LiCe(BH$_4$)$_3$Cl, a New Lithium-Ion Conductor and Hydrogen Storage Material with Isolated Tetranuclear Anionic Clusters

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ABSTRACT: Mechanochemical synthesis using CeCl$_3$-MBH$_4$ (M = Li, Na or K) mixtures are investigated and produced a new compound, LiCe(BH$_4$)$_3$Cl, which crystallizes in a cubic space group $I4_3$m, $a = 11.7204(2)$ Å. The structure contains isolated tetranuclear anionic clusters $[\text{Ce}_4\text{Cl}_4(\text{BH}_4)_4]^{12-}$ with a distorted cubane $\text{Ce}_4\text{Cl}_4$ core, charge-balanced by Li$^+$ cations. Each Ce atom coordinates three chloride ions and three borohydride groups via the $\eta^1$-$\text{BH}_3$ faces, thus completing the coordination environment to an octahedron. Combination of synchrotron radiation powder X-ray diffraction (SR-PXD), powder neutron diffraction and density functional theory (DFT) optimization show that Li cations are disordered, occupying 2/3 of the 12$\text{a}$ Wyckoff site. DFT calculation indicates that LiCe(BH$_4$)$_3$Cl is stabilized by higher entropy rather than lower enthalpy, in accord with the disorder in Li positions. The structural model also agrees well with the very high lithium ion conductivity measured for LiCe(BH$_4$)$_3$Cl of 1 $\times$ 10$^{-4}$ Scm$^{-1}$ at $T = 20$ °C. In situ SR-PXD reveals that the decomposition products consist of LiCl, CeB$_6$ and CeH$_2$. The Sieverts measurements show that 4.7 wt % H$_2$ is released during heating to 500 °C. After rehydrogenation at 400 °C and $p(\text{H}_2) = 100$ bar for 24 h an amount of 1.8 wt % H$_2$ is released in the second dehydrogenation. The $^1$H MAS NMR spectra of the central and satellite transitions for LiCe(B(D/H)$_3$)$_3$Cl reveal highly asymmetric manifolds of spinning sidebands from a single $^{11}$B site, reflecting dipolar couplings of the $^{11}$B nuclear spin with the paramagnetic electron spin of the Ce$^{3+}$ ions.

KEYWORDS: lithium ion conductor, hydrogen storage, borohydride, powder X-ray diffraction, reversibility

INTRODUCTION

The transition toward a sustainable, environmentally friendly and carbon free energy system that can fulfill the increasing energy demands is considered one of the greatest challenges in the 21st century. One, in particular, a safe, compact, and efficient means of storage of renewable energy still remains to be identified. Chemical storage of energy as hydrogen or electricity in a battery is among the most promising approaches with a potential to reach the required high energy contents. This has prompted the present research project where a new lithium- and cerium -based borohydride chloride is prepared and characterized.

Hydrogen is abundant, easy to produce by electrolysis, and has the potential to be stored efficiently in the solid state, e.g., as metal borohydrides, which currently receive increasing interest. Unfortunately, many of the known borohydrides exhibit poor thermodynamic and kinetic properties, which hamper their utilization in technological applications. Therefore, significant focus has been on synthesis and characterization of novel bimetallic borohydrides because of their somewhat tunable decomposition temperatures.

Furthermore, recent studies of metal borohydrides reveal a remarkable diversity in the structural topologies illustrated by a new nanoporous magnesium borohydride $\gamma$-Mg(BH$_4$)$_2$ with 33% empty volume. The compounds LiZn$_2$(BH$_4$)$_3$ and NaZn$_2$(BH$_4$)$_3$ are built from two identical interpenetrated three-dimensional frameworks consisting of isolated complex anions, $[\text{Zn}_3(\text{BH}_4)_4]^{-}$, whereas NaZn(BH$_4$)$_3$ consists of isolated anions of $[\text{Zn}(\text{BH}_4)_3]^{-}$ counter balanced by sodium. Isolated complex anions have also been observed in other structures, such as $[\text{Sc}(\text{BH}_4)_4]^{-}$ in $\text{MeSc}(\text{BH}_4)_4$ ($\text{M} = \text{Li, Na or K}$) or $[\text{Zn}(\text{BH}_4)_2\text{Cl}_2]^{-}$ in the heteroleptic borohydride, KZn(BH$_4$)$_2$Cl$_2$. Several of these mixed-metal borohydrides exhibit improved thermodynamic and kinetic properties, e.g. LiSc(BH$_4$)$_4$ and NaSc(BH$_4$)$_4$ are found to decompose in the temperature ranges 140 to 260 °C and 167 to 267 °C, respectively. These are significantly lower temperatures as compared to the corresponding alkali borohydrides, LiBH$_4$ and NaBH$_4$, which decompose at approximately 380 and 400 °C, respectively. The complex borohydride ion may resemble the halide ions in the solid state, which may facilitate anion substitution in metal borohydrides. The halide stabilized lithium borohydride...
LiBH₄−LiX, X=Cl, Br, I, form solid solutions, Li(BH₄)ₓ−ₓXₓ, which tend to stabilize the hexagonal polymorph to room temperature. The hexagonal halide stabilized polymorphs h-Li(BH₄)ₓ−ₓXₓ were found to have very high lithium ion conductivities in the range 1 × 10⁻⁴ to 1 × 10⁻³ S cm⁻¹ at room temperature, RT, which increase to about 1 × 10⁻² S cm⁻¹ at 150 °C. These materials are considered as possible electrolytes for solid-state lithium batteries. Structural, thermodynamic and kinetic properties as well as thermal stability and decomposition reactions are of vital importance for possible applications of reversible hydrogen carriers and rechargeable lithium battery materials. In some cases, metal borohydrides may release gaseous boranes, such as diborane, which leads to decreasing storage capacity of the hydrogen storage system. Therefore, formation of metal borides during decomposition is an important indication of possible reversibility, since boron is kept in the solid state. Furthermore, formation of metal borides is preferred to formation of elemental boron due to the high stability of the latter. Therefore, detailed characterization of new lithium containing metal borohydrides may open new routes for design of carriers and rechargeable lithium battery materials. In some cases, metal borohydrides may release gaseous boranes, such as diborane, which leads to decreasing storage capacity of the hydrogen storage system. Furthermore, formation of metal borides during decomposition is an important indication of possible reversibility, since boron is kept in the solid state. Therefore, detailed characterization of new lithium containing metal borohydrides may open new routes for design of carriers and rechargeable lithium battery materials.

