Supporting Information

From $M(BH_4)_3$ (M = La, Ce) borohydride frameworks to controllable synthesis of porous hydrides and ion conductors

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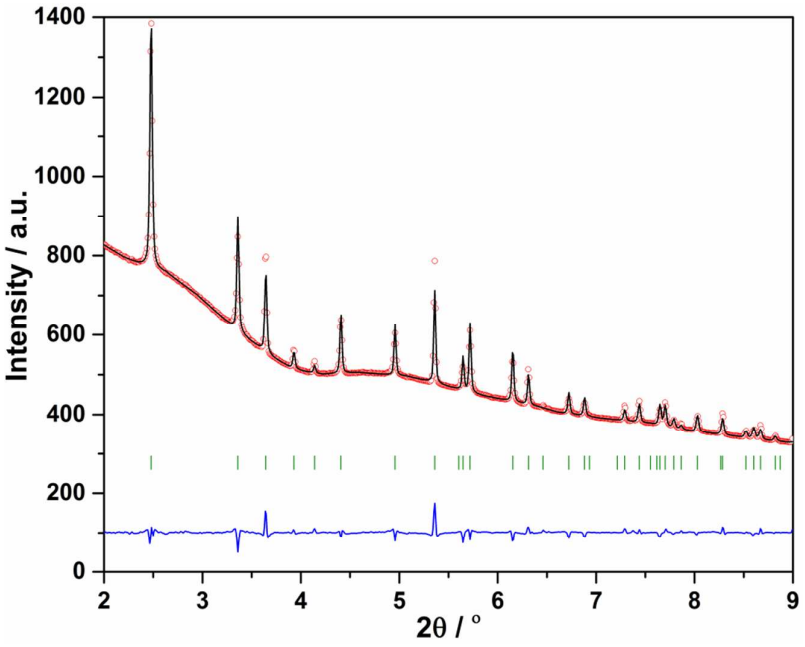

Figure S1 Rietveld refinement of SR-PXD data from *r*-$La(BH_4)_3$ (beam line P02.1, Petra III, DESY, λ = 0.2309 Å, room temperature after annealing at T = 140 °C). Tic marks: *r*-$La(BH_4)_3$.

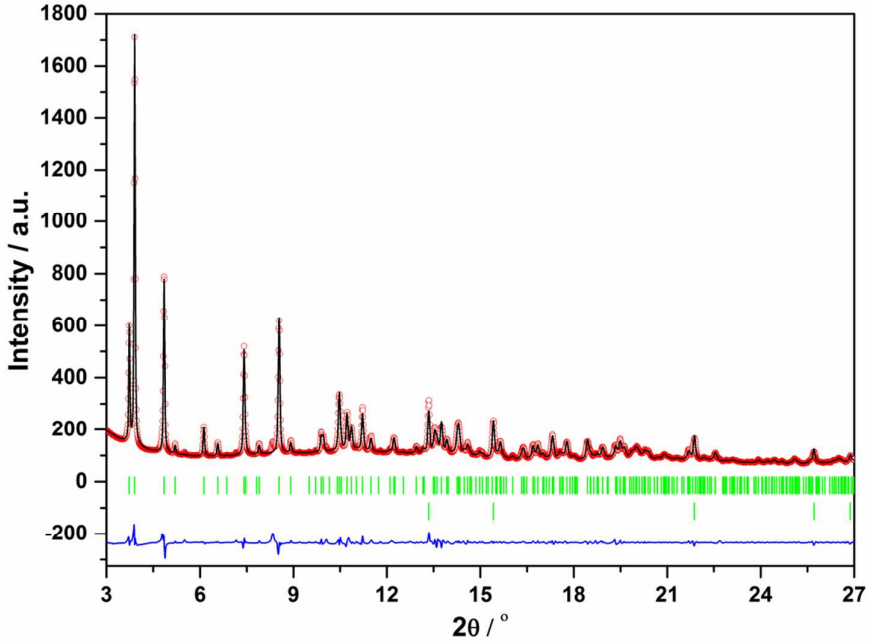

Figure S2 Le Bail refinement of the SR-PXD data obtained from $LiCe(BH_4)_3Cl{\cdot}nEt_2O$ (BM01A, SNBL, ESRF, λ = 0.688423 Å, room temperature). Tic marks: Top $LiCe(BH_4)_3Cl{\cdot}nEt_2O$, bottom LiCl.

