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# Experimental observation of polymerization from $\text{BH}_4^-$ to $\text{B}_{12}\text{H}_{12}^{2-}$ in mixed-anion $\text{A}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$ ( $\text{A} = \text{Rb}^+, \text{Cs}^+$ )

P. Schouwink<sup>a</sup>, Y. Sadikin<sup>a</sup>, W. van Beek<sup>b</sup>, R. Černý<sup>a,\*</sup>

<sup>a</sup> Department of Quantum Matter Physics, Laboratory of Crystallography, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva, Switzerland

<sup>b</sup> Swiss – Norwegian Beamlines, ESRF, BP 220, Grenoble 38043, France

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## ABSTRACT

It has often been suggested that reversible hydrogen storage is hampered by the formation of higher boranes  $M_pB_nH_m$  ( $M =$  alkaline or earth alkaline metal), acting as a boron sink in the solid state during decomposition processes of the borohydride. The thermodynamic stability of these materials poses high barriers for rehydrogenation. Though assumed to be key component in storage system optimization, the ultimate proof, being the crystal structure, has never been determined on a higher borane *in-situ* during thermal decomposition. We herein present a case study on a double-perovskite, significantly substantiating such assumptions and providing thorough experimental evidence based on synchrotron X-ray diffraction. It is shown on the basis of thermogravimetric measurements (TGA), *in-situ* mass spectroscopy and *ex-situ* nuclear magnetic resonance (NMR) spectroscopy that the double perovskites  $\text{Cs}_3\text{Y}(\text{BH}_4)_6$  and  $\text{Cs}_2\text{LiY}(\text{BH}_4)_6$  release 2.9 mol  $\text{H}_2$  during polymerization to the inverse perovskite,  $\text{Cs}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$ , containing both *closo* and *borohydride* anions. Novel phases are solved *ab-initio* and *in-situ* Raman and mass spectroscopy are employed to follow the polymerization reaction.

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## Introduction

In order to make one of the greener energy vectors available to society, the storage of hydrogen in the solid state, progress is needed to overcome practical and safety issues specified by the automobile transportation industry, which are currently not met by compressed gas tanks nor the impractically heavy intermetallic hydrides. The light-metal complex hydrides have experienced an uprisal in the research community

during the first years of the millenium, owed to their extreme hydrogen densities and low unit mass. One of the remaining unsolved challenges concerns the cycling of the respective borohydride-based materials, i.e. the rehydrogenation of the “used” product. Suffering from slow kinetics and unfavourable thermodynamics, a key issue is thought to lie in formation of higher boranes acting as boron sinks in the hydrogen sorption loop, as for instance suggested for the main contenders  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{LiBH}_4$  and  $\text{Mg}(\text{BH}_4)_2$  [1–5]. The presence of  $\text{MgB}_{12}\text{H}_{12}$  in the desorption process of  $\text{Mg}(\text{BH}_4)_2$  does

\* Corresponding author. Tel.: +41 223796450; fax: +41 223796108.

E-mail address: [radovan.cerny@unige.ch](mailto:radovan.cerny@unige.ch) (R. Černý).

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however remain a matter of debate [6]. Decomposition intermediates based on higher boranes such as  $B_{10}H_{10}^{-2}$ ,  $B_{12}H_{12}^{-2}$  or  $B_xH_y^{-2}$  have been reported by numerous groups, their direct characterization during desorption processes however being restricted to spectroscopic (Infrared, Raman, NMR) and thermogravimetric datasets, albeit their crystal structures are known. The appearance of “broad lumps” in the diffraction pattern has often been attributed to these higher boranes. However, the pending proof by means of X-ray investigations on the crystal structure has hitherto not been provided due to the bad crystallinity of the phases corresponding to such lumps. Recently, we reported on a series of complex hydride perovskites based on the tetrahydroborate anion,  $BH_4^-$  [7]. Therein, a compound  $A_3BH_4B_{12}H_{12}$  ( $A = Rb, Cs$ ) was mentioned, observed during decomposition of the double-perovskites  $A_3Y(BH_4)_6$  and  $A_2LiY(BH_4)_6$  [7,8]. In the following we present a detailed structural investigation of a mixed-anion borohydride-closoborane forming *in-situ* during decomposition of the poly-metal borohydrides  $Cs_2LiY(BH_4)_6$  and  $Cs_3Y(BH_4)_6$ . We thus provide the pending crystallographic evidence for the widely accepted scheme implying higher boranes as decomposition intermediates. At the same time the missing link between metal borohydrides and metal closoboranes is presented with the first members of a new family of anion-mixed materials, containing both the tetrahydroborate  $BH_4^-$  and the dodecahydroborate  $B_{12}H_{12}^{2-}$  anions in the same crystal structure.

