Electronic Supplementary Information

M[Y(BH$_4$)$_4$] and M$_2$Li[Y(BH$_4$)$_5$Cl] (M=Rb, Cs): New Borohydride Derivatives of Yttrium and Their Hydrogen Storage Properties

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Table S1. Description of the samples and the results of quantitative phase analysis. Dominating yttrium-containing products are bolded. + - “present”; —— - “absent”. M = Rb: x = 2.28; M = Cs: x = 1.8 (refined for samples Rb A165 and Cs B175, respectively).

Sample	**Rb 0**	**Rb A**	**Rb A165**	**Rb A175**	**Rb A180**	**Rb A185**	**Rb A190**	**Rb A225**	**Rb A300**
Method of preparation	$RbCl + LiBH_4$ milled 60 min. + $Y(BH_4)_3$ & 3LiCl milled 20 min.	$RbBH_4 + Y(BH_4)_3$ & 3LiCl milled 60 min.	**Rb A** heated to 165 °C and rapidly cooled to RT	**Rb A** heated to 175 °C and rapidly cooled to RT	**Rb A** heated to 180 °C and rapidly cooled to RT	**Rb A** heated to 185 °C and rapidly cooled to RT	**Rb A** heated to 190 °C and rapidly cooled to RT	**Rb A** heated to 225 °C and rapidly cooled to RT	**Rb A** heated to 300 °C and rapidly cooled to RT
Phase analysis (normalised to 3 mol of Cl) [molar fractions]									
$Rb[Y(BH_4)_4]$	**0.66**	**0.90**	**0.67**	**+**	**+**	**——**	——	——	——
$Rb_2Li[Y(BH_4)_{6-x}Cl_x]$	——	——	0.078	**+**	**+**	**+**	**+**	**+**	——
$Y(BH_4)_3$	0.03	——	——	——	——	——	——	——	——
LiCl	3.00	3.00	2.82	+	+	+	+	+	+
Remarks	——	very weak diffraction peaks from unidentified phase(s)	——	diffraction peaks from unidentified phase(s)	diffraction peaks from unidentified phase(s)	very **strong** diffraction peaks from unidentified phases	very **strong** diffraction peaks from unidentified phase(s)	diffraction peaks from unidentified phase(s) slightly extinct	diffraction peaks from **$RbBH_4$**, **$Rb(BH_4)_{1-x}Cl_x$**; weak diffraction peaks from unidentified phase(s)

Sample	**Cs 0**	**Cs A**	**Cs A130**	**Cs A215**	**Cs A300**	**Cs B**	**Cs B175**
Method of preparation	$CsCl + LiBH_4$ milled 60 min. + $Y(BH_4)_3$ & 3LiCl milled 30 min.	$CsBH_4 + Y(BH_4)_3$ & 3LiCl milled 60 min.	**Cs A** heated to 130 °C and rapidly cooled to RT	**Cs A** heated to 215 °C and rapidly cooled to RT	**Cs A** heated to 300 °C and rapidly cooled to RT	$2CsBH_4 + Y(BH_4)_3$ & 3LiCl milled 30 min.	**Cs B** heated to 175 °C and rapidly cooled to RT
Phase analysis (normalised to 3 mol of Cl) [molar fractions]							
$Cs[Y(BH_4)_4]$	**+**	**0.36**	**0.82**	**0.50**	——	——	——
$Cs_2Li[Y(BH_4)_{6-x}Cl_x]$	**+**	**0.26**	0.057	**0.21**	——	**+**	**0.82**
$Y(BH_4)_3$	+	**0.16**	——	——	——	——	——
LiCl	+	2.54	2.90	2.63	+	+	1.53
Remarks	——	——	——	——	diffraction peaks from **$CsBH_4$**; weak diffraction peaks from unidentified phase(s)	poorly crystalline sample	improved crystallinity in respect to **Cs B**; very weak diffraction peaks from unidentified phase(s)

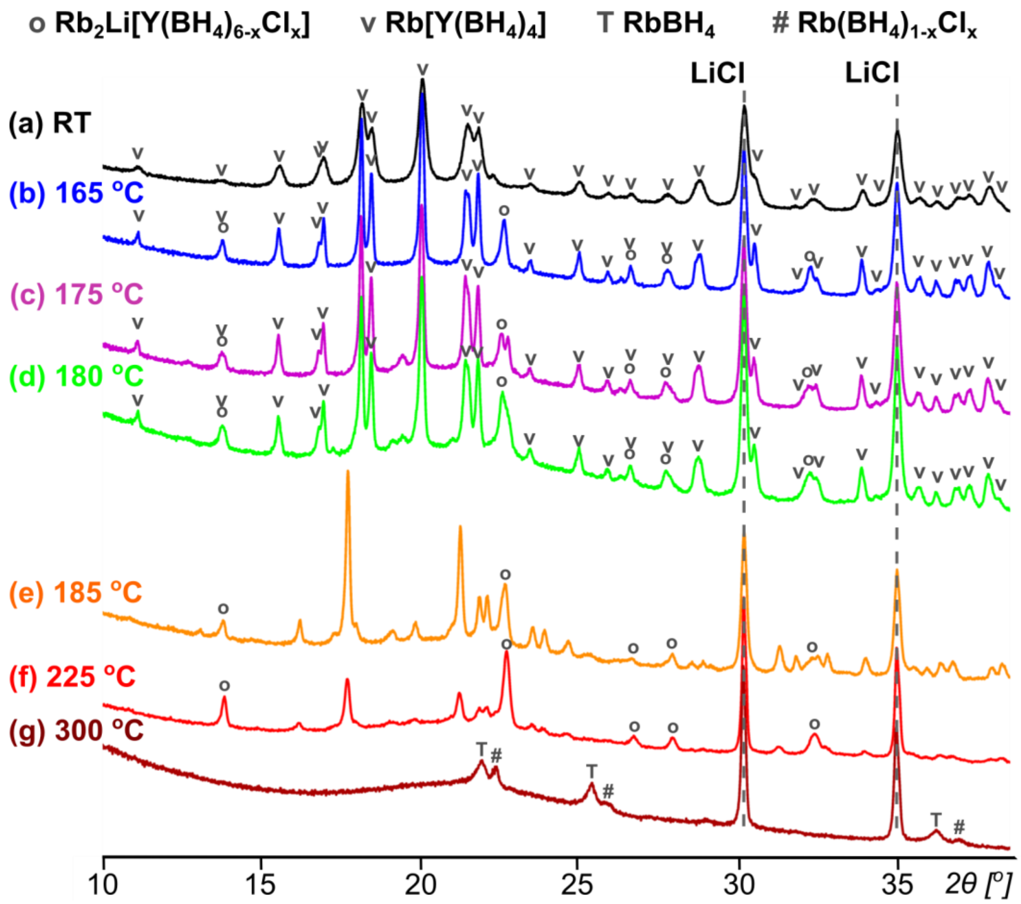

*Figure S1. PXD patterns of the sample **Rb A** heated to specified temperatures and quickly cooled to RT.*

