

Al₃Li₄(BH₄)₁₃: A Complex Double-Cation Borohydride with a New Structure

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Abstract: The new double-cation Al–Li–borohydride is an attractive candidate material for hydrogen storage due to a very low hydrogen desorption temperature (~70 °C) combined with a high hydrogen density (17.2 wt %). It was synthesised by high-energy ball milling of AlCl₃ and LiBH₄. The structure of the compound was determined from image-plate synchrotron powder diffraction supported by DFT calculations. The material shows a unique 3D framework structure within the borohy-

drides (space group = *P*-43*n*, *a* = 11.3640(3) Å). The unexpected composition Al₃Li₄(BH₄)₁₃ can be rationalized on the basis of a complex cation [(BH₄)Li₄]³⁺ and a complex anion [Al(BH₄)₄]⁻. The refinements from synchrotron powder diffraction of different samples revealed the presence of

limited amounts of chloride ions replacing the borohydride on one site. In situ Raman spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG) and thermal desorption measurements were used to study the decomposition pathway of the compound. Al–Li–borohydride decomposes at ~70 °C, forming LiBH₄. The high mass loss of about 20 % during the decomposition indicates the release of not only hydrogen but also diborane.

Keywords: borohydrides • density functional calculations • hydrogen storage • metathesis • X-ray diffraction

Introduction

For the last ten years, metal borohydrides have attracted great interest in terms of on-board hydrogen storage due to their high gravimetric and volumetric hydrogen density.^[1] Many of these compounds appear to be too stable and con-

sequently decompose at very high temperatures (e.g. LiBH₄, Mg(BH₄)₂).^[2,3] Other borohydrides are too unstable and decompose at quite low temperatures under desorption of diborane (e.g. Ti(BH₄)₃, Zn(BH₄)₄).^[4] The desorption temperature of the borohydrides decreases with the Pauling electronegativity (χ_P) of the cation.^[5] A suitable χ_P for hydrogen applications is expected in the range of 1.2 to 1.5.^[5]

Up to now, there are only a few reports on double-cation borohydrides A_xM_y(BH₄)_z, but first theoretical and experimental studies point to an intermediate stability of the corresponding single-cation borohydrides.^[6,7,8] Therefore, the decomposition temperature can be adjusted by an appropriate combination of the cations. Recently, LiK(BH₄)₂,^[8] LiSc(BH₄)₄^[9] and NaSc(BH₄)₄^[10] were synthesized but their desorption temperatures are still too high for applications with values of 380, 177, and 150 °C, respectively. As LiBH₄ is very stable it should be combined with a cation forming a borohydride of low desorption temperature. Indeed, a series of Zn-based mixed-metal borohydrides showed lower decomposition temperatures, ranging from 95 to 127 °C.^[11] Another suitable candidate for the cation is Al since its borohydride has a very low decomposition temperature of ~70 °C.^[4] LiBH₄–Al composites show improved dehydrogenation and rehydrogenation properties.^[12] Furthermore, Al is

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a very light metal and a cheap and abundant material. Replacement of the Sc^{3+} cation by Al^{3+} in $\text{LiSc}(\text{BH}_4)_4$ was discussed in reference [9] and the existence of the $[\text{Al}(\text{BH}_4)_4]^-$ anion was claimed in reference [13]. A double-cation borohydride $\text{LiAl}(\text{BH}_4)_4$ was suggested as a product of the reaction between lithium and aluminium borohydride in ether solutions;^[14] however, no structural details were reported. DFT calculations of various double-cation borohydrides by Hummelshøj et al.^[6] showed that $\text{LiAl}(\text{BH}_4)_4$ might be stable at ambient conditions. It was possibly synthesized before by Li et al.,^[15] but no structural information was provided, which was the aim of our work.

Herein, we report on the synthesis and detailed structural, physical and chemical characterisation of the complex Al–Li–borohydride. The structure was determined by the combination of synchrotron powder diffraction and DFT calculations. Further structural characterisation was carried out by vibrational spectroscopy (Raman and IR). The compound under study is a new and promising material for on-board hydrogen storage due to its low decomposition temperature ($\sim 70^\circ\text{C}$) combined with a high gravimetric hydrogen density (17.2 wt%). Therefore, it has the potential to meet the requirements for applications, for example, in PEM fuel cells.