## Experimental part

### Sample preparation

$RbBH_4$  and  $CsBH_4$  were prepared from MOH ( $M = Rb, Cs$ ) and  $NaBH_4$  [9].  $LiBH_4$  (>95%) was purchased from Sigma–Aldrich and  $Y(BH_4)_3$  was prepared according to [10]. The reactants were mixed in nominal compositions to provide the double-cation and triple-cation perovskites  $Cs_3Y(BH_4)_6$  and  $Cs_2LiY(BH_4)_6$ , and milled at 600 rpm in a Fritsch Pulverisette 7 premium line planetary ball mill in a two-step milling process of 60 repetitions where milling intervals of 2 min are followed by breaks of 2 min to avoid overheating of the sample in the grinding bowl. The powder-to-ball mass ratio was approximately 1:50. All sample handling was done in a glovebox under argon atmosphere.

### Synchrotron X-ray powder diffraction

The data used for crystal structure solution and refinements in this study were collected between room temperature (RT) and 673 K. At the Swiss-Norwegian Beamlines of ESRF (European Synchrotron Radiation Facility, Grenoble, France) a Dectris Pilatus M2 detector was used for data acquisition at a wavelength of 0.8272 and 0.8230 Å. The temperature was controlled with a hot air blower and the 2-dimensional images were integrated and treated with FIT2D [11]. High resolution data used for phase indexing were obtained at the Materials Science Beamline of the Swiss Light Source of PSI (Villigen, Switzerland) on a curved MYTHEN-II silicon strip detector at a wavelength of 0.8271 Å, temperature control was achieved

with the STOE high-temperature attachment, the Oxford Cryostream 700+ or hot air blower. Crystal structures were solved *ab-initio* using the software FOX [12] and refined with the Rietveld method using TOPAS [13].

### In-situ mass spectroscopy

The evolution of  $H_2$  and  $B_2H_6$  was monitored *in-situ* at the Swiss-Norwegian Beamlines using a Pfeiffer-GSD301 100 spectrometer while taking diffraction data. The evolution of the released gases was hence directly matched to the temperature and phase evolution. The sample was enclosed in a glass tube and the gas flow (Ar) was controlled by a Bronkhorst Mass Flow Controller.

### Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetry (TGA) were performed with a Netzsch STA449 F3 Jupiter apparatus under nitrogen flow using alumina crucibles. Calibration runs were done prior to experiment on empty crucibles.

### Vibrational spectroscopy

Raman spectroscopy was performed *in-situ* with a Renishaw InVia confocal microscope using a green laser (514 nm). Infrared spectra were collected with a Biorad Excalibur instrument equipped with a Specac Golden Gate heatable ATR setup, providing a spectral resolution of  $2\text{ cm}^{-1}$ .

### NMR spectroscopy

$^{11}B$  NMR was performed at 298 K on selected samples which were thermally treated under Ar-atmosphere in high pressure autoclaves and quenched to room temperature. 5 mg of powder were dissolved in 600 ml of DMSO- $d_6$ . Proton-decoupled spectra collected on a Bruker AVANCE III HD-NanoBay 400 MHz spectrometer, equipped with a 5 mm CryoProbe Prodigy (CPPBBO BB-1H/19F/D) and measured at a frequency of 128.38 MHz are shown in the [Supplementary Information \(Fig. S4\)](#).