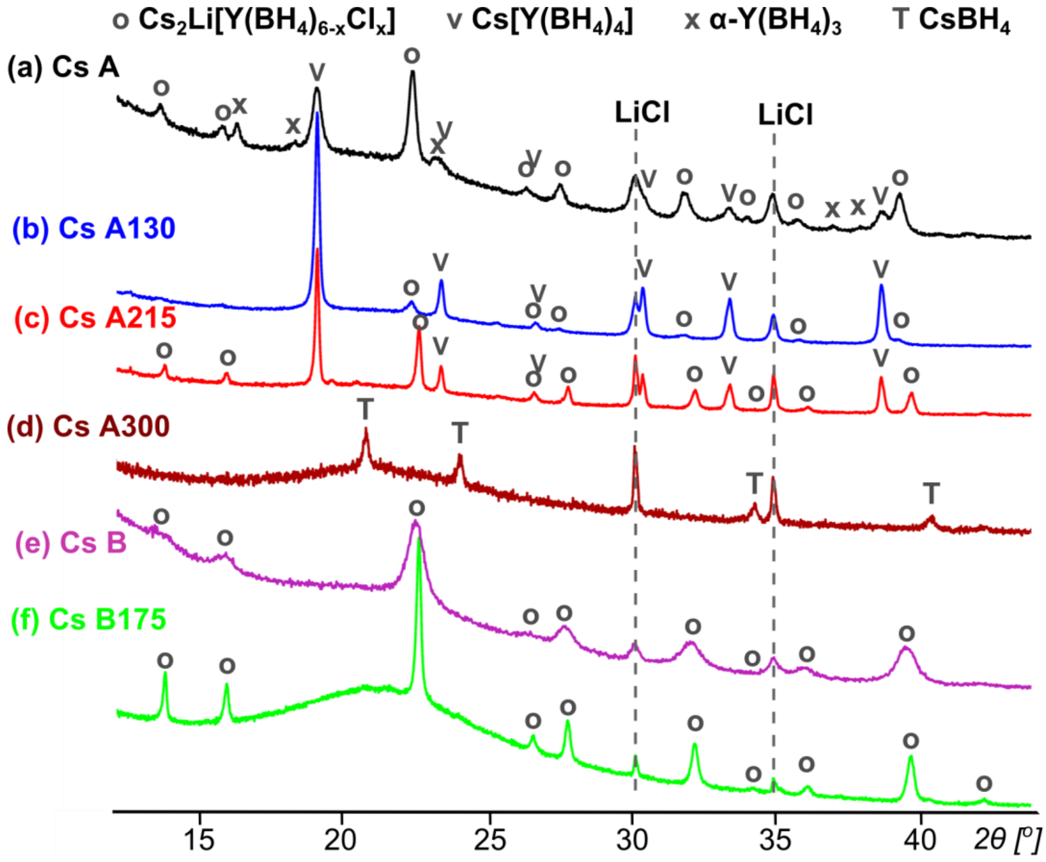

Figure S2. PXD patterns of the samples of caesium compounds heated to specified temperatures and quickly cooled to RT.

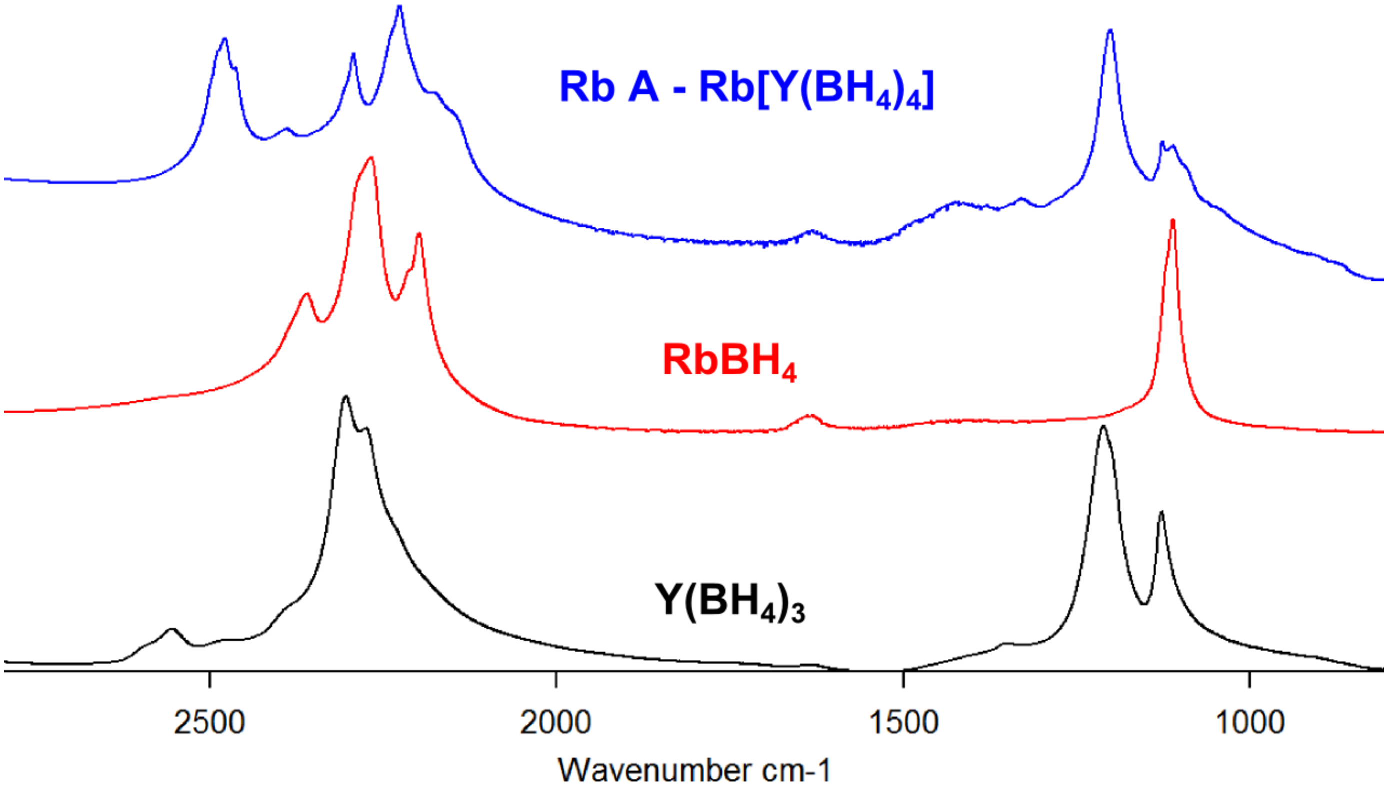

*Figure S3. The FTIR spectra of Rb[Y(BH$_4$)$_4$], sample **Rb A**, and the reactants, RbBH$_4$ and Y(BH$_4$)$_3$.*