EXPERIMENTAL SECTION

Synthesis. The title compound was prepared from samples of CeCl₃−LiBH₄ in the molar ratios 1:2, 1:3, and 1:4, denoted samples (s8 and s9) were subjected to the same ball milling conditions as used for sample s1−s5. The CeCl₃−NaBH₄ samples (s6 and s7) were also initially ball milled using these conditions, however, as no reaction occurred, the samples were subsequently ball milled for additional 30 repetitions applying 2 min BM and 2 min pauses with speeds of the main disk and the planetary disks of 250 and 625 rpm, respectively.

All preparation and manipulation of the samples were performed in a glovebox with a circulation purifier maintained under an argon atmosphere with <1 ppm of O₂ and H₂O. The chemicals used were anhydrous cerium chloride, CeCl₃ (Sigma-Aldrich 99.9%), lithium borohydride, LiBH₄ (Sigma-Aldrich, 95%), lithium borodeuteride, Li²BD₄ (KatChem, 95%), sodium borohydride (Sigma-Aldrich, 95%) and potassium borohydride (Sigma-Aldrich, 95%). All chemicals were used as received.

Laboratory Powder X-ray Diffraction. All samples were initially investigated using laboratory powder X-ray diffraction (PXD) in order to identify the reaction products and estimate the crystallinity of the samples. PXD measurements were performed in Debye–Scherrer transmission geometry using a Stoe diffractometer equipped with a curved Ge(111) monochromator (Cu Kα radiation, λ = 1.54060 Å) and a curved position sensitive detector. Data were collected at RT from 4 to 127° 2θ with counting times of ~960 s per step. Air-sensitive samples were mounted in a glovebox in 0.5 mm glass capillaries sealed with glue.

In situ Synchrotron Radiation Powder X-ray Diffraction. In situ SR-PXD data was collected at the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A glass capillary (o.d. 0.5 mm) containing the sample was heated from RT to 500 °C at a rate of 8 °C/min, while SR-PXD data was collected. The temperature was controlled with a Cyberstar hot air blower. The data were collected using a MAR345 image plate detector at a sample to detector distance of 250 mm, and a selected X-ray wavelength of λ = 0.709637 Å. The capillary was oscillated 30° during X-ray exposure of the sample for 30 s.

All obtained raw images were transformed to powder patterns using the FIT2D program, which was also used for calibration of the X-ray wavelength and the sample–detector distance using a SR-PXD data collected at the standard ILL-type Orang crysta1 at −271, −248, −223, and 25 °C.

Structure Solution of LiCe(BH₄)₂Cl. SR-PXD data collected at ~160 °C for CeCl₃−LiBH₄ (1:4, s4), containing the highest fraction of the new compound, was used for indexing and structure solution. Indexing of the diffraction peaks was performed using the program Dicvol in a body centered cubic cell (a = 11.7204(2) Å). The structure was solved in space group I4₃m by global optimization in direct space using the program FOX, using one Ce, one Li, and one Cl atom, and a rigid tetrahedral BH₄ group as optimized units and a number of antibump restraints. The structure contains one cerium and one chloride atom located on 8i and 8j, Wyckoff sites, while boron is located on the 24g Wyckoff site. The crystallographic positions of Ce, B, and Cl determined from PXD and PND, respectively, are similar. However, SR-PXD data alone showed some ambiguity for the Li positions. Therefore, the position was determined from the combination of SR-PXD data, PND data and DFT optimization of the resulting models (discussed in more detail below). The only Li position consistent with all diffraction data and energy minimizations is the 12d Wyckoff site. The Li occupancy refines to ca. 2/3, corresponding to the expected 8 Li atoms per unit cell. A symmetry check in Platon did not suggest higher metric or crystallographic symmetry. According to the
multiplicity \( Z = 8 \), the crystallographic density for the \( \text{LiCe(BH}_4\text{)}_3\text{Cl} \) compound is \( \rho = 1.87 \) g cm\(^{-3}\).