## Results and discussion

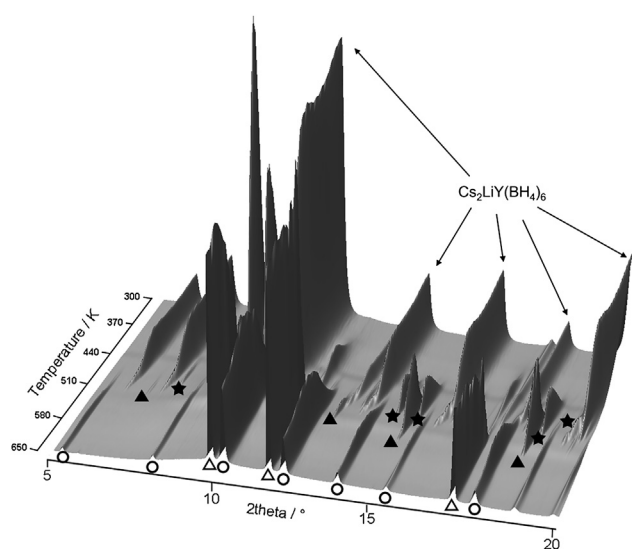
### Phase analysis and crystal structures

The phase diagram of both bi- and trimetallic compositions is dominated by the stability of the perovskite structure, occurring in different polymorphs. To exemplify this we will discuss it on the basis of the samples of composition  $CsBH_4 : Y(BH_4)_3$  3:2 ( $CsY_{32}$ ) and  $CsBH_4 : LiBH_4 : Y(BH_4)_3$  2:1:1 ( $CsLiY_{211}$ ). These samples were selected from the mixtures studied in [8], presently allowing for a more detailed view thanks to higher quality and more extensive data collections. Though we consider  $Cs_3Y(BH_4)_6$  as a model compound due to its chemical simplicity, throughout this report we will primarily focus on the characterization of  $Cs_2LiY(BH_4)_6$ , owed to the superior crystallinity of the prepared samples and hence higher quality

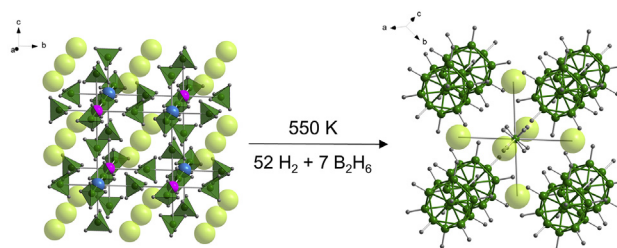
diffraction data. The *in-situ* synchrotron X-ray powder diffraction data are shown as a function of temperature in Fig. 1 for the trimetallic mixture CsLiY\_211, which results in a pure phase sample of the chemically ordered double-perovskite Cs<sub>2</sub>LiY(BH<sub>4</sub>)<sub>6</sub>, crystallizing in space group F23 with an ordered distribution of Y and Li atoms on Wyckoff sites 4d and 4c. In the bimetallic mixture CsY\_32 and various other samples xCsBH<sub>4</sub>:yY(BH<sub>4</sub>)<sub>3</sub> the main phase is still a double-perovskite, which however contains significant amount of chemical disorder on the B-site (B = octahedral site of perovskite, not boron), which is occupied by Cs and Y atoms in this case. The compound Cs<sub>2</sub>LiY(BH<sub>4</sub>)<sub>6</sub> formed during milling is marked by arrows in Fig. 1.