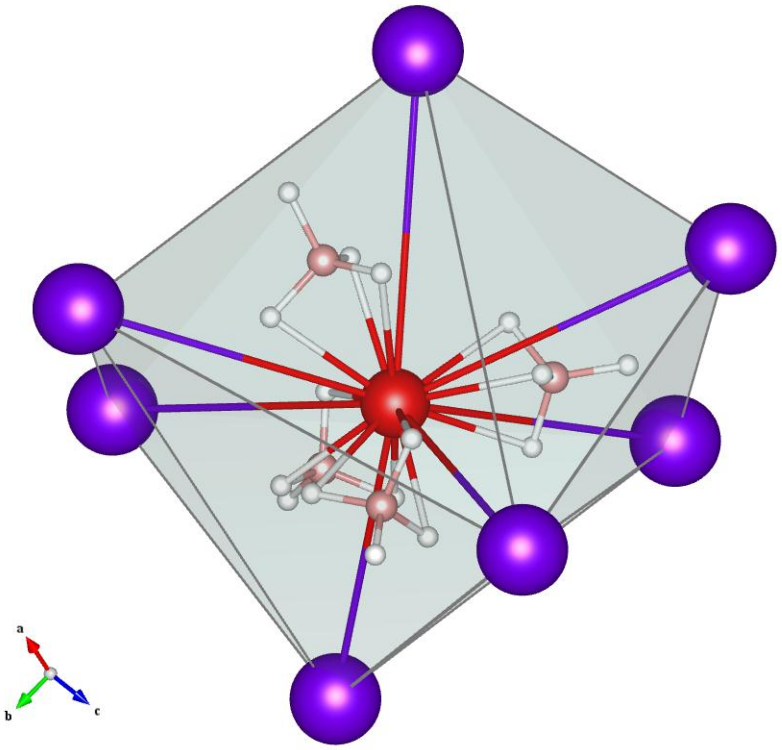

Figure S4. Coordination of [Y(BH$_4$)$_4$]$^-$ anion by Rb$^+$ cations in Rb[Y(BH$_4$)$_4$].

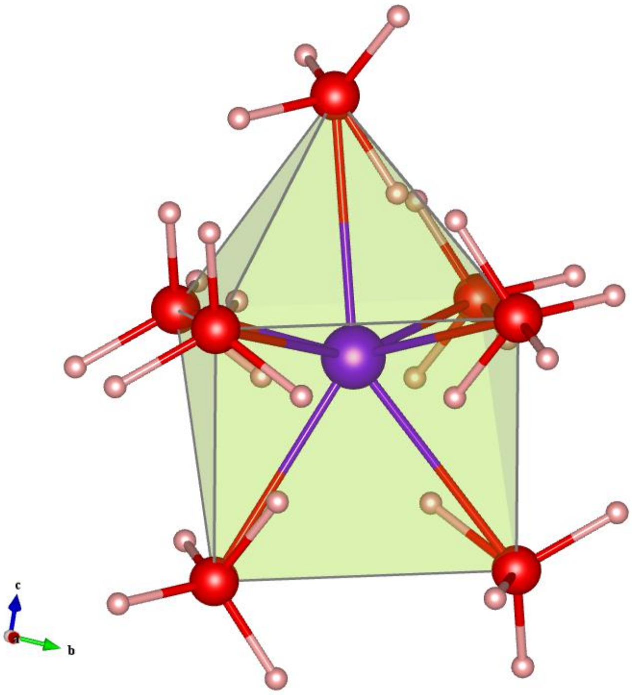

Figure S5. Coordination of Rb^+ *by* $[Y(BH_4)_4]^-$ *anions in* $Rb[Y(BH_4)_4]$.

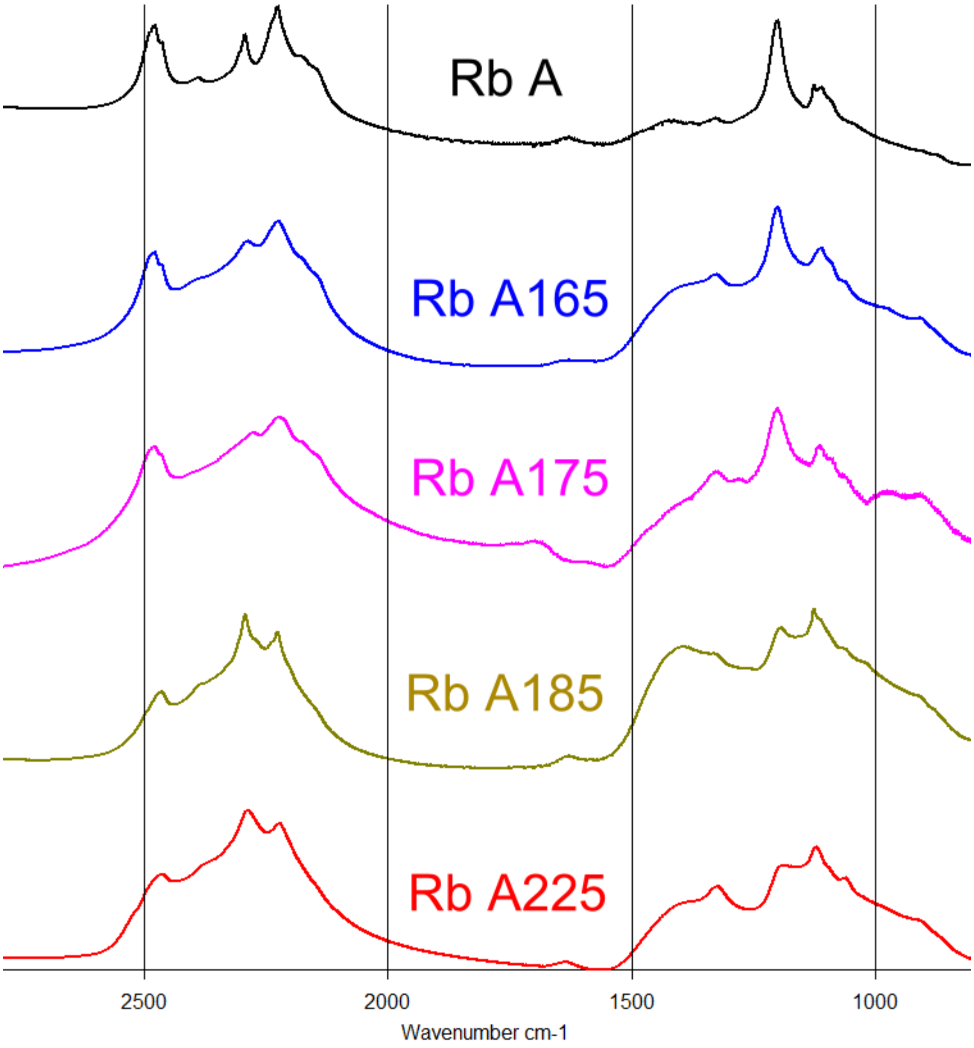

Figure S6. The FTIR spectra of the solid decomposition products of $Rb[Y(BH_4)_4]$.

