Channeltron detector capable of multi ion detection. The transfer line was heated at 300 °C. Samples were loaded in Al2O3 crucibles and heated from RT to 500 °C (ΔT/Δt = 10 °C/min) under Ar flow (50 mL/min). Differential scanning calorimetry (DSC) was also performed using a Netzsch DSC...
204 F1. Samples were loaded in Al crucibles, which were sealed in the glovebox. Just before the experiment, holes were made in the crucible lids to allow gas release. Samples were heated from RT to 500 °C (ΔT/Δt = 10 °C/min) under Ar flow (200 mL/min).

The hydrogen release and uptake of LaCl−LiBH4 (1:3, s1), GdCl3-LiBH4 (1:3, s2), and solvent-extracted Gd(BH4)3 (s3) were studied using Sieverts measurements in a PCTPro 2000 apparatus.37,38 One desorption and one absorption cycle were measured for ca. 100 mg of material. Hydrogen desorption data were collected during heating from RT to 450 °C (ΔT/Δt = 2 °C/min) and then keeping the temperature constant at 450 °C for 1 h with a back pressure of p(H2) = 1 bar. Hydrogen absorption measurements were performed at 400 °C and p(H2) = 85 bar for 12 h. All samples were studied using FTIR and PXD following the absorption measurement.

RESULTS AND DISCUSSION

Synthesis and Initial Phase Analysis. Lithium lanthanum borohydride chloride, LiLa(BH4)3Cl, was synthesized by mechano-chemistry; i.e., ball-milling LaCl−LiBH4 (1:3, s1) and the SR-PXD data measured at RT shows diffraction peaks from LiLa(BH4)3Cl, LiCl, and LaCl4. The reaction between LaCl3 and LiBH4 is a complex reaction, which is believed to be a coupled metathesis and addition reaction leading to the formation of LiLa(BH4)3Cl and LiCl according to eq 1. The optimal stoichiometry between reactants according to reaction 1 is 1:3. However, the reaction does not take place to a full extent during ball milling, as unreacted LaCl3 is identified by PXD.

LaCl3 + 3LiBH4 → LiLa(BH4)3Cl + 2LiCl (1)

A PXD pattern measured at ~115 °C reveals a sample composition of LiLa(BH4)3Cl 57 wt % (24 mol %), LiCl 33 wt % (72 mol %), and LaCl4 10 wt % (4 mol %) (see Figure 1a). Lithium borohydride is not observed in the synthesis product by SR-PXD and may be present as an amorphous phase.13

Gadolinium borohydride, Gd(BH4)3, is produced by ball-milling GdCl3-LiBH4 (1:3, s2) according to the metathesis reaction in eq 2. Indeed, Gd(BH4)3 is isostructural to α-Y(BH4)3.31 This reaction is also similar to that observed for the formation of α-Y(BH4)3. According to the reaction scheme, the optimal ratio is again 1:3. However, as for the lanthanum system, the reaction is not complete during BM. At RT, diffraction peaks from Gd(BH4)3, GdCl3, and LiCl are visible, and Rietveld refinement reveals a sample composition of Gd(BH4)3 32 wt % (18 mol %), LiCl 20 wt % (53 mol %), and GdCl3 48 wt % (29 mol %). However, during heating at T > 63 °C, the reaction in eq 2 continues. At 193 °C, GdCl3 is almost entirely consumed, and the novel compound LiGd(BH4)3Cl begins to form by an addition reaction between Gd(BH4)3 and LiCl according to eq 3.

GdCl3 + 3LiBH4 → Gd(BH4)3 + 3LiCl (2)

Gd(BH4)3 + LiCl → LiGd(BH4)3Cl (3)

Rietveld analysis of the SR-PXD data collected for GdCl3-LiBH4 (1:3, s2) at ~225 °C shows an overall composition of LiGd(BH4)3Cl 58 wt % (20.6 mol %), Gd(BH4)3 2 wt % (0.9 mol %), LiCl 38 wt % (77.9 mol %), and GdCl3 2 wt % (0.6 mol %) (see Figure 1b).