Assessing new *in-situ* diffraction data the appearance of two sets of peaks at 420 K and 440 K is observed. The first is explained as crystallization of unreacted ball milled CsBH<sub>4</sub> (open triangles in Fig. 1), while the second is related to its reaction with unreacted (amorphous) Y(BH<sub>4</sub>)<sub>3</sub>, producing Cs<sub>3</sub>Y(BH<sub>4</sub>)<sub>6</sub>. Both events are visible as weak endothermic signals in Fig. 3. The unit cell metric marked by stars in Fig. 1 was attributed to a superstructure of Cs<sub>3</sub>Y(BH<sub>4</sub>)<sub>6</sub> in [8], crystallizing in a subgroup. The supergroup, lower in unit cell volume and marked with triangles in Fig. 1, is recovered during a phase transition visible as an endothermic signal at 480 K in Fig. 3, which was wrongly interpreted in [8] as melting of Cs<sub>2</sub>LiY(BH<sub>4</sub>)<sub>6</sub>. The present diffraction data show a positive unit-cell volume shift of Cs<sub>2</sub>LiY(BH<sub>4</sub>)<sub>6</sub> around 470 K, which we interpret as a Li-exsolution occurring in discrete steps (visible e.g. around 19 2theta in Fig. 1), where Li is replaced by Cs stemming from the unreacted CsBH<sub>4</sub>.

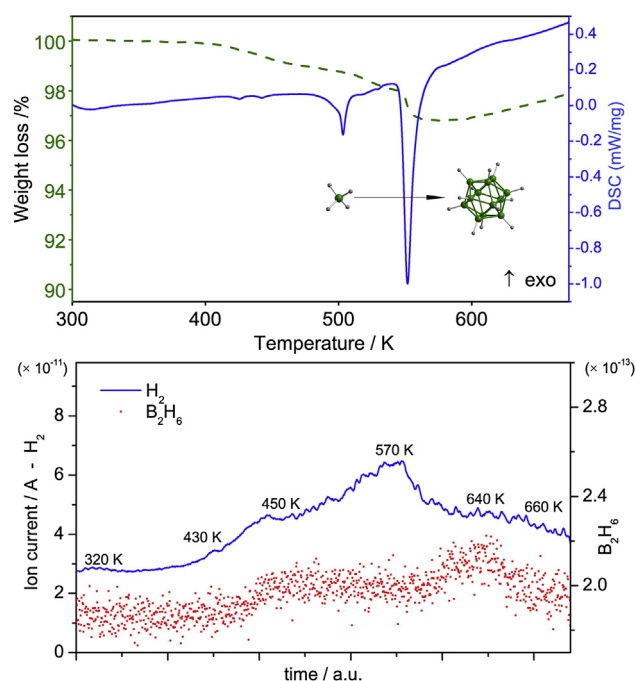
The main subject of this article, the decomposition of double perovskite-type Cs<sub>3</sub>Y(BH<sub>4</sub>)<sub>6</sub> and Cs<sub>2</sub>LiY(BH<sub>4</sub>)<sub>6</sub> to anti-perovskite-type Cs<sub>3</sub>BH<sub>4</sub>B<sub>12</sub>H<sub>12</sub> (open circles in Fig. 1, crystal structures in Fig. 2), is complicated by the concurrent decomposition of Cs<sub>3</sub>Y(BH<sub>4</sub>)<sub>6</sub>, and only the global



**Fig. 1 – In-situ powder diffraction data for the sample of composition CsBH<sub>4</sub>:Y(BH<sub>4</sub>)<sub>3</sub>:LiBH<sub>4</sub> 2:1:1. The phases labelled are: Superstructure of Cs<sub>3</sub>Y(BH<sub>4</sub>)<sub>6</sub> (stars), Cs<sub>3</sub>Y(BH<sub>4</sub>)<sub>6</sub> F23 (filled triangles), Cs<sub>3</sub>BH<sub>4</sub>B<sub>12</sub>H<sub>12</sub> (open circles), CsBH<sub>4</sub> (open triangles).**