Results and Discussion

High-energy ball milling was used to run the metathesis reaction between AlCl_3 and LiBH_4 . Structure analysis by XRD in transmission geometry points to the formation of LiCl as a byproduct. Therefore Li cations in LiBH_4 are partially substituted by Al, forming the complex Al–Li–borohydride. The presence of the non-reacted AlCl_3 in the 1:4 ratio of starting materials, and non-reacted LiBH_4 in the 1:5 starting mixture points to a stoichiometric composition at an intermediate ratio, which is different from the 1:4 ratio expected for the $\text{LiAl}(\text{BH}_4)_4$ composition.^[6,14]

The new Al–Li– BH_4 phase reveals a remarkable chemical structure as shown by synchrotron radiation powder X-ray diffraction (SR-PXD). The composition was found to be $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ in contrast to the earlier reported $\text{LiAl}(\text{BH}_4)_4$.^[6,14,15] The material (Figure 1) has a cubic unit cell (space group $P-43n$, $a = 11.3640(3) \text{ \AA}$), and its unexpected composition can be rationalized on the basis of a complex cation $[(\text{BH}_4)\text{Li}_4]^{3+}$ and anion $[\text{Al}(\text{BH}_4)_4]^-$.

The complex cation is an anion-centred complex with four Li atoms coordinated to the $(\text{BH}_4)^-$ group via the tetrahedral faces, located on a crystallographic site with point-group symmetry 23, but holding the ideal tetrahedral geometry. A similar arrangement of Li atoms around the $(\text{BH}_4)^-$ group, with a point-group symmetry $3m$, was observed in the high-temperature form of LiBH_4 .^[16] The complex anion is a cation-centred complex with four $(\text{BH}_4)^-$ groups coordinated to the Al^{3+} cation via the tetrahedral edges, as is the case in most metal borohydrides.^[16] The anion has a tetrahedral geometry deformed (B–Al–B $100.0(1)$ – $130.8(2)^\circ$) to-

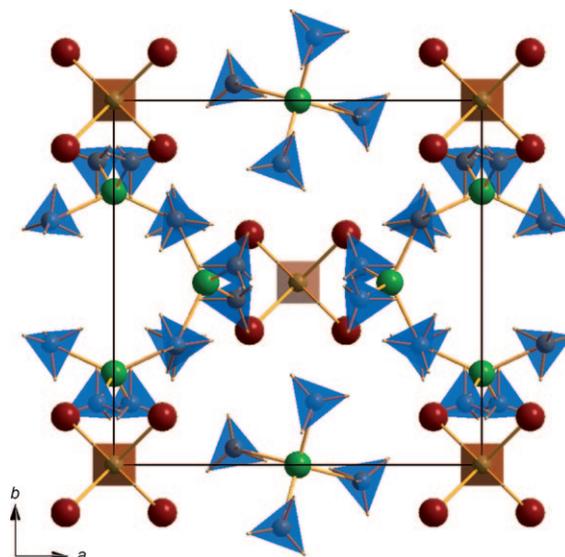
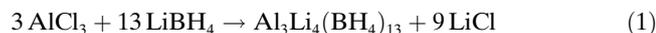


Figure 1. Unit cell of $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$. Four $(\text{BH}_4)^-$ tetrahedra (blue) and one Al^{3+} cation (green) form the complex anion $[\text{Al}(\text{BH}_4)_4]^-$. Four Li^+ cations (red) bonded to one $(\text{BH}_4)^-$ tetrahedron (brown) in the centre form the complex cation $[\text{Li}_4(\text{BH}_4)]^{3+}$.