Crystalline Structure of LiM(BH4)3Cl (M = La, Gd). The new compounds LiLa(BH4)3Cl and LiGd(BH4)3Cl are isostructural to the previously investigated compound LiCe(BH4)3Cl.13 Both structures contain isolated tetranuclear anionic clusters of [M4Cl4(BH4)12]4− (M = La or Gd) with a distorted cubane M4Cl4 core,39 charge-balanced by Li+ cations (cf. Figure 2). In

Figure 2. (a) Crystal structure of the novel compounds LiLa(BH4)3Cl and LiGd(BH4)3Cl. The BH4 groups are shown as light blue tetrahedra and the metals La or Gd in blue. The M−B coordinates are shown as dashed lines and M−Cl as full lines. The Li atoms (in red) are shown with full occupancy but are in fact disordered and only occupy 2/3 of the 12d Wyckoff site. (b) Isolated tetranuclear anionic clusters [M4Cl4(BH4)12]4− (M = La or Gd) with a distorted cubane M4Cl4 core.
positions to obtain charge neutrality. The lithium ion occupancy is challenging to determine accurately using X-ray scattering due to low scattering power of Li compared to the heavier elements in the structure. Neutron diffraction data would possibly provide a more accurate result for the Li ion occupancy, as obtained previously for the isostructural compound LiCe(BH₄)₃Cl. The orientation of the BH₄⁻ groups is adopted from structural refinement of LiCe(BH₄)₃Cl using PND, data and the Li⁺ ions coordinate tetrahedrally to four BH₄⁻ groups. The BH₄⁻ group is coordinated via the face by the heavy atoms (BH₄⁻ groups) and via a tetrahedral edge by Li⁺, i.e., BH₂ coordination scheme for M = La, Gd) and via a tetrahedral coordinated by Li⁺ ions, i.e., BH₂ coordination scheme. 

Ionic and Electronic Conductivities. Electrical conductivities of the samples LaCl₃−LiBH₄ (1:3, s4) and GdCl₃−LiBH₄ (1:3, s5) were measured by electrochemical impedance spectroscopy, at T = 20 °C. Figure 3 reveals Warburg impedances related to the semi-infinite diffusion at the electrodes for both samples. In the case of La, the beginning of a semicircle assigned to the lithium ion mobility can be seen at high frequencies; as a matter of fact, frequencies higher than 1 MHz would be needed to fully plot this semicircle. The shapes of the observed impedance spectra are typical for good conductors, and conductivities can be calculated from the intercepts with the real axis (Z_m). Ionic conductivities of 2.3 × 10⁻⁴ and 3.5 × 10⁻⁴ S·cm⁻¹ are found at 20 °C for LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl, respectively. These values are slightly higher than the conductivity of 1.0 × 10⁻⁴ S·cm⁻¹ previously reported for LiCe(BH₄)₃Cl and are much higher than that measured for α-LiBH₄, 8.6 × 10⁻⁸ S·cm⁻¹ at T = 20 °C, using the same experimental conditions. As a comparison, the impedance spectra recorded for LiBH₄ is shown in the Supporting Information (Figure S3). From the diameter of the semicircle observed at high frequency, which is related to the lithium ion mobility, a conductivity of 8.6 × 10⁻⁸ S·cm⁻¹ is found in good agreement with the values reported for orthorhombic α-LiBH₄. The conductivities of the LiM(BH₄)₃Cl, M = La, Ce, or Gd, samples are therefore more than 3 orders of magnitude higher than that of α-LiBH₄ at RT and are similar to that found for the hexagonal h-LiBH₄−LiI solid solution. 