The final Rietveld refinement was performed using the PND data measured at \(-248 \) °C on \( \text{CeCl}_3\text{−LiBH}_4 \) \((1:3, s4)\) and subsequently the SR-PXD data measured at \(-160 \) °C on \( \text{CeCl}_3\text{−LiBH}_4 \) \((1:4, s3)\). The SR-PXD data region 18.7° was described by linear interpolation between selected points. Due to the used weighting scheme: 1/\( \sigma^2 \). The refinement factors from the PND data are examined by density functional theory calculations. The calculations were performed within the generalized-gradient approximation by Perdew, Burke, and Ernzerhof as implemented in the Vienna Ab-initio Simulation Package. Projector augmented wave (PAW) potential with a planewave cutoff energy of 600 eV is used. For each atomic species, Li, Ce, B, H, and Cl, the PAW potentials \( \text{Li}_v \), \( \text{Ce}_3 \), B, H, and Cl are used, respectively. Three valence electrons are included in the \( \text{Li}_v \) potential, and a 4f electron in Ce is frozen to core in the \( \text{Ce}_3 \) potential.

A primitive cell having four formula units of LiCe\((\text{BH}_4\text{)}_3\text{Cl} \) is used. Regular \( k \)-point meshes of 2 × 2 × 2 in the first Brillouin zone including is \( \Gamma \) point are sampled, which ensures energy convergence within 0.2 meV/f.u. Structural optimization was performed until the force on each atom became smaller than 0.005 eV/Å. During the optimization the lattice parameter was fixed to the experimental value from the SR-PXD analysis. Partial occupation at the 12d or 24g (discussed in detail below) sites is modeled in the DFT optimization by removing the 3-fold axes along the \((111)\) directions, which reduces the symmetry to the space group \( \text{I} \). In order to find the best-fit atomic positions, the DFT procedure was performed using GAUSSIAN 03. The resulting atomic coordinates \( \langle a \rangle \) were derived by applying 3-fold rotation along the \( \text{Li} \) axis for \( \text{LiBH}_4 \) (reference sample) and \( \text{LiCe(BH}_4)\text{Cl} \) respectively. The conductivity measurements were performed on five pellets made from sample \( \text{CeCl}_3\text{−LiBH}_4 \) \((1:3, s5)\). The pellets with a diameter of 10 mm and with thicknesses in the range 0.5 to 2.0 mm were prepared by using a uniaxial press (900 MPa). Sintering of the pellets was performed at RT due to possible decomposition of the materials at elevated temperatures. The pellets densities were ca. 2.42 g cm\(^{-3}\), which corresponds to a compactness of 93%, calculated using the density of sample \( \text{CeCl}_3\text{−LiBH}_4 \) \((1:3, s5)\) derived from the Rietveld refined composition, \( \rho(s) = 2.61 \) g cm\(^{-3}\).

Conductivity Measurements. The cyclic reversibility of hydrogen release and uptake was studied by Sieverts’ measurements using a PCTPro 2000 apparatus. Three
desorption and two absorption cycles were measured for ca. 150 mg of material. Hydrogen desorption was collected during heating from RT to 500 °C (ΔT/Δt = 1 °C/min) and then keeping the temperature constant at 500 °C for 3 h with a back pressure of p(H2) = 1 bar. Hydrogen absorption measurements was performed before the second and third desorption cycle at 400 °C and p(H2) = 100 bar for 24 h.

RESULTS AND DISCUSSION

Synthesis and Initial Phase Analysis. Lithium cerium borohydride chloride, LiCe(BH4)3Cl was synthesized by a mechano-chemistry, i.e. ball milling (BM) of samples CeCl3−LiBH4 (1:3, s2) and (1:4, s3). The SR-PXD data, collected at RT after BM, show diffraction peaks from LiCe(BH4)3Cl, LiCl, and CeCl3, indicating that the reaction shown in (1) occurs.

CeCl3 + 3LiBH4 → LiCe(BH4)3Cl + 2LiCl

The gravimetric and volumetric hydrogen density for LiCe-(BH4)3Cl is \( \rho_{\text{g}} = 5.37 \) wt % H2 and \( \rho_{\text{v}} = 99.8 \) kg H2/m3, respectively. The reaction between CeCl3 and LiBH4 is a complex reaction, which is believed to be a coupled metathesis and addition reaction leading to the formation of LiCe-(BH4)3Cl and LiCl. The optimal stoichiometry between reactants according to reaction 1 is 1:3. However, the reaction is not completed using the selected ball milling conditions, as unreacted CeCl3 is identified by PXD.

Upon heating, the reaction between CeCl3 and LiBH4 continues from 100 to 160 °C, where the maximum amount of LiCe(BH4)3Cl is observed by SR-PXD. The composition of s3 at 160 °C found by Rietveld refinement is LiCe(BH4)3Cl 62 wt % (32 mol %), LiCl 22 wt % (61 mol %), and CeCl3 16 wt % (7 mol %). s4 used for the PND experiment and \(^{11}\)B MAS NMR analysis was also analyzed with SR-PXD measured at RT, and the overall sample composition was LiCe(B12D2)3Cl 66 wt % (28 mol %), LiCl 29 wt % (70 mol %) and CeCl3 5 wt % (2 mol %), which indicates that reaction 1 has occurred to a higher extent during BM for this sample. Crystalline lithium borohydride is not observed in the synthesis products for any of the samples by SR-PXD or PND. However, LiBH4 was confirmed to be present in an amorphous state by NMR analysis (see below). Prolonged ball milling times or conditions facilitating higher energy during ball milling are possibly needed to complete reaction 1.\(^{40}\) The samples CeCl3−NaBH4 and CeCl3−KBH4 were treated at similar mechano-chemical conditions as compared to the CeCl3−LiBH4 samples but no indications for chemical reaction were observed.