wards a square plane more than $[\text{Sc}(\text{BH}_4)_4]^-$ in $\text{LiSc}(\text{BH}_4)_4$ ^[9] (B–Sc–B 96.5 – 125.4°) and in $\text{NaSc}(\text{BH}_4)_4$ ^[10] (B–Sc–B 100.7 – 119.1°). The $[\text{Al}(\text{BH}_4)_4]^-$ complex anion has been observed in the solid state for the first time. The complex cation $[(\text{BH}_4)\text{Li}_4]^{3+}$ is important in understanding the unexpected $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ stoichiometry, relative to other double-cation borohydrides, such as $\text{LiK}(\text{BH}_4)_2$,^[8] $\text{LiSc}(\text{BH}_4)_4$ ^[9] and $\text{NaSc}(\text{BH}_4)_4$.^[10] This composition can be rationalized by a simple formula, $[(\text{BH}_4)\text{Li}_4][\text{Al}(\text{BH}_4)_4]_3$, in which the packing of the structural units corresponds to the structure type Cr_3Si (A15), a Frank–Kasper phase with 14 and 12-coordinated sites. The hydrogen-rich highly symmetric Li cluster is also of a theoretical interest.^[17] The Al–Li–borohydride represents a novel type of borohydride since it contains both a complex cation and a complex anion.

Formation of the complex cations and anions is caused by the directional metal– $(\text{BH}_4)^-$ interaction.^[16] Aggregation of Li and $(\text{BH}_4)^-$ groups in structural units, such as layers, has been noted previously in pure LiBH_4 ,^[18,19] and a concept of the anion-centred complexes was used to explain the composition, structure and properties of complex hydrides.^[16,20,21] The directional coordination of the $(\text{BH}_4)^-$ ion by metal atoms clearly indicates the non-spherical nature of the $(\text{BH}_4)^-$ anion, with geometrical and electronic preferences in metal– $(\text{BH}_4)^-$ interactions, responsible for the formation of doubly interpenetrated 3D frameworks in $\text{MZn}_2(\text{BH}_4)_5$ ^[11] and porous 3D frameworks in $\alpha\text{-Mg}(\text{BH}_4)_2$.^[22] The $(\text{BH}_4)^-$ -centred complex is not isolated: the Li–B distance within the $[(\text{BH}_4)\text{Li}_4]^{3+}$ complex is $2.59(1)$ versus $2.46(1) \text{ \AA}$ between the Li atom and the $[\text{Al}(\text{BH}_4)_4]^-$ anion. The similar distances allow us to describe the structure also as a 3D framework. A notable void at $1/4, 0, 1/2$ with a centre 2.89 \AA from the nearest atom (H22) is located between the

complex cations and anions, and its size and a total 12% porosity of the structure suggest that $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ is not closely packed, and therefore the directionality of metal– $(\text{BH}_4)^-$ interactions plays an important role. Rationalization of the bonding in terms of the complex anion and cation likely reflects these interactions and may explain the complex and unexpected stoichiometry. As the observed stoichiometry requires a molar $\text{AlCl}_3/\text{LiBH}_4$ ratio of 1:4.33, the complete metathesis reaction [Eq. (1)] is as follows:



Temperature-resolved diffraction studies of the ball-milled mixtures revealed a linear thermal expansion of $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ at lower temperatures (see Figure 2), with the

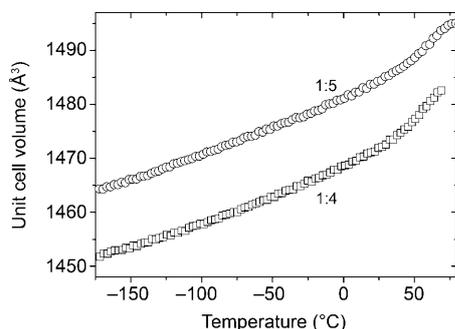


Figure 2. Thermal expansion of the unit cell of $\text{Al}_3\text{Li}_4(\text{BH}_4)_{13}$ in a mixture with the molar ratio of 1:4 (\square) and 1:5 (\circ).

coefficient of volumetric thermal expansion $\alpha_v = 6.16(7) \times 10^{-5} \text{ K}^{-1}$. However, the unit-cell volume of the Al–Li–borohydride is larger at the 1:5 than at the 1:4 molar ratio. Detailed analysis indicates an incorporation of some chloride anions on the $(\text{BH}_4)^-$ site in the anion-centred complex, similar to the one observed in $\text{LiBH}_4\text{--LiCl}$ mixtures.^[23,24] Rietveld refinement suggests $\sim 42\%$ occupation of this site by Cl in the 1:4 and $\sim 26\%$ occupation in the 1:5 mixture.