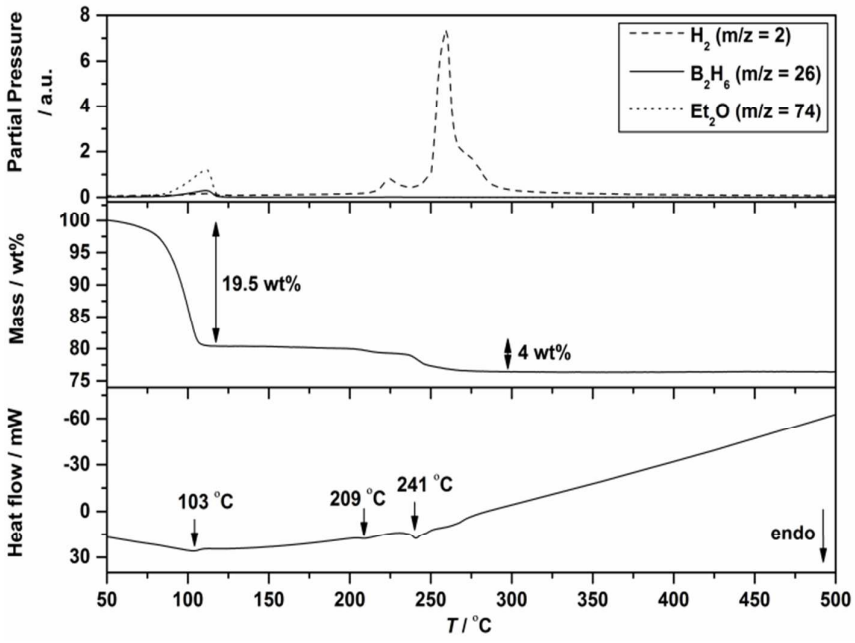

Figure S3 Thermal analysis and mass spectrometry of $LiCe(BH_4)_3Cl{\cdot}nEt_2O$, DSC (bottom), TGA (middle) and MS (top), $\Delta T/\Delta t$ = 5 °C/min, argon flow.