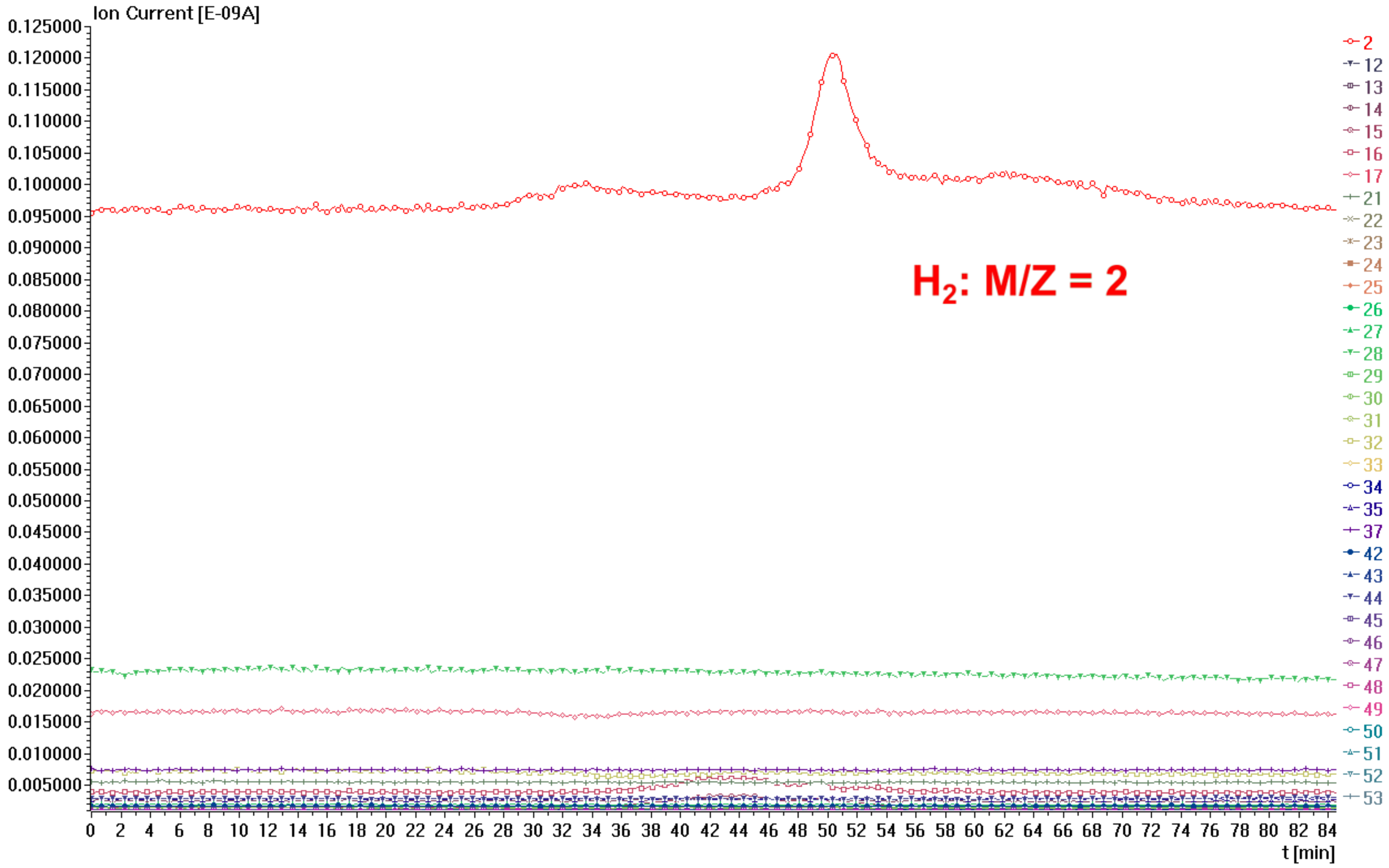

Figure S7. Time-resolved mass spectra of gaseous decomposition products of the sample ***Rb A****. Note the absence of meaningful amount of volatile boron hydrides. Heating rate: 5 K min^{-1}.*