Temperature-dependent conductivity measurements were also performed for LiM(BH₄)₃Cl (M = La or Gd) samples. The complex impedance spectra recorded for LaCl₃−LiBH₄ (1:3, s4) and GdCl₃−LiBH₄ (1:3, s5) can be found in Figure S4 and Figure S5 (Supporting Information), respectively. For both samples, the resistance rapidly decreases when increasing the temperature. Figure 4 presents the evolution of the electrical conductivities for LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl. The lanthanum containing compound has ionic conductivity of 5.5 × 10⁻³ S·cm⁻¹ at 90 °C, which may exceed 1 × 10⁻² S·cm⁻¹ at T ∼ 100 °C. The conductivities follow a linear Arrhenius behavior when ln(σT) is plotted as a function of 1/T as depicted in Figure 5. From the slope of the linear fittings, activation energies, E_a = 57 kJ·mol⁻¹ (0.59 eV) and 37 kJ·mol⁻¹ (0.38 eV), are found for LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl, respectively. The latter E_a value is lower than those reported for LiBH₄ (E_a = 66 kJ·mol⁻¹ (0.69 eV) and 51 kJ·mol⁻¹ (0.53 eV) for the orthorhombic LT and the hexagonal HT polymorph, respectively), and this highlights the high mobility of the Li⁺ cations within the newly reported crystal structure of LiGd(BH₄)₃Cl.
To demonstrate that the conductivity is purely ionic, direct current conductivity experiments were performed at \( T = 20 \) °C for both \( \text{LaCl}_3-\text{LiBH}_4 \) (1:3, s4) and \( \text{GdCl}_3-\text{LiBH}_4 \) (1:3, s5), which provide the electronic conductivities using Ohm’s law. Figure S6 in the Supporting Information shows linear evolutions of the current \( I \) when increasing the applied voltage \( U = 2.0, 2.5, \text{and} \ 3.0 \) V. From the slopes of the ohmic plots, resistances of 23 300 and 3040 kΩ = 2.0, 2.5, and 3.0 V. From the slopes of the ohmic plots, evolutions of the current \( I \) when increasing the applied voltage \( U = 2.0, 2.5, \text{and} \ 3.0 \) V. From the slopes of the ohmic plots, the electronic conductivities are therefore about 4 orders of magnitude lower than the ionic conductivities found from the impedance spectroscopy experiments. This confirms that the electric conductivity measured for \( \text{LiM(BH}_4)_3\text{Cl} \) (M = La or Gd) samples solely originates from the high mobility of \( \text{Li}^+ \).

These conductivity measurements suggest that the \( \text{LiM(BH}_4)_3\text{Cl} \) compounds could be considered as promising materials for solid electrolytes in lithium-ion batteries. Electrochemical cycling at low temperatures \( (T < 100 \) °C) of all solid-state lithium-ion batteries using the \( \text{MCl}_3-\text{LiBH}_4 \) (1:3) ball-milled samples as electrolytes is in progress to demonstrate such a feasibility. Furthermore, the conductivity measurements reported in this study were performed on pellets, which were composed of \( \text{LiM(BH}_4)_3\text{Cl} \) and \( \text{LiCl} \) 1:2 (see eqs 1–3). Higher conductivities are expected for a sample of pure \( \text{LiM(BH}_4)_3\text{Cl} \), since \( \text{LiCl} \) is a nonconducting material.

**Thermal Analysis and Sieverts Measurements.** The sample \( \text{LaCl}_3-\text{LiBH}_4 \) (1:3, s4) was studied by simultaneous TGA/DTA/MS and DSC (see Figures 6 and 8). TGA shows that a mass loss of 2.87 wt % is observed in the temperature range 200–400 °C, which is 1 wt % smaller than the theoretical hydrogen content for the sample, 3.89 wt % \( \text{H}_2 \) (including \( \text{LiCl} \)). The onset of the mass loss is associated with a smaller endothermic peak at 226 °C. A larger endothermic DSC event is observed with peak value at 266 °C associated with the main mass loss from the decomposition of \( \text{LiLa(BH}_4)_3\text{Cl} \). Mass spectroscopy measurement reveals that hydrogen is released in the temperature range 226–300 °C with a smaller amount with maximum release rate at 226 °C and a larger amount at 266 °C. There is no indication of contaminating borane species, i.e., \( \text{B}_2\text{H}_6 \) (no peak is detected for \( m/z = 28 \)).