Vibrational spectroscopy was used for further structural characterisation. Raman measurements at RT are shown in Figure 3a for the 1:4 and 1:5 mixtures as well as the predicted 1:4.33 molar ratio. Modes of the non-reacted LiBH_4 (2277 and 2299 cm^{-1})^[25] are observed in the 1:5 powder as well as some traces in the 1:4.33 mixture. The Raman spectra of the 1:4 ratio powder shows shifts only corresponding to the new Al–Li–borohydride. It shows several internal modes of the $(\text{BH}_4)^-$ tetrahedron: four stretching modes between 2200 and 2500 cm^{-1} and three bending modes between 1000 and 1500 cm^{-1} . The four stretching modes originate from the low symmetry $[\text{Al}(\text{BH}_4)_4]^-$ tetrahedron. In agreement with the determined structure, the $[\text{Al}(\text{BH}_4)_4]^-$ complex is observed with the bidentate coordination of the $(\text{BH}_4)^-$ group. Therefore, the modes at 2210 and 2250 cm^{-1} belong most probably to the inward B–H bonds, whereas the modes at 2440 and 2480 cm^{-1} are related to the outward pointing B–H bonds. The vibration at 1450 cm^{-1} can be as-

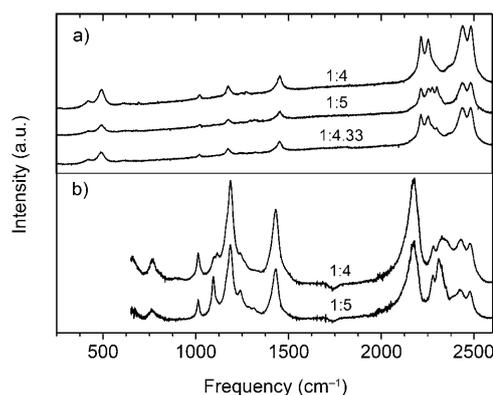


Figure 3. Raman (a) and IR (b) measurements of the as-milled powders with the molar ratios of 1:4, 1:5 and 1:4.33.

signed to the BH_2 bending mode in the $[\text{Al}(\text{BH}_4)_4]^-$ complex, which is observed at higher frequencies than the corresponding mode in the $[\text{Sc}(\text{BH}_4)_4]^-$ complex^[4,9] due to the bidentate binding. Two further bending modes are observed at 1170 and 1020 cm^{-1} , which appear at lower frequencies than in LiBH_4 . The mode at 490 cm^{-1} corresponds to the $[\text{Al}(\text{BH}_4)_4]^-$ complex since a strong Raman Al–B band appears in $\text{Al}(\text{BH}_4)_3$.^[26] These Raman shifts recall the pattern reported previously for the $[\text{Sc}(\text{BH}_4)_4]^-$ complex.^[4,9] The other lower bands (90 and 420 cm^{-1}) may correspond to the external modes of the $[\text{Li}_4(\text{BH}_4)]^{3+}$ tetrahedron because they are close to those observed in LiBH_4 .^[25] However, these modes do not show any shift in different compositions as expected for Cl substitution.

The IR spectra for the 1:4 and 1:5 ratio compounds are shown in Figure 3b. Above 2400 cm^{-1} , two bands appear at 2420 and 2480 cm^{-1} for the $[\text{Al}(\text{BH}_4)_4]^-$ complex, which are also Raman active. These bands correspond to the two outward pointing B–H bonds of the $[\text{Al}(\text{BH}_4)_4]^-$ complex, whereas a single mode would indicate one terminal hydrogen as in the $[\text{Sc}(\text{BH}_4)_4]^-$ complex.^[9] The strong band at 2180 cm^{-1} could correspond to the IR-active stretching mode of the highly symmetrical $[\text{Li}_4(\text{BH}_4)]^{3+}$ complex. As observed by Raman measurement, the mode at 1450 cm^{-1} shows the BH_2 bending of the $[\text{Al}(\text{BH}_4)_4]^-$ complex. Its strong intensity proves the local symmetry of the $(\text{BH}_4)^-$ ion to be quite different from tetrahedral because this mode would be IR inactive in the tetrahedral symmetry. The sharp band around 1020 cm^{-1} is also observed in the Raman measurements and may be attributed to the $[\text{Li}_4(\text{BH}_4)]^{3+}$ complex.