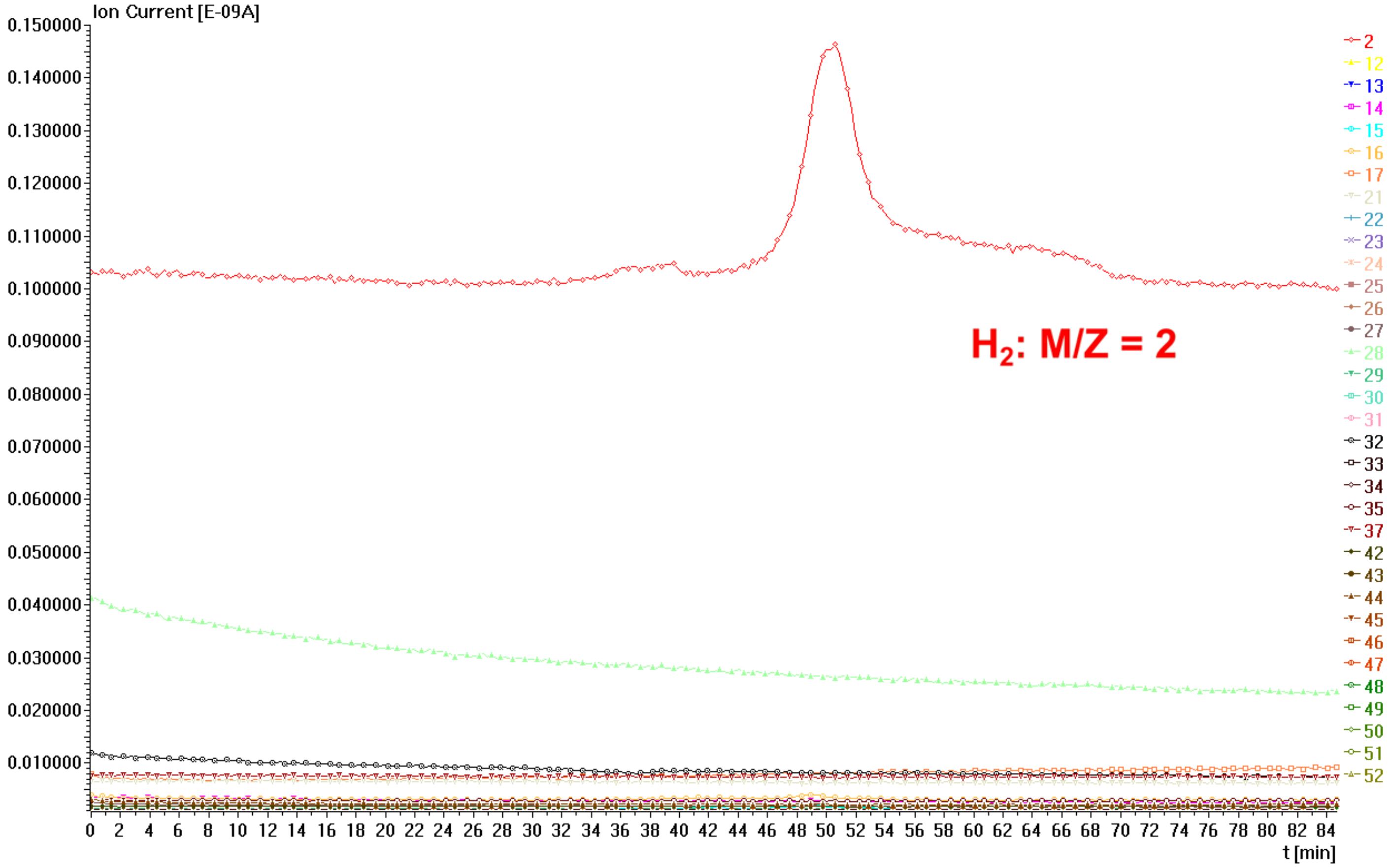

Figure S8. Time-resolved mass spectra of gaseous decomposition products of the sample ***Cs A****. Note the absence of meaningful amount of volatile boron hydrides. Heating rate: 5 K min^{-1}.*

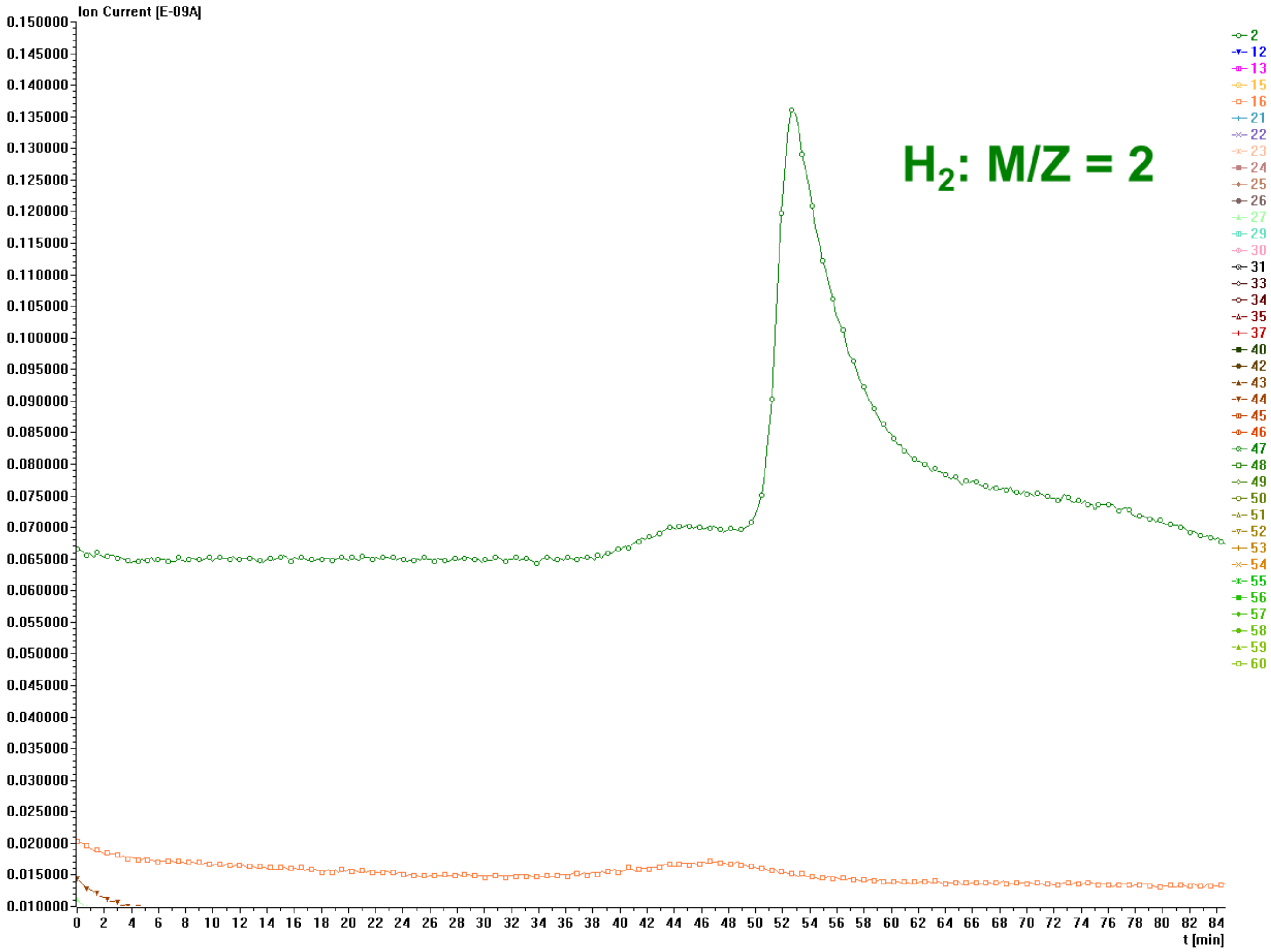

*Figure S9. Time-resolved mass spectra of gaseous decomposition products of the sample **Cs B**. Note the absence of meaningful amount of volatile boron hydrides. Heating rate: 5 K min^{-1}.*