Simultaneous TGA/DTA/MS and separately recorded DSC for sample \( \text{GdCl}_3-\text{LiBH}_4 \) (1:3, s5) (see Figures 7 and 8) reveal that hydrogen is released in a single step at 261 °C. TGA reveals a mass loss in the temperature range RT to 500 °C \( (\Delta T/\Delta t = 10 °C/min \text{in Ar flow}) \). With a heating rate of 10 °C/min in Ar flow. Figure 6. Thermogravimetric analysis, TGA (dash), and differential thermal analysis, DSC (full), measured for \( \text{LaCl}_3-\text{LiBH}_4 \) (1:3, s4) in the temperature range RT to 500 °C \( (\Delta T/\Delta t = 10 °C/min \text{ in Ar flow}) \).

Figure 7. Thermogravimetric analysis, TGA (dash), and differential thermal analysis, DSC (full), measured for \( \text{GdCl}_3-\text{LiBH}_4 \) (1:3, s5) in the temperature range RT to 500 °C \( (\Delta T/\Delta t = 10 °C/min \text{ in Ar flow}) \).

Figure 8. Mass spectroscopy signal showing hydrogen release \( (m/z = 2, \text{full}) \) and diborane, \( \text{B}_2\text{H}_6 \) \( (m/z = 28, \text{dash}) \), for \( \text{LaCl}_3-\text{LiBH}_4 \) (1:3, s4) and \( \text{GdCl}_3-\text{LiBH}_4 \) (1:3, s5) using a heating rate of \( \Delta T/\Delta t = 10 °C/min \text{ in Ar flow}) \).
from differences in the preparation procedure, where the samples have been heated to 200 and 220 °C in the case of LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl, respectively. A previous study of the GdCl₃–LiBH₄ system, where the sample was not preheated prior to the DSC experiment, revealed an endothermic peak at 211 °C. Additionally, unreacted LiBH₄ left from ball-milling might be catalyzed by the remaining metal chlorides in the sample and release hydrogen in the same temperature range as the novel compounds LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl. However, thermal treatment of the samples lead to further formation of LiM(BH₄)₃Cl, M = La or Gd; i.e., the remaining LiBH₄ and LaCl₃ or GdCl₃ is consumed prior to decomposition of LiM(BH₄)₃Cl (which is further discussed later in this paper).

Hydrogen storage properties were investigated using Sieverts (PCT) measurements for samples s1, s2, and s3 (Figure 9).

Figure 9. Sieverts measurement of LaCl₃–LiBH₄ (1:3, s1, solid line), GdCl₃–LiBH₄ (1:3, s2, dash), and solvent-extracted Gd(BH₄)₃ (s3, dot) showing the first desorption conducted in the temperature range RT to 450 °C (ΔT/Δt = 2 °C/min and p(H₂) = 1 bar).

Hydrogen absorption was not possible at the selected physical p,T conditions for our studies as shown later by FTIR and PXD. During the first desorption in the Sievert’s measurement, all three samples release 0.3–0.55 wt % H₂ from RT to 200 °C (possibly from an unidentified gas). However, no mass loss or hydrogen evolution is observed in any of the TGA/MS experiments.

The gravimetric and volumetric hydrogen densities in LiLa(BH₄)₃Cl are ρₘ = 5.36 wt % H₂ and ρₜ = 96.4 kg H₂/ m³, respectively. Sample s1 releases 0.17 wt % H₂ from 200 to 225 °C, and a major H₂ release of 2.2 wt % H₂ is observed from 225 to 270 °C. Throughout the heating to 450 °C and the following isotherm at 450 °C, 1.5 wt % H₂ is additionally released, raising the total mass loss to 3.87 wt % H₂, corresponding well to the theoretical hydrogen content of the sample of 3.9 wt % H₂.

