



Alkali metal – yttrium borohydrides: The link between coordination of small and large rare-earth



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ABSTRACT

The system Li–A–Y–BH₄ (A=K, Rb, Cs) is found to contain five new compounds and four further ones known from previous work on the homoleptic borohydrides. Crystal structures have been solved and refined from synchrotron X-ray powder diffraction, thermal stability of new compounds have been investigated and ionic conductivity measured for selected samples. Significant coordination flexibility for Y³⁺ is revealed, which allows the formation of both octahedral frameworks and tetrahedral complex anions with the tetrahydroborate anion BH₄[−] both as a linker and terminal ligand. Bi- and trimetallic cubic double-perovskites c-A₃Y(BH₄)₆ or c-A₂LiY(BH₄)₆ (A=Rb, Cs) form in all the investigated systems, with the exception of the Li–K–Y system. The compounds with the stoichiometry AY(BH₄)₄ crystallize in all investigated systems with a great variety of structure types which find their analog amongst metal oxides. *In-situ* formation of a new borohydride – closo-borane is observed during decomposition of all double perovskites.

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1. Introduction

Metal borohydrides have high gravimetric and volumetric capacities of hydrogen, and are therefore of interest for chemical hydrogen storage [1]. Recently high cation mobility was identified in some borohydrides promoting these compounds also as solid state electrolytes for battery application [2]. It was found that the paddle-wheel effect of the tetrahydroborate anion [BH₄][−] facilitates the passage of mobile species [3]. Crystal structures amongst metal borohydrides range from close packed predominantly ionic compounds [4] to 3-dimensional frameworks [5] as well as open nano-porous frameworks [6]. There exists a multitude of topologically intermediate structures, based on complex anions of the general kind [M_n^{m+}(BH₄)_p]^{(p−n^m)−} which are counterbalanced by alkali cations, [7] and most readily rationalized as salts.

Recently we reported on the first trimetallic homoleptic borohydride [8], which forms a (4,3)-connected framework not previously observed. In another recent work [9] we presented a series

of trimetallic compounds ALiM(BH₄)₄ (A=K or Rb; M=Mg or Mn) and K₃Li₂Mg₂(BH₄)₉ which represent the first two-dimensional topologies amongst homoleptic borohydrides. Our interest in trimetallic lithium containing borohydrides was motivated by a search for topologies promoting the mobility of Li⁺ cations. The general crystal chemistry relationships between metal oxides and metal borohydrides suggest that prototypical oxide ionic conductors may provide a good point of departure for such a search. As some garnet-type oxides are good ionic conductors, we have attempted the crystallization of trimetallic garnet borohydrides A₃⁺Y₂³⁺Li₃⁺(BH₄)₁₂ (A=K, Rb, Cs), with the aim of placing Li⁺ on the conducting tetrahedral site. The garnet-type was first observed amongst borohydrides as KCd(BH₄)₄ [7k]. The herein presented investigation of the systems Li–A–Y–BH₄ (A=K, Rb, Cs), has up to date not allowed to obtain garnet-type borohydrides, but a diversity of compounds revealing new structural features and connectivities associated with the Y³⁺ metal center. The dominant stable phase for A=Rb, Cs is described as a double-perovskite, the main phase for A=K is still unknown. A large number of other new compounds is observed as a function of nominal sample composition and annealing temperature, and not all of them are fully structurally characterized due to the complications posed by sample nature and phase equilibria. Our work relates to the previous investigations by Jaroń et al. [10], who previously

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investigated these systems on samples obtained from chlorine-based syntheses. The samples investigated herein however contain no halide-impurities, resulting in the discovery of five further novel compounds. The difference between chlorine-free and chlorine containing samples is discussed.

The paper is organized in the following way. First, we analyse samples obtained from different mechano-chemical syntheses, Li-A-Y-BH_4 ($A=\text{K, Rb, Cs}$), with compositions formally presenting the different discovered compounds. In this context the chemical reactions that take place during heating are established. We then continue with the discussion of solved crystal structures. In the third part the different 4- and 6-fold coordination environments of Y are discussed.

2. Material and methods

2.1. Synthesis

LiBH_4 (> 95%), KBH_4 (95%) and YCl_3 (> 99.99%) were purchased from Sigma-Aldrich. RbBH_4 and CsBH_4 were prepared from MOH ($M=\text{Rb, Cs}$) and NaBH_4 [11]. $\text{Y}(\text{BH}_4)_3$ was prepared according to Ref. [12]. The reactants were mixed in different ratios as given in Table 1, and milled at 600 rpm in a Fritsch Pulverisette 7 premium line planetary ball mill in a two-step milling process with intervals of 2 min followed by a break of 2 min, 60 repetitions. The powder-to-ball mass ratio was 1:50. All sample handling was done in a glovebox under argon atmosphere.