Finally, the decomposition pathway of the compound was analyzed by in situ Raman, synchrotron powder X-ray diffraction, differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements and by thermal desorption analysis. The decomposition products are of great interest to reload the material with hydrogen. In situ Raman measurements were carried out in Ar and in 50 bar H_2 as shown in Figure 4. The measurement under an Ar atmosphere (see Figure 4a) shows modes corresponding to ortho-

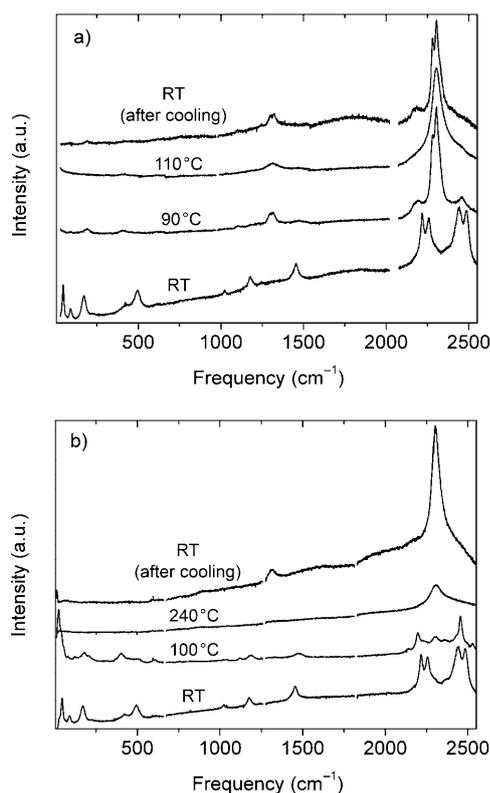


Figure 4. In situ Raman measurements of the as-milled powder in a 1:4 molar ratio at different temperatures under 1 bar of Ar (a) and 50 bar of H₂ (b).

rhombic LiBH₄ at 90°C, which indicates the complete decomposition of Al₃Li₄(BH₄)₁₃. The formation of LiBH₄ is confirmed by the Raman spectra obtained at 110°C. Here, LiBH₄ in the hexagonal phase is found since the compound undergoes a phase transformation at 110°C that is in good agreement with results of Gomes et al.^[25] When cooling the powder down to room temperature, a splitting of the bending is observed again due to the formation of LiBH₄ in the orthorhombic phase. The DSC measurement (see Figure S4 in the Supporting Information) confirms these observations: endothermic peaks are found around 70°C pointing to the decomposition of the Al–Li–borohydride and at about 100°C, which indicates the phase transformation of the decomposition product LiBH₄.

The in situ Raman measurements in 50 bar H₂ atmosphere are given in Figure 4b. In this case the Al–Li–borohydride is still observed even at 100°C due to an increased decomposition temperature at higher H₂ pressure. The Raman spectra show a change of the geometry of the anion ([Al(BH₄)₄]⁻ complex). The low frequency band at 490 cm⁻¹ is still present, confirming that Al is still bonded to (BH₄)⁻ groups. At higher temperatures, the hexagonal phase of LiBH₄ is observed due to the decomposition of the complex Al–Li–borohydride. When cooling the powder down to RT, the hexagonal phase survives. The presence of different ions decreases the phase transformation temperature considera-

bly so that the disordered high-temperature phase is still present at room temperature due to incorporated Cl.^[24,27]

For thermal desorption analysis, vacuum (see Figure 5) pressure versus temperature was monitored while heating the powders at approximately 5°Cmin⁻¹ up to 150°C. The