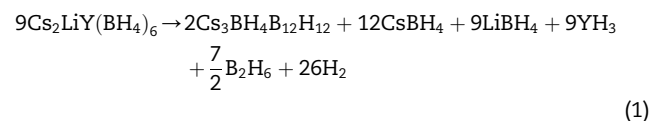


**Fig. 2 – Transformation of borohydride to closoborane borohydride showing the crystal structures of Cs<sub>2</sub>LiY(BH<sub>4</sub>)<sub>6</sub> (left) and Cs<sub>3</sub>BH<sub>4</sub>B<sub>12</sub>H<sub>12</sub> (right).**



**Fig. 3 – Top: Thermal analysis for the sample CsLiY 211, weight loss in green, heat flow in blue. Bottom: In-situ mass spectrometry showing the signals for gas releases of H<sub>2</sub> (continuous line) and B<sub>2</sub>H<sub>6</sub> (dotted line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)**

decomposition to the nominal composition of the sample can be rationalized with reaction 1. It has its onset at 480 K and peaks at 550 K, accompanied by the second crystallization of CsBH<sub>4</sub> (open triangles in Fig. 1) according to.



The refined phase composition at 658 K yields 14 %mol Cs<sub>3</sub>BH<sub>4</sub>B<sub>12</sub>H<sub>12</sub> and 86 %mol CsBH<sub>4</sub>, in good agreement with eq. (1). The decomposition of Cs<sub>3</sub>BH<sub>4</sub>B<sub>12</sub>H<sub>12</sub> was also recorded with *in-situ* diffraction and shows the formation of Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub> at approximately 650 K (Supplementary Fig. S1), further corroborating the correctness of reaction 1. The formation of

the closoborane anion  $[B_{12}H_{12}]^{2-}$  from the tetrahydroborate anion has previously been described as proceeding via a series of intermediate borane anions of the type  $[B_xH_y]^{n-}$ , for instance in  $Mg(BH_4)_2$  [14]. Such a sequence is presently also suggested. Though not observed from crystalline phases, a continuous mass loss (Fig. 3) pointed out below and the decreasing intensity of diffraction peaks could be a signature of such a stepwise polymerization.

We performed NMR spectroscopy at 298 K on various samples of  $Cs_2LiY(BH_4)_6$  in DMSO- $d_6$  thermally treated at different temperatures across the decomposition range. The decomposition of the borohydride to the closo-anion proceeds via the formation of  $B_3H_8^-$  species (the proton-decoupled spectra are shown in Supplementary Fig. S4). A second intermediate with a resonance at  $-20.4$  ppm is observed (Fig. S4), which has previously been assigned to a borane species with a B:H ratio of 1:1 and a similar closo structure as  $[B_{12}H_{12}]^{2-}$ , and is likely the phase  $B_9H_9^{2-}$  [6]. At temperatures above 530 K  $B_{12}H_{12}^{2-}$  is identified at a chemical shift of  $-15.2$  ppm.

While the antiperovskite resulting in the present decomposition is a cubic polymorph, the trigonal RT-polymorph [15] is formed also in related borohydride-closo-borane systems where the cubic polymorph presents the HT-phase, resulting from an R-3m to P23 transition, which takes place at approximately 580 K, and shows no hysteresis upon cooling within the precision of temperature measurements (about 1 K) (Supplementary Fig. S2).

The lack of hysteresis and very close structural relationship between both phases is indicative of anion-disorder being the driving mechanism of this transformation. We point out that the supposedly disordered cubic HT-polymorph was refined constraining the orientation of the closo molecule to its site symmetry, and provides a very satisfactory fit without modelling disorder, the Rietveld plot being available as Supplementary Fig. S3. However, the thermal displacement parameters on boron and hydrogen (constrained to each other) do refine to rather large values of 8. The borohydride anion is disordered in both polymorphs, hence the symmetry change is due exclusively to  $B_{12}H_{12}$  reorientations. Related to this, the transition into the superionic bcc phase of  $Na_2B_{12}H_{12}$  is a reported example of  $B_{12}H_{12}$ -controlled polymorphism [16]. The phase diagrams of these systems are rather complex due to structural disorder and low energy barriers between different polymorphs, and the role of metastable phases needs to be further investigated. It should however be kept in mind that we here stabilize the disordered polymorph to lower temperature by growing it during decomposition, a fact worth considering when attempting to lower the transition temperature to the conducting phase of the promising Na-conductor  $Na_2B_{12}H_{12}$ .