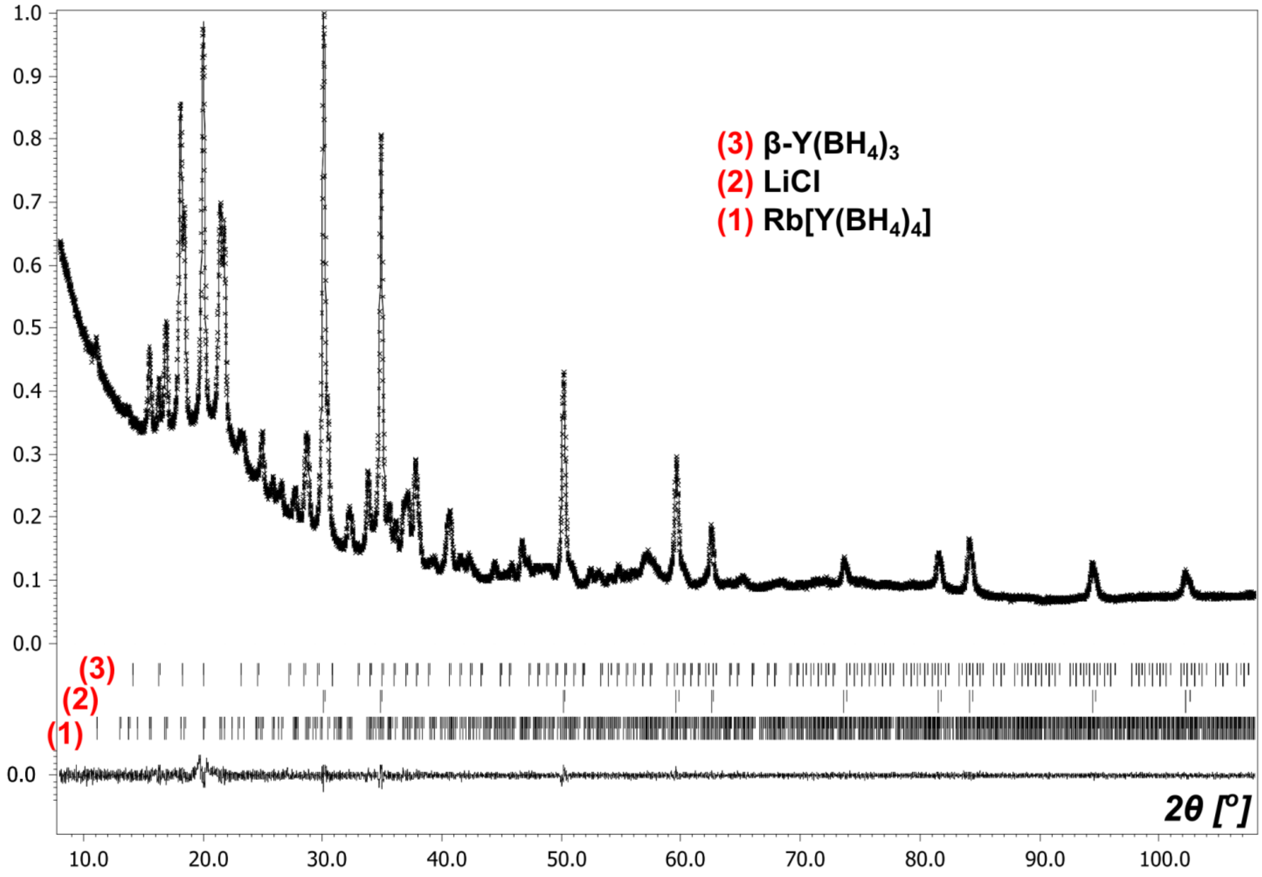

Figure S10. Rietveld plot of the sample ***Rb 0****. The Bragg reflections of the three crystalline phases present in the sample have been marked.*

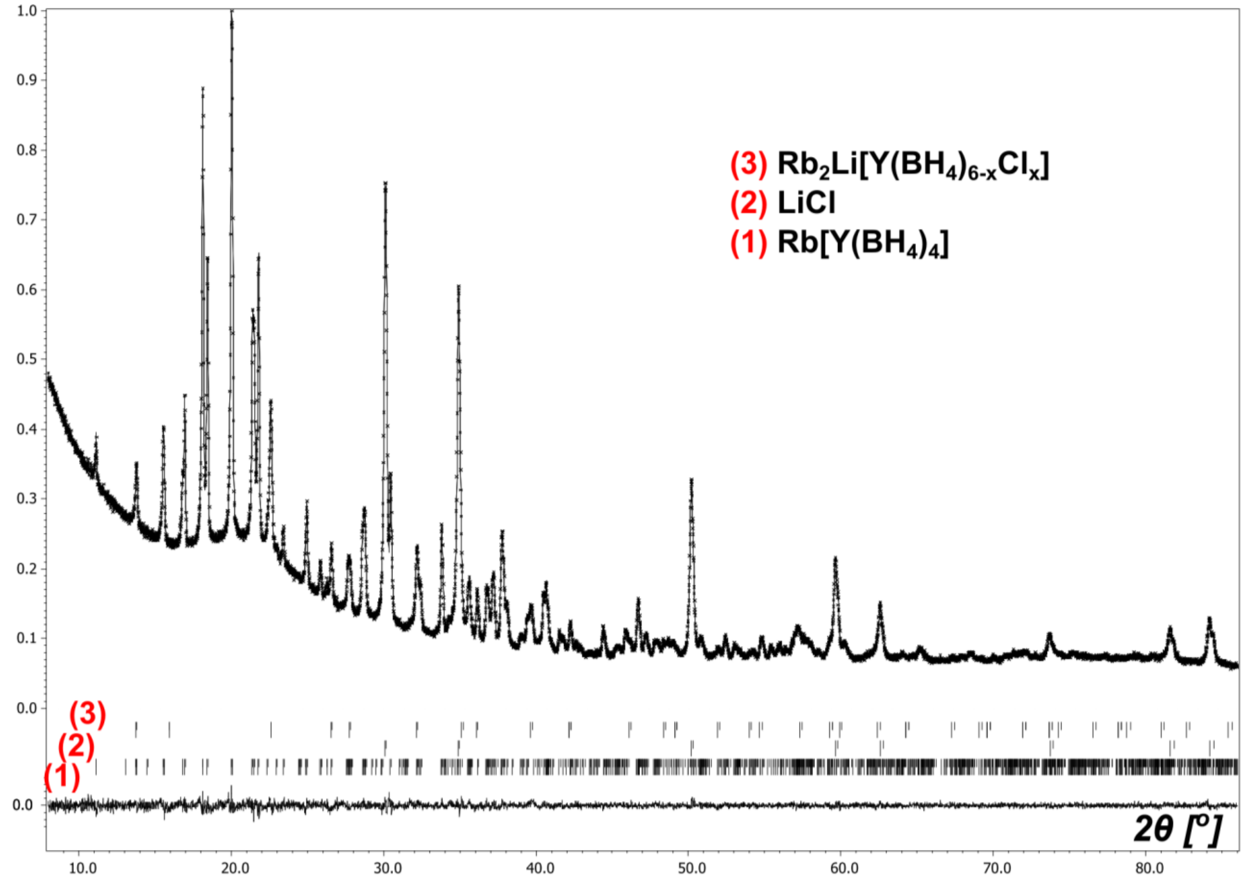

Figure S11. Rietveld plot of the sample ***Rb A165****. The Bragg reflections of the three crystalline phases present in the sample have been marked.*