Crystal Structure of LiCe(BH4)3Cl. LiCe(BH4)3Cl crystallizes in a cubic unit cell, \( a = 11.7204(2) \) Å, with space group symmetry \( I\overline{4}3m \) (see Figure 2). The positions of Ce, B and Cl ions were readily determined from the SR-PXD data. The structure contains isolated tetranuclear anionic clusters of \([\text{CeCl3(BH4)}]_{12}^{4+} \) with a distorted cubane Ce4Cl4 core,\(^{41}\) charge-balanced by Li⁺ cations (see Figure 3). Rietveld refinement of the PND data measured at –248 °C reveal a \( \eta^4\text{−BD}_{4}\text{−Ce} \) coordination mode. The angles \( \angle\text{Cl–Ce–Cl} \) and \( \angle\text{B–Ce–B} \) are 73.26(16)° and 99.2(6)°, respectively, and the Ce–Cl and Ce–B distances are 2.961(6) and 2.742(2) Å, respectively. From the initial SR-PXD structural analysis some ambiguity existed concerning the position of the Li⁺ ions and several structural models were investigated by Rietveld refinement of SR-PXD data and PND data and by DFT optimization, revealing that Li⁺ ions are disordered, occupying 2/3 of the 12\( d \) Wyckoff site. Li⁺ ions coordinate tetrahedrally four BD₄⁺ groups via the tetrahedral edge, i.e., \( \eta^4\text{−BD}_{4}\text{−Li} \) (Figure 3). Three B–D distances are determined to be 1.181(8) Å (D1), 1.22(1) Å (D2) and 1.231(7) Å (D3). The closest D–D contact is 1.9302(82) Å (D1–D3).

As mentioned, a combined analysis of data from SR-PXD, PND and DFT optimization was utilized to locate the Li⁺ ions. Besides the structure of LiCe(BH4)3Cl described above with Li⁺ positioned on the 12\( d \) Wyckoff site two other Li⁺ positions were considered but eventually rejected (see Table 2). One of these two models corresponds to the only possible fully ordered arrangement of Li⁺ ions on the sites 2\( a \) and 6\( h \). The 2\( a \) site is situated in the center of the distorted cubane cage Ce4Cl16, resulting in Ce−Li distance of only 2.8757(14) Å. For comparison, in a similar mixed metal borohydride chloride NaY(BH4)3Cl2, the shortest Na−Y distance is 4.95 Å.\(^{43}\) Indeed, DFT calculations on a model with the 2\( a \) site filled by Li⁺ ions shows larger discrepancy for the position of Ce atoms with respect to the experimental data. Moreover, a Rietveld
refinement of the occupancy for the 2a site gives a negative value of −0.8 using the SR-PXD data, questioning the credibility of the model.

In the third structural model for LiCe(BH4)3Cl, one-third of the 24g site (a = 0.12350, z = 0.57580) is occupied by Li+ ions. However, DFT optimization showed large displacements of lithium and in particular hydrogen atom positions yielding a model inconsistent with neutron diffraction data. The Rietveld refinement using the SR-PXD data reveal unacceptable short Li–H distances of ~1.2 Å. Because of the lack of agreement between the theoretical and experimental data the third model was also rejected.

DFT optimization showed that the 12d model (see Figure S1a in the Supporting Information) has the lowest energy and that the 2a/6b and the 24g model energies are higher by 0.42 and 1.14 eV/f.u., respectively. Furthermore, the optimized (center of the cage)—Ce distance for the 12d and 2a model are 2.905 and 3.114 Å, respectively. This difference makes a noticeable change in the simulated X-ray diffraction patterns since the heaviest atom Ce most strongly scatters X-rays and the 12d model reproduces the experimental X-ray patterns more closely (see the R-values in Table 2). DFT optimization reveals that relaxation of the unit cell volume leads to a rather large expansion of 11.1% while accompanying a small decrease in energy by 0.051 eV/f.u. for the model containing the 2a site. Contrary to that, the model with 12d site remains stable, with only 0.1% variation of the cell parameter and the related total energy changes of less than 1 meV/f.u. Another ordered variant of Li+ configuration in the 12d site was modeled using DFT (see Figure S1 in the Supporting Information), which has higher energy by only 0.028 eV/f.u. and almost constant unit cell volume within 0.6% of the experimental value. The similarities in energy and volume between different hypothetically ordered 12d sites strongly support this model.

The formation energy for LiCe(BH4)3Cl from LiCl and Ce(BH4)3 has also been estimated using DFT calculations. Since the crystal structure of Ce(BH4)3 is unknown, the low temperature polymorph of Y(BH4)3 was adopted as a hypothetical “Ce(BH4)3” structure. Both LiCl and Ce(BH4)3 were simulated with the same approximations as LiCe(BH4)3Cl. The DFT optimized lattice parameter for “Ce(BH4)3” is a = 11.482 Å, which is somewhat larger than that of Y(BH4)3 (a = 10.852 Å) and rather close to that observed for LiCe(BH4)3Cl (a = 11.720 Å, this study), reflecting the relatively larger ionic radius of Ce and weaker binding as compared to Y(BH4)3. This may partly explain why formation of LiCe(BH4)3Cl is preferred to the formation of “Ce(BH4)3” under the same experimental condition. The reaction energy for (2) is estimated to be slightly endothermic.