The gravimetric and volumetric hydrogen densities in LiGd(BH₄)₃Cl are ρₘ = 4.95 wt % H₂ and ρₜ = 102.6 kg H₂/ m³, respectively. Sample s2 also releases 0.17 wt % H₂ from 200 to 225 °C, and a major H₂ release of 2.15 wt % H₂ is observed from 225 to 250 °C. A total of 1.25 wt % H₂ is released from s2 during the final heating to 450 °C and the following isotherm at 450 °C, giving a total mass loss of 3.6 wt %, which also compares well to the theoretical hydrogen content of 3.7 wt % for the sample. The observed desorption temperatures confirm that the hydrogen storage properties of LiLa(BH₄)₃Cl and LiGd(BH₄)₃Cl are indeed very similar, possibly due to similar electronegativities for lanthanum and gadolinium and that the two compounds are isostructural. The mass loss observed in the Sieverts measurement for s2 is larger than the mass loss observed for s2 in the TGA/DTA experiment. The difference may originate from the use of a slower heating rate. Additionally, the isotherm at 450 °C applied in the Sieverts measurement facilitates a more complete desorption, where the metal hydride produced from the decomposition of the parent metal borohydride may also decompose.

The solvent-extracted sample of Gd(BH₄)₃ (s3) releases 0.6 wt % H₂ from 200 to 225 °C compared to 0.2 wt % H₂ for the ball-milled sample. From 225 to 250 °C, the sample releases 2.35 wt % H₂ and additionally 2.8 wt % H₂ at higher temperatures, providing a total mass loss of 5.75 wt % H₂, which is comparable to the total hydrogen content ρₚ(Gd(BH₄)₃) = 5.99 wt % H₂. Indeed, the removal of LiCl facilitates the full hydrogen desorption capability of Gd(BH₄)₃. An interesting observation is that the onset temperatures are similar, 200 or 225 °C, respectively, for the different steps in the decomposition. No measurable difference in the onset temperatures is observed between the two samples containing gadolinium, even though most of the LiCl has been removed from the solvent-extracted sample. Indeed, the reduced formation of the novel compound LiGd(BH₄)₃Cl does not have an effect on the decomposition temperature or the steps in the decomposition. In both samples, the decomposition takes place in a two-step mechanism, a small mass loss followed by a rather abrupt mass loss in a very narrow temperature range of 25 °C.

Infrared Spectroscopy. The samples s1, s3, and s5 were further investigated by Fourier transform infrared spectroscopy (FTIR), as shown in Figure S8 (Supporting Information). The FTIR spectrum for s1 reveals the signatures of [BH₄]⁻ vibrations at 1092 cm⁻¹ and stretching at 2305 cm⁻¹, which are located in the typical B–H vibrational range for borohydrides and are expected to originate from the LiLa(BH₄)₃Cl compound. The FTIR spectrum of sample s5 shows that when an as-milled sample of GdCl₃–LiBH₄ (1:3) is heated to produce LiGd(BH₄)₃Cl the stretching and bending modes of the borohydride group are less intense. However, signatures of [BH₄]⁻ bending modes at 1184 cm⁻¹ and stretching at 2259 cm⁻¹ reveal that the borohydride chloride is still present. Additionally, the FTIR spectrum of the solvent-extracted sample of Gd(BH₄)₃ shows that some ether solvent remains in the sample after extraction, as revealed by the C–H stretching modes at 2922 cm⁻¹ and bending at 1185 cm⁻¹. However, as for the two other samples, [BH₄]⁻ bending modes at 1123 cm⁻¹ and stretching at 2263 cm⁻¹ reveal the presence of the borohydride group in Gd(BH₄)₃.

The presence of diethyl ether in a form of crystalline complexes is not detected in any of the diffraction experiments. The samples used in the Sieverts measurement were also studied using FTIR spectroscopy (see Figure S9, Supporting Information). A minor and broad absorption is observed in the spectrum for s3 at 1373 cm⁻¹, which was not assigned. No bending or stretching modes are observed for the two other samples, confirming that the
physical conditions applied here for hydrogen absorption are not sufficient to allow formation of borohydrides.