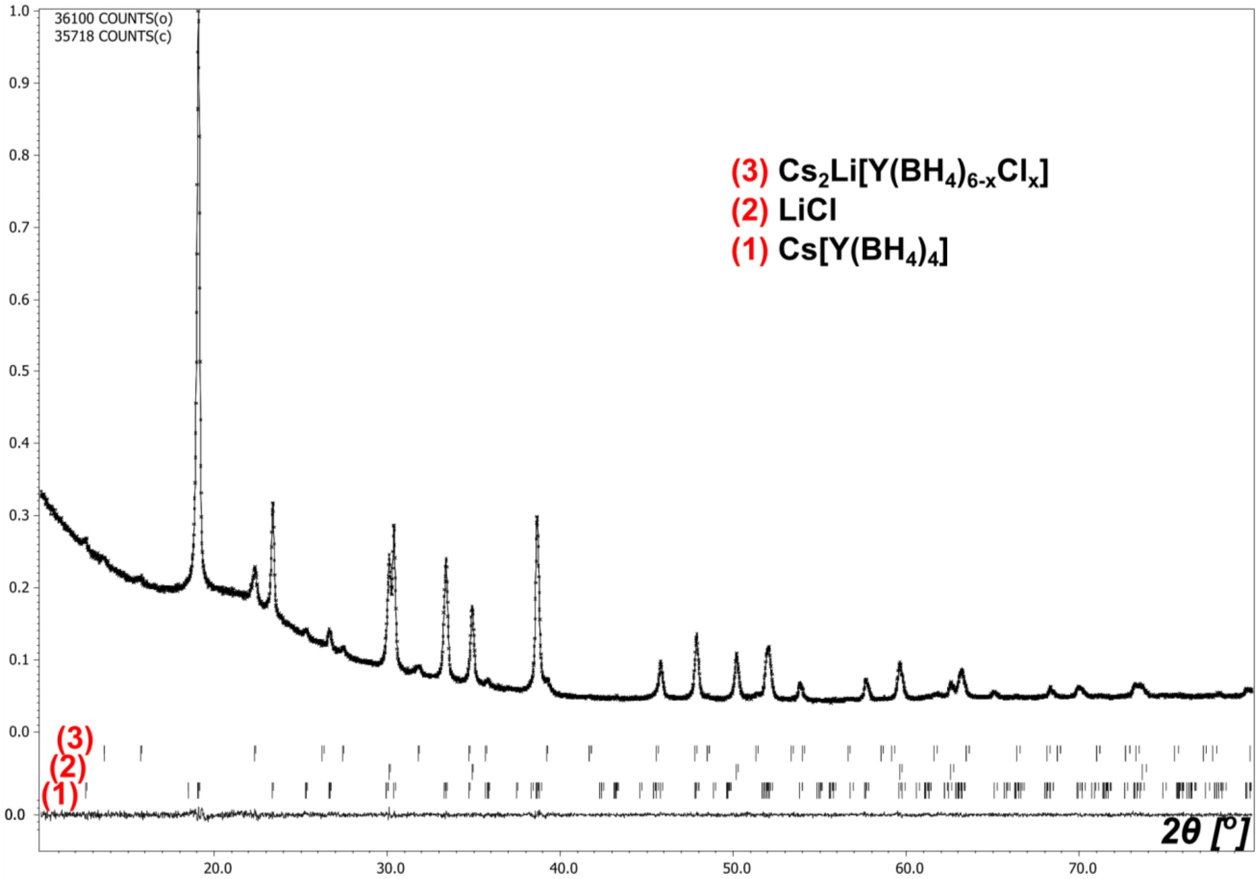

*Figure S12. Rietveld plot of the sample **Cs A130**. The Bragg diffraction peaks of the three crystalline phases present in the sample have been marked.*

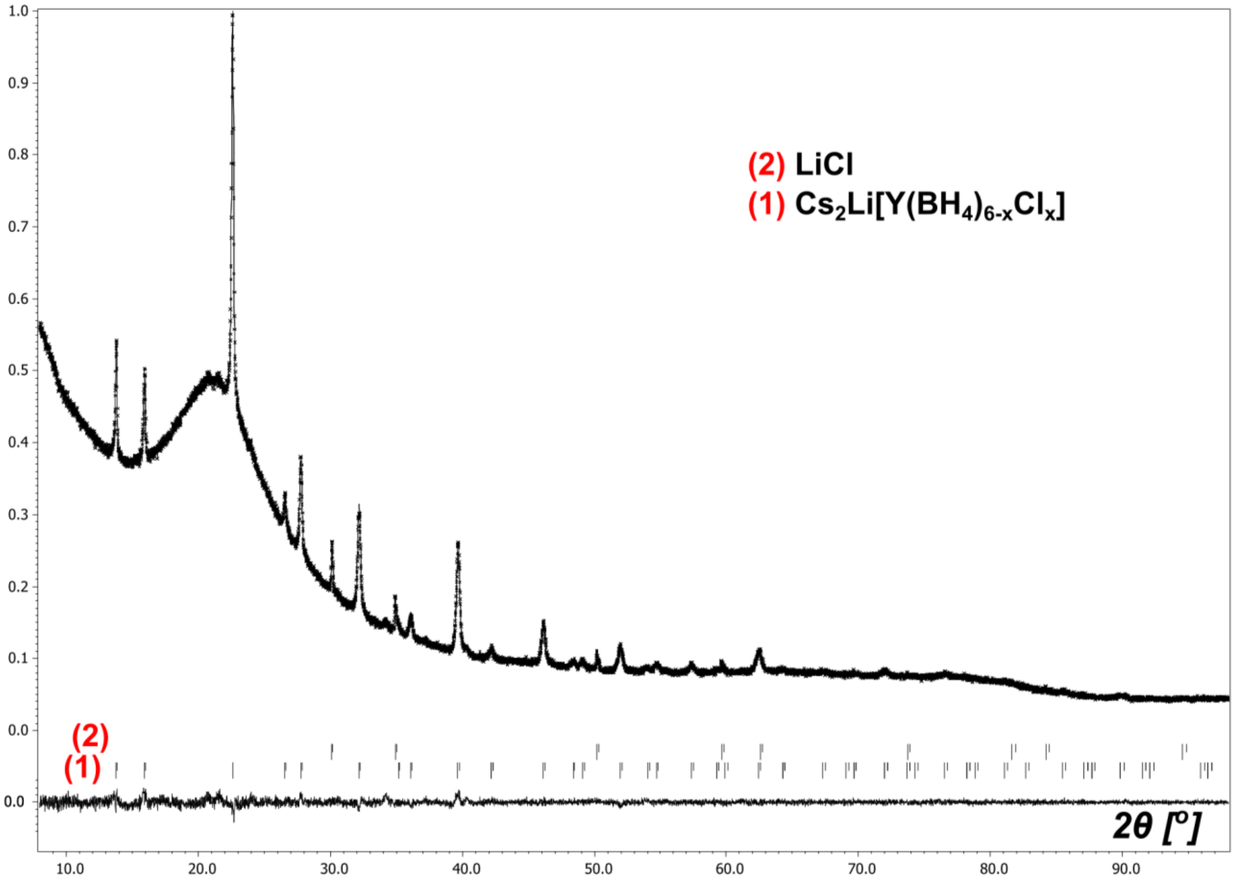

*Figure S13. Rietveld plot of the sample **Cs B175**. The Bragg reflections of the two crystalline phases present in the sample have been marked.*