<table>
<thead>
<tr>
<th>Li+ Wyckoff site</th>
<th>PXD Rθ (°)</th>
<th>PND Rθ (°)</th>
<th>DFT eEnergy (eV/f.u.)</th>
<th>idealized occupancy</th>
</tr>
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<tr>
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<td>5.50</td>
<td>0</td>
<td>2/3</td>
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<tr>
<td>2a, 6b</td>
<td>3.38</td>
<td>6.96</td>
<td>0.42</td>
<td>1 (for both sites)</td>
</tr>
<tr>
<td>24g</td>
<td>2.51</td>
<td>5.19</td>
<td>1.14</td>
<td>1/3</td>
</tr>
</tbody>
</table>

“Not corrected for background. Energy is calculated with respect to the lowest energy structure.

Table 2. Overview of the Three Models for the Li Positions in Space Group I43m, Showing the Position and Idealized Occupancy of Li Sites

\[ \text{LiCl + Ce(BH}_4\text{)}_3 \rightarrow \text{LiCe(BH}_4\text{)}_3\text{Cl} \ \Delta E = 13.9 \text{ kJ/mol (or 0.144 eV) (2)} \]

Temperature effects are not taken into account and \( \Delta E \) is the DFT total energy difference. Since the bonding characters are largely preserved between the reactants and the product, \( \Delta H (T = 298 \text{ K}) \) would not be significantly different from \( \Delta E (T = 0 \text{ K}) \). Therefore, the structure of LiCe(BH4)3Cl may be stabilized by higher entropy rather than lower enthalpy, and this result again favors the 12d model because disorder in Li positions would certainly contribute to the entropy.

In this study, a bimetallic borohydride chloride LiCe(BH4)3Cl is discovered, in contrast to other rare earth metal borohydrides produced mechano-chemically from similar metalborohydride-metalchloride reaction mixtures, i.e. LiSc(BH4)3, Y(BH4)3, Gd(BH4)3, and Ce(BH4)3. This dissimilarity might be due to differences in ionic ratio (given in parentheses) for the lanthanides as compared to lithium, i.e. Li+ (0.76 Å) \( \approx \) Sc3+ (0.75 Å) < Y3+ (0.90 Å) < Gd3+ (0.94 Å) < Ce3+ (1.02 Å). Apparently, anionic structures are preferred for the smallest ions, as in LiSc(BH4)3, and formation of monometallic framework structures seems to be more favorable for the slightly larger lanthanides, e.g., Y(BH4)3 and Gd(BH4)3. The largest lanthanides appear to facilitate formation of more complex framework structures, as for LiCe(BH4)3Cl, which contains isolated tetranuclear anionic clusters [Ce4Cl4(C2H4)i2]- with a distorted cubane Ce2Cl4 core, charge-balanced by Li+ cations.

**Solid-State 11B MAS NMR.** The 11B MAS NMR spectra of the central and satellite transitions for the deuterated sample ClCe3–Li11BD4 (1:4, s4) recorded at 14.1 and 9.4 T (Figure 4) reveal manifolds of spinning side bands (ssb) from a single 11B site, in agreement with the present crystal-structure determination. The appearance of the ssb manifolds in the three spectra is highly asymmetric and thereby deviates from the symmetric ssb patterns reported earlier for the 11B central and satellite transitions in borohydride compounds.19,47,50 Although asymmetries in the ssb intensities from the central and satellite transitions may arise from the combined effect of the 11B quadrupole coupling and chemical shift anisotropy interactions, as demonstrated in 11B MAS NMR spectra of borates,51 the asymmetry in the present spectra reflects strong 11B nuclear spin – paramagnetic electron-spin dipolar interactions52,53 present along with the 11B quadrupole coupling. Thus, the 11B nuclear spin couples to the surrounding free electrons of the paramagnetic Ce3+ ions, in accordance with curium present as the Ce5+ ion in LiCe(BH4)3Cl, i.e., the Ce4+ ion would result in a diamagnetic compound. In addition to the asymmetry of the ssb manifolds, these couplings also result in a significant line broadening of the individual ssbs. The fact, that the individual 11B spins couple to the paramagnetic electron from several Ce3+ ions in different distances to the 11B site and that these couplings are additive,52 prevents a straightforward simulation of the ssb manifolds by consideration of the mutual effects from the 11B quadrupole coupling and 11B nuclear spin – paramagnetic electron-spin dipolar couplings. However, the observation of these heteronuclear dipolar couplings strongly suggests that the paramagnetic electron is localized in a Ce3+ bonding and that it is nonconducting. It is unlikely that the well-defined 11B MAS NMR spectra shown in Figure 4 could have observed if the unpaired electrons were conducting. An estimation of the 11B quadrupole coupling constant (CQ) can...
be achieved from the width of the ssb manifolds, which equals $C_Q$ for a spin $I = 3/2$, assuming that the width is dominated by the first-order quadrupole interaction for the satellite transitions.\textsuperscript{54} The $^{11}$B MAS NMR spectra in Figure 4 are shown on identical widths in Hz, demonstrating that this is an acceptable approximation, and resulting in the estimated quadrupole coupling of $C_Q = 420$ kHz and an axially symmetric quadrupole coupling tensor ($\eta_Q = 0$). Although these values are nearly identical, the apparent chemical shift for LiCe(BD$_4$)$_3$Cl in s4 is significantly shifted to high frequency as compared to the $^{11}$B chemical shift range observed for BD$_4^-$ sites in diamagnetic borohydrides (e.g., roughly from −35 to −47 ppm). This high-frequency shift may reflect that the $^{11}$B spin − paramagnetic electron-spin interactions also contribute with a Knight shift of the $^{11}$B resonance. $^{11}$B MAS NMR spectra have also been acquired for the hydrogen samples, i.e. LiCe(BH$_4$)$_3$Cl in s1 − s3 (not shown), which reveal the same centerband ($\delta = 26$ ppm) and ssb manifold as observed for the deuterated sample (Figure 4) along with a centerband resonance at $\delta_{iso} = 41.2$ ppm and a few associated ssbs from LiBH$_4$ in the samples. LiBD$_4$ is also observed in the s4 sample, as most clearly seen in the 9.4 T spectrum recorded with a spinning speed of $\nu_R = 12.0$ kHz (Figure 4b). However, evaluation of the intensities for the two compounds in this spectrum gives the intensity ratio $I$(LiBD$_4$)$:I$(LiCe(BH$_4$)$_3$Cl) $= 0.03$, demonstrating that the amount of LiBD$_4$ is very small in the s4 sample.