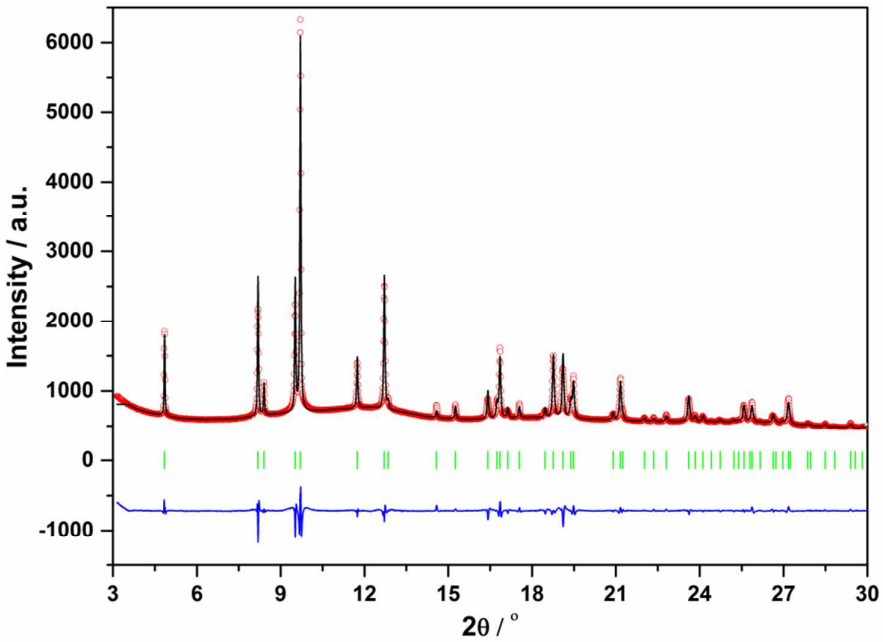

Figure S4 Le Bail refinement of the SR-PXD data obtained from $La(BH_4)_3 \cdot mS(CH_3)_2$ (I11, Diamond, $\lambda = 0.827120$ Å, $T = 117$ °C). Tic marks: $La(BH_4)_3 \cdot mS(CH_3)_2$.

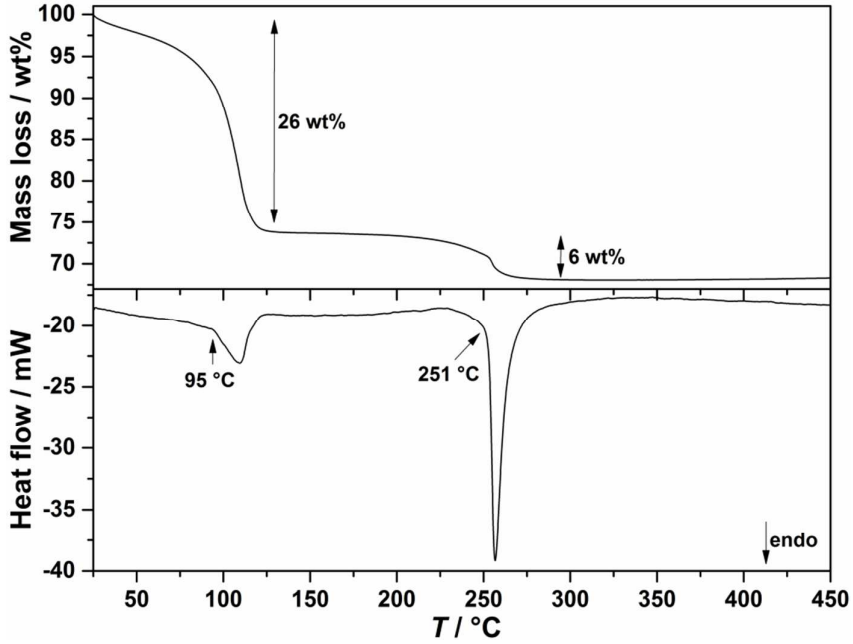

Figure S5 Thermal analysis of $Ce(BH_4)_3 \cdot nS(CH_3)_2$, DSC (bottom) and TGA (top), $\Delta T/\Delta t = 5$ °C/min, argon flow.