Table S2. Symmetrisation of the Y–Rb sublattice of Rb[Y(BH$_4$)$_4$]

Max deviation	0.0529 Å	
Tolerance used	0.2 Å	
Symmetry group	Pnma	(was P2$_1$/c)
IT number	62	(was 14)
Option	Origin-1	
a, b, c	12.239 Å, 8.1635 Å, 10.4712 Å	(were 8.1635 Å, 12.2390 Å, 13.2299 Å)
alpha, beta, gamma	90.00, 90.00, 90.00	(were 90.00, 127.678, 90.00)

Table S3. Symmetrisation of the Y–Cs sublattice of Cs[Y(BH$_4$)$_4$]

Max deviation	0.000 Å	
Tolerance used	0.001 Å	
Symmetry group	I4$_1$/amd	(was I4$_1$/a)
IT number	141	(was 88)
Option	Origin-1	
a, b, c	7.60845 Å, 7.60845 Å, 18.5560 Å	(no change)
alpha, beta, gamma	90.00, 90.00, 90.00	(no change)

Remarks on the thermal stability of mixed-cation borohydrides.

As it is well known, metal hydrides (including complex hydrides such as alanates and borohydrides) are thermodynamically and thermally stabilised in a basic environment [see e.g. ref. 18]. In the most simple case of a metal hydride, $M^{(n+)}H_n$, Lewis bases decrease the net charge of a cation $M^{(n+)}$, which in turn causes stabilisation of compound, i.e. decrease the electrochemical potential – the driving force for $M^{(n+)}$ reduction to M^0.

Such stabilisation may be achieved for metal borohydrides, $M(BH_4)_n$, by forming quasi-ternary $M[Y(BH_4)_4]$ salts:

$$MBH_4 + Y(BH_4)_3 \rightarrow M[Y(BH_4)_4]. \qquad \text{(S1)}$$

Yttrium borohydride, crystallising as a 3D network with bridging borohydride groups forming a distorted octahedron around Y^{3+} cation, acts as a Lewis acid in reaction with the most basic among the tested MBH_4 substrates, resulting in derivatives which show discrete $[Y(BH_4)_4]^-$ anions.

Based on systematic investigations for a series of derivatives of yttrium borohydride as model systems we can now qualitatively verify the influence of Lewis acidity of cation M^+ on the thermal stability of $M[Y(BH_4)_4]$ systems. Although these materials constitute a single-crystalline phase or may be a fine mixture of MBH_4 and $Y(BH_4)_3$ (for M=Li, Na), and they may decompose according to various mechanisms, yet their thermal stabilities (as quantified here by the temperature of the fastest mass loss), reveal a simple trend, Fig. S14.

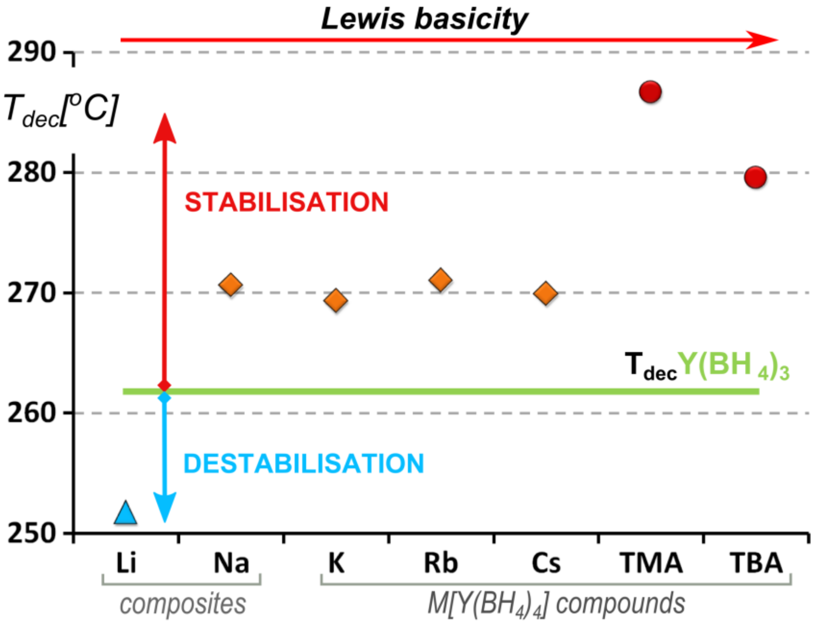

Fig. S14. The temperature of maximum rate of mass loss (DTG) for a series of derivatives of yttrium borohydride, i.e. composites $MBH_4/Y(BH_4)_3$*, M = Li, Na, and compounds* $M[Y(BH_4)_4]$*, M = K, Rb, Cs,* $(CH_3)_4N$ *– TMA,* $(n\text{-}C_4H_9)_4N$ *– TBA as compared with parent* $Y(BH_4)_3$*. Heating rate: 5 K* min^{-1}*; every sample was synthesised in similar conditions and contained LiCl.*

While the relation is not monotonic (due to a lot of factors influencing the thermal stability of a particular compound or composite), the investigated systems may be divided easily into three groups with increasing thermal stability along with Lewis basicity: Tdec(M=Li) << Tdec(M=Na)≈Tdec(M=K)≈Tdec(M=Rb)≈Tdec(M=Cs) << Tdec(M=TMA) > Tdec(M=TBA).

The highest decomposition temperatures are observed for the two compounds containing tetraalkylammonium cations, R_4N^+ (TMA, TBA) which are the least acidic (in a Lewis sense) among the borohydrides studied. These organic cations are bulky enough to place their positive charge away from the $[Y(BH_4)_4]^-$ anion and increase T_{dec} by up to 25 °C as compared to $Y(BH_4)_3$. On the opposite extreme, $LiBH_4$ acts as a strong Lewis acid; its presence decreases the thermal decomposition temperature of $LiBH_4/Y(BH_4)_3$ composite by 10 °C with respect to parent $Y(BH_4)_3$. These effects are not large but they qualitatively agree with what is expected based on the Lewis basicity scale. Recall that Li^+ forms $KLi(BH_4)_2$ salt with basic KBH_4, but its Lewis acidity is insufficient to form $Li(BH_4)_2^-$ anion with $Y(BH_4)_3$. Li-based system behaves unlike the system composed of the heavier alkaline metals, M = Na, K, Rb, Cs which show almost invariant T_{dec}. Such dissimilarity of lithium compounds to the rest of alkaline metals is also very well exemplified in the structural and other aspects of chemistry of borohydrides of alkaline metals.

The influence of Lewis basicity of M^+ cation on the decomposition temperature clearly allows for fine property tuning of metal borohydrides. It does not lead to particularly impressive impact on the T_{dec} value for yttrium salts, but it is a valid concept which could be used for other $M\text{-}BH_4$ systems as well.