**Lithium Ion Conductivity.** Conductivities are measured for LiBH$_4$ (Sigma-Aldrich, as received) and LiCe(BH$_4$)$_3$Cl (sample CeCl$_3$ $\cdot$ LiBH$_4$ 1:3, s5) pellets between steel disks acting as ionically blocking electrodes by impedance spectroscopy, at $T = 20 \, ^{\circ}$C. The impedance spectra recorded for LiBH$_4$ is shown in the Supporting Information, Figure S2. From the diameter of the semicircle observed at high frequency, which is related to the lithium ion mobility, a resistance of $R = 8.35 \times 10^5 \, \Omega$ is measured for a 0.56 mm pellet thickness. This leads to a conductivity of $8.6 \times 10^{-8}$ S cm$^{-1}$ at 20 $^{\circ}$C in good agreement with the values reported for orthorhombic $\alpha$-LiBH$_4$.\textsuperscript{55} No signature of the electrode interface or the grain boundaries are observed on the impedance spectra.

For LiCe(BH$_4$)$_3$Cl, impedance spectra were recorded on pellets of different thicknesses and Figure 5 reveal that the impedances are much lower than that of $\alpha$-LiBH$_4$ in all cases. Only Warburg impedances related to the semi-infinite diffusion at the electrodes are observed and frequencies higher than 1 MHz are needed to fully plot the semicircles assigned to the lithium ion mobility in the material. Nevertheless, the shape of the impedance spectra is typical of a good conductor and the conductivity can be calculated from the intercept with the real axis ($Z_{re}$ value). Figure 6 reveals for LiCe(BH$_4$)$_3$Cl a linear relationship between the resistance and the pellet thickness.
The extrapolated resistance for a zero thickness is very low (Rs = 42 Ω) highlighting the quality of our electrode-material interface. The slope of the linear fit is R = 1232 Ω mm⁻¹, which corresponds to a high conductivity of 1.03 × 10⁻⁴ S cm⁻¹ measured at T = 20 °C.

To investigate more in detail the nature of the conduction, we also carried impedance spectroscopy out on a pellet sandwiched between lithium foils acting as ion non-blocking electrodes. On Figure 7, the resistivity is given for both the metallic lithium electrodes. On Figure 7, the resistivity is given for both the metallic lithium electrodes and the shape of the impedance curve resembles a curve for a good conductor. From the intercept with the real axis, a conductivity of 7 × 10⁻⁴ S cm⁻¹ is obtained at 20 °C. This suggests that the LiCe(BH₄)₃Cl sample CeCl₃−LiBH₄ (1:3, s5) is a good lithium ion conductor. The high lithium ion conductivity in LiCe(BH₄)₃Cl may be attributed to empty Li⁺ sites in the structure. According to the structural model for LiCe(BH₄)₃Cl, only 2/3 of the Li positions (12 d Wyckoff site) are occupied in a disordered manner. These first conductivity measurements suggest that LiCe(BH₄)₃Cl could be considered as a future candidate for a solid electrolyte in the next-generation lithium-ion batteries. Recently, extremely high Li ion conductivity of 1.2 × 10⁻² S cm⁻¹ was reported for the novel compound Li₁₀GeP₂S₁₂. Li NMR experiments are in progress to demonstrate the high Li⁺ mobility and to definitively conclude that the ionic conductivity originates solely from Li⁺ cations.

Thermal Analysis and Sievert Measurements. Thermogravimetric (TGA) and differential scanning calorimetric (DSC) measurements for samples CeCl₃−LiBH₄ (1:3, s2) and (1:4, s3) are shown in Supporting Information, Figure S3, and Figure 8, respectively. Sample s3 shows a mass loss of 0.7 wt % in the temperature range 150 to 240 °C and a larger loss in the range 240 to 290 °C of 3.0 wt %. Thus, the observed mass loss for sample s3 is 3.7 wt % in the temperature range RT to 500 °C, which is less than the calculated hydrogen content of the sample, 4.84 wt % H₂. The observed and calculated mass losses for sample s2 are 3.2 and 3.88 wt % H₂, respectively. Considering that the decomposed samples contain cerium dihydride, CeH₂, the calculated hydrogen contents of the samples s2 and s3 are 3.23 and 4.23 wt % H₂.