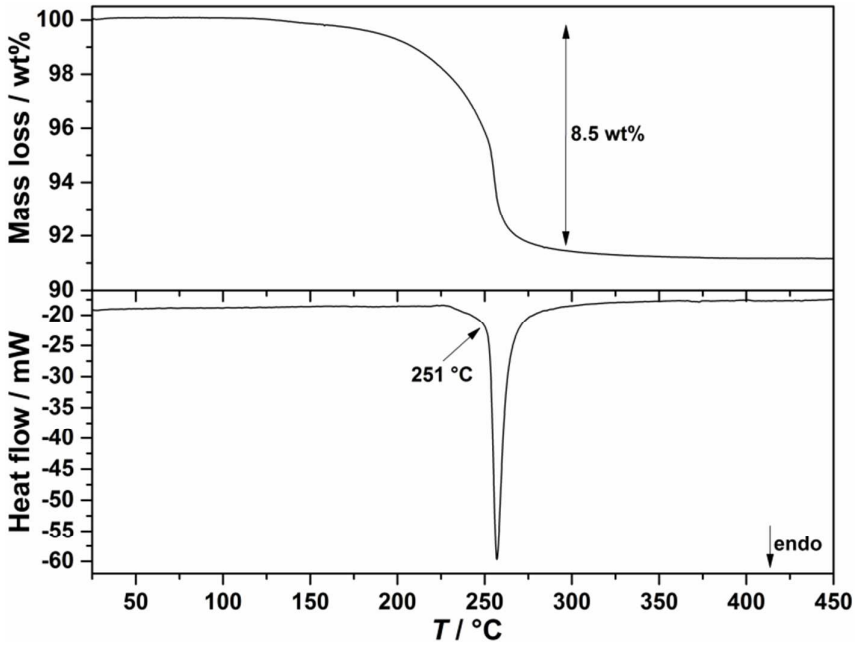

Figure S6 Thermal analysis for $Ce(BH_4)_3$, DSC (bottom) and TGA (top), from room temperature to 450 °C, $\Delta T/\Delta t$ = 5 °C/min, argon flow.

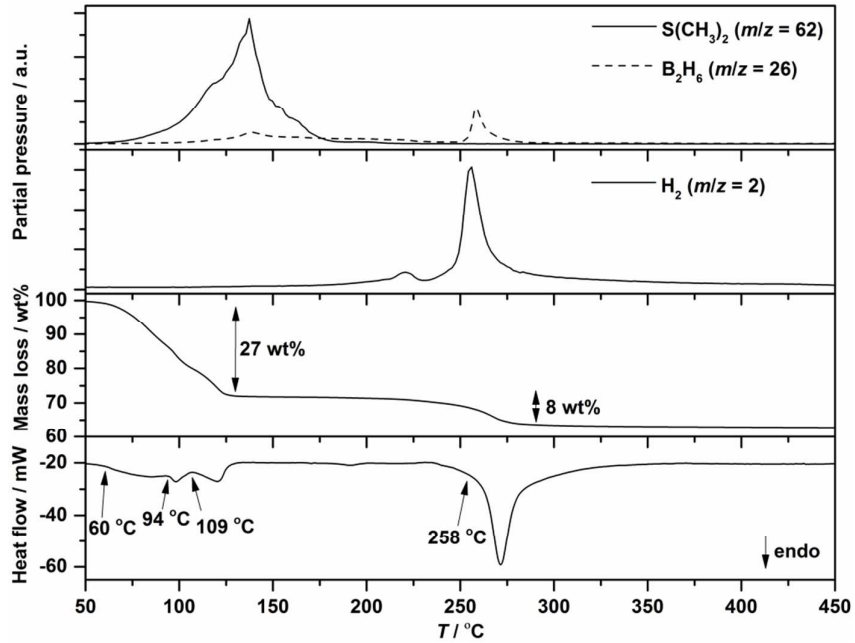

Figure S7 Thermal analysis for $La(BH_4)_3 \cdot nS(CH_3)_2$, DSC (bottom), TGA (middle) and MS (top two rows) from room temperature to 450 °C, $\Delta T/\Delta t$ = 5 °C/min, argon flow.

Table S1 Atomic positions for *r*-$Ce(BH_4)_3$ (space group *R*-3*c*, *a* = 7.3745(1) Å, *c* = 20.1567(2) Å, *T* = 180 °C) determined by Rietveld refinement of the SR-PXD data.

Atom	Wyck.	x/a	y/b	z/c
Ce	**6*b***	**0**	**0**	**0**
B	**18*e***	**0.632(2)**	**0**	**1/4**
H1	**36*f***	**0.461(2)**	**-0.094(5)**	**0.261(2)**
H2	**36*f***	**0.759(2)**	**0.026(5)**	**0.288(2)**

Table S2 Atomic positions for *c*-$Ce(BH_4)_3$ (space group *Fm*-3*c*, *a* = 11.7106(6) Å, *T* = 180 °C) determined by Rietveld refinement of the SR-PXD data.

Atom	Wyck.	x/a	y/b	z/c
Ce	**8*b***	**0**	**0**	**0**
B	**24*c***	**0**	**0**	**1/4**
H1	**96*i***	**0**	**0.4075(1)**	**0.3104(1)**