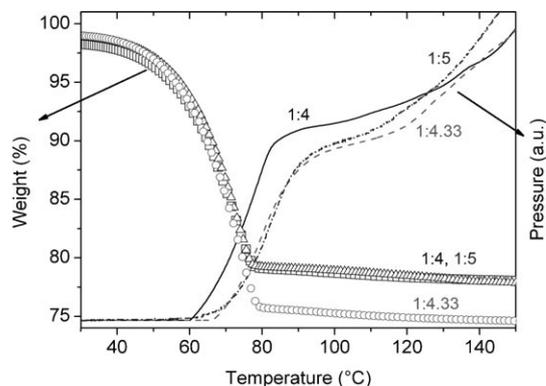


Figure 5. Pressure versus temperature (lines) and TG measurements (symbols) for the as-milled powders with molar ratios of 1:4, 1:4.33 and 1:5.

pressure increase starts in a single step at about 60°C for the 1:4 ratio compound and at about 70°C for the 1:4.33 and 1:5 ratio compounds due to the decomposition of the Al–Li–borohydride under formation of LiBH₄ as shown by in situ Raman measurements. The desorption temperature of the 1:4 ratio compound is lower due to a higher content of incorporated Cl in the Al–Li–borohydride. In situ SR-PXD (see Figure S3 in the Supporting Information) showed the formation of LiBH₄ at 77°C for the 1:4 ratio and at 95°C for the 1:5 ratio, respectively. The gas desorption is in good agreement with the mass loss observed by TG analysis under an Ar atmosphere (see Figure 5). The weight just before the TG measurement is found to be less than 100% because the material loses mass already during the purging cycle. In all three mixtures a significant mass loss was observed at around 70°C. About 20.8% mass loss was measured for the 1:4 and 1:5 ratio compound. The 1:4.33 ratio showed 24.4% weight loss. Based on the reaction in Equation (1) with the ideal reaction yield the 1:4.33 ratio should contain 44.2 wt% Al–Li–borohydride, whereas the 1:5 ratio should contain 41.5 wt% Al₃Li₄(BH₄)₁₃ and the 1:4 mixture 42.1 wt%, respectively. However, SR-PXD gives an additional unknown phase in the 1:4 mixture so that this value is not reliable. According to the decomposition reaction [Eq. (2)] a loss of nine of the thirteen (BH₄)⁻ tetrahedral as B₂H₆ and H₂ can be assumed during the decomposition of the Al–Li–borohydride leading to the formation of LiBH₄.



Therefore, a mass loss of 18.3% for the 1:5 and 21.6% for the 1:4.33 ratio compound, respectively, is expected. A higher mass loss than the theoretical one is observed experi-

mentally because Al can most likely be desorbed from the material as alane upon heating as reported by Hara et al.^[28] and as supported by the absence of diffraction peaks of the crystalline Al.

Conclusion

The complex double-cation borohydride Al–Li–borohydride presented here has a unique structure within a large group of metal borohydrides. It consists of the anion-centred $[(\text{BH}_4)\text{Li}_4]^{3+}$ complex and a new $[\text{Al}(\text{BH}_4)_4]^-$ anion. This system improves the knowledge on the chemistry of the other double-cation systems. Al–Li–borohydride decomposes at moderate temperatures of about 70 °C leading to the formation of LiBH_4 . An optimization of the reaction pathways for both hydrogen release and uptake seems to be possible. For now, the release of diborane (B_2H_6) and the Al evaporation restrict reversibility, which might be eliminated by the formation of a boride. Thus, the new Al–Li–borohydride with an extremely high volumetric (117 kg m^{-3}) and gravimetric (17.2 wt %) hydrogen density, in combination with a low dehydrogenation temperature, is a potential candidate material for on-board hydrogen storage.

Experimental Section

General: AlCl_3 (Merck, purity 98 wt %) and LiBH_4 (Aldrich, purity 95 wt %) mixed in different molar ratios (1:2, 1:3, 1:4, 1:4.33 and 1:5) were ball-milled for 5 h under an argon atmosphere (Fritsch P6, 500 rpm) with a ball-to-powder ratio of 40:1. All manipulations of the chemicals were performed in argon-filled glove boxes. During the milling process, pressure and temperature were continuously in situ monitored to follow any hydrogen evolution processes (evico magnetics device).^[29,30] Transmission X-ray diffraction measurements were done in 0.7 mm capillaries with a STOE Stadi P ($\text{MoK}\alpha$) in Debye–Scherrer geometry with a step size of $0.02^\circ 2\theta$ at room temperature. The diffractometer is equipped with a curved Ge(111) monochromator and a 6° linear position sensitive detector with a resolution of about $0.06^\circ 2\theta$ at full width at half maximum