### Thermal analysis and mass spectrometry

Following reaction 1, one mol of  $Cs_2YLi(BH_4)_6$  (also  $Cs_3Y(BH_4)_6$ ) releases 2.9 mol  $H_2$  during polymerization to the borohydride-closoborane. To directly associate this gas release with the crystallization of the mixed-anion compound we performed *in-situ* mass spectrometry during temperature-dependent powder diffraction. The observed ion current (not quantified) is shown in Fig. 3 for the species  $H_2$  and  $B_2H_6$ . The

gas release was quantified from thermogravimetric analysis also shown in Fig. 3 (top), the molar amount of released gases corresponding to the measured weight loss of the sample. The transformation of borohydride to borohydride-closoborane corresponds to an initial mass loss with a flat slope, its onset located around 480 K, and becomes stronger at 540 K. The total observed weight loss observed at 550 K amounts to approximately 3.3 %wt, which matches the theoretical value quite well (3.7%), in order to comply with reaction 1. The minor discrepancy could be due to an additional boron-containing phase in the decomposed material. We note at this point that a mass increase is observed at temperatures above 600 K. This is very likely owed to  $N_2$ -uptake by the sample due to the reaction with the  $LiBH_4$  that is released during reaction 1. This however does not influence our conclusions, since the processes take place above 600 K, where our discussion has already ended. The integrated reaction enthalpy of  $Cs_2LiY(BH_4)_6 \rightarrow Cs_3BH_4B_{12}H_{12}$  amounts to 55(3) kJ/mol (decomposition included).

This value compares quite well, for instance, to the experimentally observed dehydrogenation of  $Mg(BH_4)_2$ , 67(7) kJ/mol (22.3 kJ/mol  $H_2$ ) [17], while the theoretical expected value is reported as 40 kJ/mol  $H_2$  [14] (dehydrogenation to the elements). According to reaction 1, the determined enthalpy per mol  $H_2$  amounts to 19 kJ/mol  $H_2$  for the decomposition of the double-perovskite. According to van't Hoff's relation, albeit a severe simplification in this case (does not account for  $B_2H_6$ , nor multiple phases taking part in the event), this experimentally obtained value would suggest dehydrogenation of the double-perovskite far below room temperature. Thus, kinetic energy barriers must be at the origin of the much higher observed temperature, again similar to  $MgB_{12}H_{12}$ . A due question arises in the present case as to why the borohydride-closoborane is so much better crystallized than any other suggested decomposition higher borane previously suggested. A likely scenario is that the thermolysis of  $Cs_2YLi(BH_4)_6$  produces diborane in a first step which then reacts with the  $BH_4^-$  anions to form successively higher borane anions. This mechanism has been reported and even applied to the synthesis of both borohydrides as well as closoboranes [18,19], and was also studied by *in-situ* powder diffraction [20]. In the case of  $Cs_2LiY(BH_4)_6$  the minimum diffusion path is very short as opposed to gas–solid reactions, statistically less than one unit cell length for a  $B_2H_6$  molecule, which results in a swift and efficient conversion sequence to the closo anion and hence in a good crystallinity. The observation of higher boranes other than  $B_{12}H_{12}^{2-}$  with NMR spectroscopy provides evidence for the  $B_2H_6$ -mediated process.

In this context it should be noted that, at the decomposition temperature of both  $Cs_2LiY(BH_4)_6$  and  $Cs_3Y(BH_4)_6$  of 540 K, the thermal stability of  $Y(BH_4)_3$  and  $B_2H_6$  has been exceeded [21]. This signifies that decomposition kinetics of the released  $Y(BH_4)_3$  fraction itself may be slightly altered to provide a more efficient/sudden release of diborane, again favouring the crystallization of the borohydride-closoborane material.