Decomposition Mechanisms Observed by in situ SR-PXD. The thermal decompositions of samples LaCl₃–LiBH₄ (1:3, s1), GdCl₃–LiBH₄ (1:3, s2), and Gd(BH₄)₃ (s3) were studied by in situ SR-PXD (see Figures 10, 11, and 12). The first SR-PXD pattern in the series for s1 (Figure 10) measured at RT shows diffraction peaks from LiLa(BH₄)₃Cl, LaCl₄, and LiCl. LaCl₄ remains in the sample during the complete heating run, but peaks corresponding to lanthanum chloride decrease in intensity at $T > 50 \, ^\circ\mathrm{C}$. Above $50 \, ^\circ\mathrm{C}$, the diffracted peak intensity from LiLa(BH₄)₃Cl increases due to the continuation of reaction eq 1. The Bragg diffraction peaks from LiLa(BH₄)₃Cl disappear at $185 \, ^\circ\mathrm{C}$ due to melting corresponding to results from TGA/MS and DSC measurements where decomposition was observed at $T \sim 266 \, ^\circ\mathrm{C}$. Melting of LiLa(BH₄)₃Cl is correlated with a minor increase in the diffracted intensity from LiCl. Diffraction peaks from an unknown compound appear at $165 \, ^\circ\mathrm{C}$. The unknown compound may be a ternary salt, which may explain the decreasing diffracted intensity from LiCl in this region. A ternary salt, NaYCl₄, is also observed during the decomposition of NaY(BH₄)₂Cl₂.¹¹ Sample s1 used in the Sieverts measurement was studied using PXD after the absorption experiment (see Figure S10, Supporting Information). Lanthanum hydride and lanthanum boride, LaH₂ and LaB₆, were observed, which lead to a reaction scheme (eq 4) as a possible overall decomposition reaction for LiLa(BH₄)₃Cl. The unknown/ unidentified compound 1 may form in a side reaction.

$$\text{LiLa}(\text{BH}_4)_3\text{Cl} \rightarrow 1/2\text{LaH}_2 + 1/2\text{LaB}_6 + 11/2\text{H}_2 + \text{LiCl}$$

(4)

Initially, Gd(BH₄)₃, GdCl₃, and LiCl are present at RT in sample s2 (see Figure 11). When the temperature reaches $80 \, ^\circ\mathrm{C}$, the diffracted intensity from Gd(BH₄)₃ and LiCl starts to increase in intensity, and simultaneously the GdCl₃ peak intensity decreases according to eq 2. At $200 \, ^\circ\mathrm{C}$, Gd(BH₄)₃ reacts with LiCl, forming LiGd(BH₄)₃Cl according to eq 3. This is also associated with a decrease in intensity of the Bragg peaks belonging to LiCl. At $240 \, ^\circ\mathrm{C}$, diffraction peaks from LiGd(BH₄)₃Cl vanish due to decomposition, simultaneous with formation of an unknown compound 2 (see Figure 11). Bragg peaks from 2 can be indexed by a monoclinic unit cell, $a = 7.76(1)\, \AA$, $b = 12.71(5)$, $c = 3.62(1)\, \AA$, and $\beta = 94.7(2)^\circ$. However, structure solution has not yet been possible. Bragg peaks from 2 disappear at $290 \, ^\circ\mathrm{C}$. At the end of the heating, peaks from GdB₆ and an unknown compound 3 appear (see Figure 11). Compound 3 has peak positions similar to 1 observed in the La system, and the two compounds may be structurally related.

A PXD diagram at RT of solvent-extracted Gd(BH₄)₃ measured from RT to $400 \, ^\circ\mathrm{C}$ ($\Delta T/\Delta t = 5 \, ^\circ\mathrm{C}/\text{min}, p(Ar) = 1 \text{ bar}, \lambda = 0.753377\, \AA$). Symbols: open down triangle, Gd(BH₄)₃; black down triangle, LiGd(BH₄)₃Cl; black box, LiCl; gray diamond, GdCl₃; black box, LiCl; and gray circle, Unknown 1.

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Figure 10. In situ SR-PXD data for LaCl₃–LiBH₄ (1:3, s1) measured from RT to $220 \, ^\circ\mathrm{C}$ ($\Delta T/\Delta t = 1 \, ^\circ\mathrm{C}/\text{min}$, $p(Ar) = 1 \text{ bar}, \lambda = 0.69736\, \AA$). Symbols: black triangle, LiLa(BH₄)₃Cl; gray triangle, LaCl₃; black box, LiCl; and gray circle, Unknown 1.