2.2. Synchrotron radiation X-ray powder diffraction (SR-XPD)

The data used for crystal structure solution and refinements in this study were collected between RT and 773 K at three different sources. At the Swiss–Norwegian Beamlines of ESRF (European Synchrotron Radiation Facility, Grenoble, France) data was measured on a Dectris Pilatus M2 detector at a wavelength of 0.82727(1) and 0.82307(1) Å. The temperature was controlled with the Oxford Cryostream 700+ or hot air blower and the 2-dimensional images were integrated and treated with FIT2D [13]. At the Materials Science Beamline of the Swiss Light Source of PSI (Villigen, Switzerland) high-resolution data were obtained on a curved MYTHEN-II silicon strip detector at a wavelength of 0.82711(1), 0.81811(1) and 0.77505(1) Å and the temperature was controlled with the STOE high-temperature attachment or with the Oxford Cryostream 700+ or hot air blower. At beamline I11 of the Diamond synchrotron source (Didcot, UK) high-resolution data were

obtained on a curved MYTHEN-II silicon strip detector at a wavelength of 0.82712(1) Å and the temperature was controlled with the Oxford Cryostream 700+ or hot air blower. For all measurements the samples were loaded into borosilicate capillaries of diameter 0.5 mm, which were spun during data acquisition. The wavelength was calibrated using the external NIST SRM660b LaB_6 standard.

The data from the SLS and Diamond have higher resolution in reciprocal space, and narrower profile of the diffraction peaks, and were therefore preferred for indexing. On the other hand, data from the 2-dimensional detector at the SNBL benefit from better powder averaging leading to less sensitivity to the grainy state of powder samples, that can be induced by reactions or liquid–solid transitions.

2.3. Differential scanning calorimetry (DSC)/thermogravimetry (TG)

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were carried out on a Netzsch STA449 F3 Jupiter from RT to 673 K at a ramping rate of 5 K/min using Al_2O_3 crucibles with lid as sample holder. The measurements were conducted under Nitrogen protective gas with a flow rate of 20 ml/min. Approximately 10 mg of sample was used for each run.

2.4. FTIR

Temperature dependent Fourier transform infrared spectroscopy (FTIR) was performed on solid samples using a Biorad Excalibur Instrument equipped with a Specac Golden Gate heatable ATR set-up. The spectral resolution was set to 2 cm^{-1} .

2.5. Impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was performed using a HP4192A LF impedance analyzer (frequency range 10 Hz–13 MHz, applied voltage 100 mV). The powder was pressed into a pellet (diameter 10 mm, thickness 0.8 mm) and sandwiched between two gold discs as electrodes inside a Novocontrol sample cell BDS 1200.

3. Theory/calculation

3.1. Crystal structure solution

Indexing the powder patterns of individual phases is possible thanks to “decomposition-aided indexing” by means of temperature-ramps [14], *i.e.* separating the peaks of individual phases by correlating them to their temperature-dependent vanishing from the diffraction pattern. After assigning peaks this way indexing of each novel phase was tempted on the basis of 10–15 peaks with the dichotomy routine implemented in Fox [15]. The correct indexing was selected not only according to the highest figure-of merit as implemented in each indexing program, but also according to systematic extinctions, obtained by a careful visual inspection of powder patterns, which should be crystallographic, *i.e.* corresponding to crystallographic space groups. Structure solution was always attempted in the highest symmetry space group compatible with the extinction symbol. In the case of *o*- $\text{KY}(\text{BH}_4)_4$, *o*- $\text{RbY}(\text{BH}_4)_4$, *t*- $\text{CsY}(\text{BH}_4)_4$ and the double perovskites their structural relation to the known borohydride structures or halide prototype was recognized at this moment. The structures were modeled with Y, Li and K, Rb, Cs, as free atoms and BH_4 groups as rigid bodies with fixed B–H distances (1.13 Å), and solved in direct space using Fox. The stoichiometric composition of the unknown phases was found by using an excess of the heavier Y and K, Rb, Cs, atoms, which were rapidly localized, excess atoms being merged by the dynamic occupancy

Table 1
Samples prepared by ball milling different molar ratios Li:A:Y , ($A=\text{K, Rb, Cs}$).

Sample name	Nominal composition
LiKY_332	$3\text{LiBH}_4 + 3\text{KBH}_4 + 2\text{Y}(\text{BH}_4)_3$
LiKY_333	$3\text{LiBH}_4 + 3\text{KBH}_4 + 3\text{Y}(\text{BH}_4)_3$
LiKY_343	$3\text{LiBH}_4 + 4\text{KBH}_4 + 3\text{Y}(\text{BH}_4)_3$
LiKY_431c	$1.5\text{LiBH}_4 + 3\text{KBH}_4 + 1$ $(\text{YCl}_3 + 3\text{LiBH}_4)$
LiKY_632c	$3\text{LiBH}_4 + 3\text{KBH}_4 + 2$ $(\text{YCl}_3 + 3\text{LiBH}_4)$
RbY_32	$3\text{RbBH}_4 + 2\text{Y}(\text{BH}_4)_3$
LiRbY_332	$3\text{LiBH}_4 + 3\text{RbBH}_4 + 2\text{Y}(\text{BH}_4)_3$
LiRbY_121	$1\text{LiBH}_4 + 2\text{RbBH}_4 + 1\text{Y}(\text{BH}_4)_3$
LiRbY_541	$5\text{LiBH}_4 + 4\text{RbBH}_4 + 1\text{Y}(\text{BH}_4)_3$
CsY_11	$1\text{CsBH}_4 + 1\text{Y}(\text{BH}_4)_3$
CsY_32	$3\text{CsBH}_4 + 2\text{Y}(\text{BH}_4)_3$
LiCsY_332	$3\text{LiBH}_4 + 3\text{CsBH}_4 + 2\text{Y}(\text{BH}_4)_3$
LiCsY_121	$1\text{LiBH}_4 + 2\text{CsBH}_4 + 1\text{Y}(\text{BH}_4)_3$

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