With the aim of producing a single phase sample of  $Cs_3BH_4B_{12}H_{12}$  we attempted to synthesize the compound mechano-chemically as an adduct from both the precursors  $CsBH_4$  and  $Cs_2B_{12}H_{12}$  (NMR spectra in Fig. S4). The resulting

product (R-3m) was badly crystallized and did not improve its crystallinity upon heating above the decomposition temperature of  $\text{Cs}_2\text{LiY}(\text{BH}_4)_6$ , where diffusion would be expected to be comparable in both cases. The phase transition to the P23 phase did however occur at a temperature of 580 K.

These present findings suggest that the diffusion of the borane species formed *in-situ* in the material itself by  $\text{BH}_4^-$  decomposition is favoured as compared to the diffusion of borohydride or closoborane groups, leading to an enhanced nucleation of  $\text{Cs}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$  in the double-perovskite matrix.

A question that remains to be answered is that of thermodynamic equilibrium. If the decomposition reaction forming well-crystallized  $\text{Cs}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$  proceeds under equilibrium conditions it would be plausible that the ball-milled adduct anneals upon thermal treatment at the same or higher temperature, which is not the case. We can rule out any considerable difference in formation enthalpies between both phases, which could explain the formation of the cubic phase during decomposition (prior to the trigonal–cubic transition temperature). Both polymorphs transform into each other by rotational dynamics of the closo anion (no atomic rearrangements), and the phase transition does occur in the ball-milled adduct.

We would like to note that we have investigated many mixed-metal closoborane systems (to be published elsewhere) and that the *as-milled* products are always badly crystallized or unreacted, without exception. The crystallinity usually improves greatly across chemical solid–solid or solid–vapour reactions or simply upon heat treatment above 500–600 K. This observation is equally well reflected in the broad lumps defined as decomposition products of binary alkaline-earth or alkali-borohydrides.

## Conclusion

Thermolysis of the double-perovskite type metal borohydrides  $\text{Cs}_2\text{LiY}(\text{BH}_4)_6$  and  $\text{A}_3\text{Y}(\text{BH}_4)_6$  (A = Rb, Cs) results in a gas release of 2.9 mol  $\text{H}_2$  yielding an antiperovskite type mixed-anion compound containing both  $\text{BH}_4^-$  and  $\text{B}_{12}\text{H}_{12}^{2-}$  anions. The crystal structures observed *in-situ* during temperature-dependent powder diffraction for the first time provide crystallographic evidence for the generally accepted decomposition scheme of alkaline and alkaline-earth borohydride via polymerization of the borohydride group to higher boranes.

The “out of equilibrium” decomposition of  $\text{Y}(\text{BH}_4)_3$  results in a well-crystallized borohydride-closoborane and may explain why binary metal borohydrides tend to form broad lumps in the diffraction pattern due to a sluggish formation process of the higher borane. The reported crystal structures can provide valuable input to correlate the presently experimentally observed  $\text{BH}_4^-$  polymerization with thermodynamic calculations. From a materials science point of view, it is highly interesting that the disordered borohydride-closoborane polymorph can be formed below its bulk transition temperature when produced by the decomposition of the borohydride.

While the prevalent opinion in the literature agrees on the presence of higher boranes in the thermal decomposition/polymerization of metal borohydrides the stability of the

precursor  $[\text{BH}_4]^-$  next to the product  $[\text{B}_{12}\text{H}_{12}]^{2-}$  has never been discussed in this context. Mixed-anion compounds based on these two molecules present a new group of materials prone to exhibit specific features of both compound families and with the potential of raising new questions regarding the thermodynamic stability of the borohydride anion, in particular its presence side by side with the polymerized product.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2015.06.022>.

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