In Figure 8, the resistivity is measured for the CeCl₃−LiBH₄ (1:3, s5) recorded with steel and Li metal electrodes at T = 20 °C.

The DSC data for s3 (see Figure 8) show two small endothermic peaks at 93 and 109 °C, which may correspond to the onset temperature for the reaction between CeCl₃ and LiBH₄ in the sample (see reaction scheme 1) and to the polymorphic phase transition from orthorhombic to hexagonal LiBH₄. An endothermic peak observed at 213 °C may correspond to the melting of LiCe(BH₄)₃Cl. A smaller
endothermic event observed at 240 °C may be associated with the initial decomposition of LiCe(BH₄)₃Cl. Indeed, the decomposition may consist of multiple reactions visible as shoulders at 257 and 261 °C at the major DSC signal with peak value at 266 °C. The endothermic events at 213 and 266 °C are correlated with the mass loss observed in the TGA data.

Reversible hydrogen storage properties were investigated using Sieverts measurements for sample s3 and s2 and the data is shown in Figure 9 and the Supporting Information, Figure S4, respectively. Desorption data for sample s3 is collected in the Supporting Information, Table S3. Sample s3 releases 0.5 wt % H₂ from RT to 220 °C and a major H₂ release of 3.25 wt % H₂ is observed from 220 to 270 °C, which corresponds to the observations by TGA and DSC. Additionally, 0.80 wt % H₂ is released during heating from 270 to 500 °C and 0.15 wt % H₂ is released after heating the samples for 3 h at a constant temperature of 500 °C. Hence, the total observed H₂ release is 4.7 wt % H₂ for sample s3. In a previous study of the CeCl₃−LiBH₄ system gas analysis revealed a very small amount of diboran during hydrogen desorption. In the present study, the mass loss from the samples are all below the theoretical content of hydrogen; for this reason, the release of diboran from the samples is assumed to be at a minimum.

The Sieverts measurements for the second (d2) and third (d3) desorption follow a different trend since only 0.25 wt % H₂ is released in the temperature range RT to 270 °C. In contrast, desorptions d2 and d3 release 1.25 and 1.15 wt % H₂ from 270 to 500 °C and 0.5 and 0.4 wt % H₂ during 3 h at a constant temperature of 500 °C. Thus, the desorption d2 and d3 does not show the expected hydrogen release in the temperature range RT to 270 °C for the decomposition of LiCe(BH₄)₃Cl revealing that the sample is not fully rehydrogenated at the selected conditions for hydrogen absorption. In total, the desorption d2 and d3 release 2.0 and 1.8 wt % H₂, which is slightly higher than the calculated hydrogen content assuming that CeH₂ or CeH₃ is formed during absorption of sample s3, i.e., 0.60 or 0.91 wt % H₂, respectively. The sample s3 contains one equivalent excess LiBH₄ which may be rehydrogenated and the calculated hydrogen release from a sample s3 containing CeH₂ and 1 equiv. of LiBH₄ is 2.12 wt % H₂. In contrast, sample s2 release 3.75 wt % H₂ in the first cycle (d1) and 1.25 and 1.25 wt % H₂ in the second and third cycles, which is comparable to the calculated H₂ release of 3.88 and 0.97 wt % H₂ assuming that s2 contain LiCe(BH₄)₃Cl prior to d1 and CeH₃ for the later desorption cycles (see the Supporting Information, Figure S4).

The decomposition products for s3 after the third desorption (d3) in the Sieverts measurements (Figure 9) was investigated by Rietveld refinement of SR-PXD data (Figure 10). Desorption from the decomposition products LiCl, CeH₂, and CeB₆ are identified along with an unknown compound.

**Decomposition Mechanism for LiCe(BH₄)₃Cl Observed by In situ SR-PXD.** The thermal decomposition of samples CeCl₃−LiBH₄ (1:3, s3) and (1:4, s4) were studied by in situ SR-PXD. Both samples display similar decomposition mechanism, though the decomposition products from s2 appear more crystalline and are discussed in the following (Figure 11). The first SR-PXD patterns in the series measured at RT show diffraction peaks from LiCe(BH₄)₃Cl, CeCl₃ and LiCl. The diffraction peaks from CeCl₃ decreases slowly at T > 63 °C and disappear at 315 °C. During heating from 100 to 160 °C the amounts of LiCe(BH₄)₃Cl and LiCl increase, while that of CeCl₃ decreases because of the progress of reaction 1. The Bragg diffraction peaks from LiCe(BH₄)₃Cl disappear at 240 °C, possibly because of melting and subsequent decomposition and diffraction from an unknown compound appear at 240 °C. Peaks from CeH₃ emerge at 320 °C when CeCl₃ disappears. The unknown compound may be a ternary salt composed of lithium, cerium and chloride and remains in the sample during the rest of the heating. A ternary salt, NaYCl₄, is also observed during the decomposition of NaY(BH₄)₂Cl₂. Structural determination of the unknown compound has unfortunately not been possible, but further studies are currently being performed to elucidate the atomic composition. The reaction scheme (3) describes the idealized overall decomposition reaction for s2 omitting the unknown compound.