Synchrotron radiation in situ powder X-ray diffraction (SR-PXD) data of the 1:4 and 1:5 ratios were collected at beamline BM01A at the European Synchrotron Radiation Facility, Grenoble (France). A MAR345 detector was used and the selected X-ray wavelength was 0.77029 \AA . All 2D SR-PXD data were integrated into 1D patterns by using Fit2D.^[31] A dataset collected at 100.8 K on the mixture with 1:5 molar ratio contained a higher yield of the main phase (36.4(4) wt %), and was used for indexing and structure solution. 13 low-angle unidentified diffraction peaks were indexed by Dicvol04^[32] in a primitive cubic cell. Analysis of systematic absences by using the program Chekcell^[33] suggested two possible space groups: $Pm\bar{3}n$ and $P\bar{4}3n$. After making Le Bail fit in Fullprof^[34] the structure was solved in $P\bar{4}3n$ by using a global optimization in direct space in the program FOX.^[35] No reasonable ordered model could be obtained in $Pm\bar{3}n$. During the structure solution, the positions of one Al and one Li atom and the positions and orientations of two $(\text{BH}_4)^-$ groups were optimized. Antibump restraints on the shortest H–H distances helped to find the orientation of the $(\text{BH}_4)^-$ group. The refinement was conducted by the Rietveld method by using the program Fullprof.^[34] The background was described by linear interpolation between selected points. One coordinate parameter was refined for the Li atom, whereas Al and the $(\text{BH}_4)^-$ group are located on special positions with no refinable coordinate parameters. The $(\text{B}_2\text{H}_4)^-$ group is located on a general po-

sition. H-atoms were refined with $1.13(1) \text{ \AA}$ restraints on the B–H distances and with $1.85(1) \text{ \AA}$ restraints on the H–H distances. During the refinement, the mixed occupancy between $(\text{BH}_4)^-$ and Cl^- anions was detected and refined. The DFT optimization of the model allowed the fit to be improved and thus the global minimum to be achieved. The final refinement converged at $R_B=2.65$, $R_F=3.17$, $R_p=2.92$, $R_{wp}=2.63\%$ (profile factors corrected for background) and $\chi^2=1020$. The high value of χ^2 reflects mainly the extremely high counting statistics of the powder diffraction data obtained from modern 2D detectors. The temperature-dependent (SR-PXD) data of the 1:4 and 1:5 mixtures were refined by using the sequential mode of Fullprof.

The SR-PXD structure was optimized within the Kohn–Sham formulation of DFT^[36,37] by performing periodic calculations with the ABINIT package,^[38–40] which is based on plane waves and pseudopotentials. We used Troullier–Martins pseudopotentials^[41] generated with the FHI98PP^[42] code in the separable Kleinman–Bylander form.^[43] The calculation was carried out in the Generalized Gradient Approximation (GGA).^[44,45] A $2 \times 2 \times 2$ Monkhorst–Pack grid^[46] and a kinetic energy cut-off of 50 Hartree were used. During the optimization, the symmetry of the system was kept fixed to the cubic space group $P\bar{4}3n$.

Raman measurements were performed with an Ar+ laser (Innova 305 Coherent) with a wavelength of $\lambda=514 \text{ nm}$. The spectra were recorded by a T-64000 spectrometer (Instruments SA) with a spectral resolution of 1 cm^{-1} . The spectrometer was calibrated before each series of measurements by using the F_{1g} mode of Si at 520.2 cm^{-1} . IR spectra were obtained at RT by using a Biorad Excalibur FTIR instrument with a nominal resolution of 1 cm^{-1} . Thermodynamic characterization was performed by DSC (Netzsch DSC 204 HP), TG (IGA Hiden Isochema) and thermal desorption analysis (Hy-Energy, PCTPro-2000) with a constant heating rate of 5 K min^{-1} . In situ Raman measurements were carried out in the same device as given above with a pressure cell especially designed for this purpose for temperature- and pressure-dependent studies. Sample preparation was carried out in a glove box with an oxygen and water content of less than 2 ppm.

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