Figure 11. In situ SR-PXD data for GdCl₃–LiBH₄ (1:3, s2) measured from RT to $400 \, ^\circ\mathrm{C}$ ($\Delta T/\Delta t = 5 \, ^\circ\mathrm{C}/\text{min}$, $p(Ar) = 1 \text{ bar}, \lambda = 0.75277\, \AA$). Symbols: open down triangle, Gd(BH₄)₃; gray down triangle, GdCl₃; black down triangle, LiGd(BH₄)₃Cl; black box, LiCl; gray diamond, GdB₆; gray star, Unknown 2; and black diamond, Unknown 3.

Figure 12. In situ SR-PXD data for solvent-extracted Gd(BH₄)₃ (s3) measured from RT to $400 \, ^\circ\mathrm{C}$ ($\Delta T/\Delta t = 5 \, ^\circ\mathrm{C}/\text{min}, p(Ar) = 1 \text{ bar}, \lambda = 0.753377\, \AA$). Symbols: open down triangle, Gd(BH₄)₃; black down triangle, LiGd(BH₄)₃Cl; black box, LiCl; and black diamond, Unknown 3.
are observed. Crystalline GdB₄ is also observed in sample S3 together with LiCl. Gadolinium hydride GdH₂ is not observed to crystallize in any of the in situ SR-PXD studies and is neither observed in S2 nor S3 after the rehydrogenation in the Sieverts measurement, but GdH₂ is reported to form in previous studies. The reaction scheme in eq 5 describes the overall idealized decomposition reaction for LiGd(BH₄)₃Cl. The unknown or unidentified compounds 2 and 3 may form in side reactions.

\[
\text{LiGd(BH}_4\text{)}_3\text{Cl} \rightarrow 1/4\text{GdH}_2 + 3/4\text{GdB}_4 + 23/4\text{H}_2
\]

\[+ \text{LiCl} \quad (5)\]

**Comparison with Related Compounds.** For LiCe(BH₄)₃Cl, the position of the Li⁺ ions was discovered by the combined use of powder X-ray and neutron diffraction and DFT optimization. After considering several models for the structure, the Li⁺ ions were positioned on the 12d Wyckoff site with an idealized occupancy of 2/3.¹³ DFT optimization indicates that the LiCe(BH₄)₃Cl structure is stabilized by higher entropy rather than lower enthalpy. The Li disorder may be the origin of the high Li-ion conductivity observed for the whole LiM(BH₄)₃Cl series of compounds, M = La, Ce, Gd. Lanthanum and cerium have similar ionic radii, for the same factor is crucial for the phase stability in LiBH₄.

The reversible hydrogen storage properties for rare earth metal borohydrides may be avoided. This may also be important in reactive hydride composite based on rare earth metal borohydrides, which remains an unexplored area of solid state hydrogen storage.

**Table 2. Hydrogen Densities, Decomposition Temperatures and Conductivities for the Three Compounds LiM(BH₄)₃Cl (M = La, Ce, or Gd)**

<table>
<thead>
<tr>
<th>compound</th>
<th>unit cell a/Å</th>
<th>ρ_m wt % H₂</th>
<th>ρ_i kg H₂ m⁻³</th>
<th>T_dec°C</th>
<th>Li-ion S·cm⁻¹</th>
<th>electronic S·cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiLa(BH₄)₃Cl</td>
<td>11.7955(1)</td>
<td>5.36</td>
<td>96.4</td>
<td>266 ± 2</td>
<td>2.3 ± 0.6</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>LiCe(BH₄)₃Cl</td>
<td>11.7204(2)</td>
<td>5.33</td>
<td>99.8</td>
<td>258 ± 2</td>
<td>1.0 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td>LiGd(BH₄)₃Cl</td>
<td>11.5627(1)</td>
<td>4.95</td>
<td>102.6</td>
<td>261 ± 2</td>
<td>3.6 ± 0.6</td>
<td>9 ± 0.9</td>
</tr>
</tbody>
</table>

*Calculated values. *Values from thermogravimetrical experiments.

**REFERENCES**