![Figure 9](image9.png)

*Figure 9. Sieverts type (PCT) measurement of the gas release from CeCl₃−LiBH₄ (1:4, s3), showing the first three desorptions, d1, d2, and d3, conducted in the temperature range RT to 500 °C (heating rate $ΔT/Δt = 1 \degree C/min$ and with a back-pressure of $p(H₂) = 1$ bar). Prior to d2 and d3, the sample was rehydrogenated at 400 °C and $p(H₂) = 100$ bar for 24 h.*

![Figure 10](image10.png)

*Figure 10. SR-PXD pattern of sample CeCl₃−LiBH₄ (1:4, s3) after the third desorption (d3) in the Sieverts measurements (Figure 8). The decomposition products CeB₆, LiCl, CeH₂ were identified by Rietveld refinement along with weak diffraction peaks from an unknown compound (ESRF, $λ = 0.696713$ Å, measured at RT). Symbols: ■ LiCl, □ CeH₂, ○ CeB₆, and Δ unknown.*

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dx.doi.org/10.1021/cm300792t | Chem. Mater. 2012, 24, 1654−1663
resonance. Very high lithium ion conductivity is in favor of our capacity of only

10−5 S/cm at moderate conditions leads to a reversible storage state. 11B MAS NMR spectra of the central and satellite mobility, which is in favor of our model of disordered Li. Solid-state measurements carried out between lithium foils suggest that the conductivity measured for the LiCe(BH4)3Cl containing calculations agree well with the very high lithium ion conductivity measured for the disorder at the Li positions. The structural model and DFT indicate by higher entropy rather than lower enthalpy, in accord with

charge-balanced by Li+ cations. The Li+ ions are disordered with a distorted cubane Ce4Cl4 core

the Li positions. The structural model and DFT indicates that LiCe(BH4)3Cl is stabilized by higher entropy rather than lower enthalpy, in accord with the disorder at the Li positions. The structural model and DFT calculations agree well with the very high lithium ion conductivity measured for the LiCe(BH4)3Cl containing sample. 1.03 × 10−4 S cm−1 at T = 20 °C. Conductivity measurements carried out between lithium foils suggest that the conductivity mainly originates from the high lithium ion mobility, which is in favor of our model of disordered Li. Solid-state 11B MAS NMR spectra of the central and satellite transitions reveal that the 11B spin interacts with the paramagnetic electron-spins (from the unpaired electron on Ce3+) which also contribute with a Knight shift of the 11B resonance. Very high lithium ion conductivity is in favor of our structural model including disordered Li. The new compound LiCe(BH4)3Cl also stores 5.33 wt % hydrogen, which is released in the temperature range 220−260 °C. Rehydrogenation at moderate conditions leads to a reversible storage capacity of only ~1 wt % H2.

CONCLUSION

The novel compound LiCe(BH4)3Cl crystallizes in the cubic crystal system with the space group I43m and the structure contains isolated tetranuclear anionic clusters [Ce4Cl4(BH4)12]4− with a distorted cubane Ce6Cl4 core charge-balanced by Li+ cations. The Li+ ions are disordered and occupy 2/3 of the 12d Wyckoff sites. The structural model was derived by the combined use of synchrotron radiation powder X-ray diffraction (SR-PXD), powder neutron diffraction (PND), and density functional theory (DFT) and would likely not have been obtained with any combination of only two of the methods. DFT indicates that LiCe(BH4)3Cl is stabilized by higher entropy rather than lower enthalpy, in accord with the disorder at the Li positions. The structural model and DFT calculations agree well with the very high lithium ion conductivity measured for the LiCe(BH4)3Cl containing sample, 1.03 × 10−4 S cm−1 at T = 20 °C. Conductivity measurements carried out between lithium foils suggest that the conductivity mainly originates from the high lithium ion mobility, which is in favor of our model of disordered Li. Solid-state 11B MAS NMR spectra of the central and satellite transitions reveal that the 11B spin interacts with the paramagnetic electron-spins (from the unpaired electron on Ce3+), which also contribute with a Knight shift of the 11B resonance. Very high lithium ion conductivity is in favor of our structural model including disordered Li. The new compound LiCe(BH4)3Cl also stores 5.33 wt % hydrogen, which is released in the temperature range 220−260 °C. Rehydrogenation at moderate conditions leads to a reversible storage capacity of only ~1 wt % H2.

ASSOCIATED CONTENT

Supporting Information

Additional tables and figures (PDF) and CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

Dr. Denis Sheptyakov, Paul Scherrer Institut, PSI, Switzerland, is thanked for the powder neutron diffraction measurements and SNBL for beamtime allocation. We thank the Danish National Science Research Councils for fundings to the Instrument Centre for Solid-State NMR Spectroscopy and the research program DanScatt. The Danish Strategic Research Council is acknowledged for financial support to the Center for Energy Materials (CEM) and The Danish National Research Foundation for fundings to the Center for Materials Crystallography (CMC). Y.-S.L. and Y.W.C. acknowledge support by the Hydrogen Energy R&D Center, funded by the Ministry of Education, Science and Technology of Korea.

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Figure 11. In situ SR-PXD data for CeCl3−LiBH4 (1:3, s) measured from RT to 500 °C (ΔT/Δt = 8 °C/min, p(Ar) = 1 bar, λ = 0.709637 Å). Symbols: • LiCe(BH4)3Cl, □ CeCl3, □ LiCl, ○ CeH2, ○ CeB6 and Δ unknown.

LiCe(BH4)3Cl + 2LiCl

→ 1/2CeH2 + 1/2CeB6 + 11/2H2 + 3LiCl

(3)