Electronic Supplementary information

Structure and thermal properties of composites with RE-borohydrides (RE = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Er, Yb or Lu) and $LiBH_4$

Jørn Eirik Olsen[1], *Christoph Frommen*[1], *Torben R. Jensen*[2], *Magnus H. Sørby*[1], *Bjørn C. Hauback*[1*]

[1] Institute for Energy Technology, Physics Department, P.O. Box 40, NO-2027 Kjeller, Norway

[2] Center for Materials Crystallography (CMC), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark.

[*] Corresponding author: E-mail: bjorn.hauback@ife.no, Phone: +47 63 80 60 78, Fax : +47 63 81 09 20

Table S1 The refined unit cell dimensions, RE-B and RE-Cl distances in the $LiRE(BH_4)_3Cl$ phases, RE = La, Ce, Pr, Nd, at RT. Estimated standard deviations in parenthesis.

Atom in $LiRE(BH_4)_3Cl$	Unit cell dimension, *a* (Å)	RE-B distance, (Å)	RE-Cl distance, (Å)
La	11.6853(1)	2.714(7)	2.978(1)
Ce	11.6243(1)	2.720(8)	2.952(2)
Pr	11.5784(1)	2.72(1)	2.932(2)
Nd	11.5480(2)	2.69(3)	2.926(5)

Table S2 Experimentally found IR active modes for the different $LiRE(BH_4)_3Cl$ phases

	RE = La	RE = Ce	RE = Pr	RE = Nd
B-H bending	1176	1175	1176	1179
	1202	1202	1203	1206
B-H stretching	2325	2324	2324	2322
	2422	2420	2416	2427
	2446	2447	2443	2452

Table S3 Crystallographic data for $LiLa(BH_4)_3Cl$ at RT from SR-PXD data

Phase data						
Compound	$LiLa(BH_4)_3Cl$					
Space group	*I*-43*m* (217)					
Unit cell parameters	*a* = 11.6853(1) Å					
Unit cell volume	1595.57(3) $Å^3$					
Z	8					
Calculated density	1.88009 g/cm^3					
Atomic parameters						
Atom	**Wyck.**	**Occ.**	***x*/a**	***y*/b**	***z*/c**	***U* [$Å^2$]**
La	8*c*	1	0.85762(3)	0.85762(3)	0.85762(3)	0.0140(1)
B	24*g*	1	0.1271(6)	0.6224(5)	0.6224(5)	0.018(1)
H1	24*g*	1	0.028(2)	0.619(2)	0.619(2)	0.024(6)
H2	48*h*	1	0.164(2)	0.659(3)	0.537(2)	0.024(6)
H3	24*g*	1	0.160(3)	0.691(1)	0.691(1)	0.024(6)
Cl	8*c*	1	0.8923(2)	0.1077(2)	0.8923(2)	0.0155(7)
Li	12*d*	0.6667	1/4	1/2	0	0.036(6)

Table S4 - Crystallographic data for $LiCe(BH_4)_3Cl$ at RT from SR-PXD data

Phase data						
Compound	$LiCe(BH_4)_3Cl$					
Space group	*I*-43*m* (217)					
Unit cell parameters	*a* = 11.6243(1) Å					
Unit cell volume	1570.74(4) $Å^3$					
Z	8					
Calculated density	1.92004 g/cm^3					
Atomic parameters						
Atom	**Wyck.**	**Occ.**	***x*/a**	***y*/b**	***z*/c**	***U* [$Å^2$]**
Ce	8*c*	1	0.85825(4)	0.85825(4)	0.85825(4)	0.0133(2)
B	24*g*	1	0.1260(7)	0.6218(6)	0.6218(6)	0.009(2)
H1	24*g*	1	0.026(3)	0.615(2)	0.615(2)	0.005(7)
H2	48*h*	1	0.155(3)	0.667(3)	0.552(3)	0.005(7)
H3	24*g*	1	0.161(4)	0.687(2)	0.687(2)	0.005(7)
Cl	8*c*	1	0.8925(2)	0.1075(2)	0.8925(2)	0.0153(9)
Li	12*d*	0.6667	1/4	1/2	0	0.011(6)

Table S5 - Crystallographic data for $LiPr(BH_4)_3Cl$ at RT from SR-PXD data

Phase data						
Compound	$LiPr(BH_4)_3Cl$					
Space group	*I*-43*m* (217)					
Unit cell parameters	a = 11.5784(1) Å					
Unit cell volume	1552.17(5) $Å^3$					
Z	8					
Calculated density	1.94977 g/cm^3					
Atomic parameters						
Atom	**Wyck.**	**Occ.**	***x*/a**	***y*/b**	***z*/c**	***U* [$Å^2$]**
Pr	8*c*	1	0.85854(4)	0.85854(4)	0.85854(4)	0.0152(2)
B	24*g*	1	0.1258(9)	0.6215(8)	0.6215(8)	0.010(2)
H1	24*g*	1	0.024(4)	0.613(3)	0.613(3)	0.012(9)
H2	48*h*	1	0.149(4)	0.668(3)	0.562(3)	0.012(9)
H3	24*g*	1	0.161(5)	0.686(3)	0.686(3)	0.012(9)
Cl	8*c*	1	0.8929(2)	0.1071(2)	0.8929(2)	0.016(1)
Li	12*d*	0.6667	1/4	½	0	0.010(7)

Table S6 Crystallographic data for $LiNd(BH_4)_3Cl$ at RT from SR-PXD data

Phase data						
Compound	$LiNd(BH_4)_3Cl$					
Space group	*I*-43*m* (217)					
Unit cell parameters	a = 11.5480(2) Å					
Unit cell volume	1540.00(7) $Å^3$					
Z	8					
Calculated density	1.9939 g/cm^3					
Atomic parameters						
Atom	**Wyck.**	**Occ.**	***x*/a**	***y*/b**	***z*/c**	***U* [$Å^2$]**
Nd	8*c*	1	0.8585(1)	0.8585(1)	0.8585(1)	0.0141(4)
B	24*g*	1	0.127(3)	0.620(2)	0.620(2)	0.0250
H1	24*g*	1	0.028(4)	0.627(7)	0.627(7)	0.0250
H2	48*h*	1	0.161(7)	0.634(9)	0.533(5)	0.0250
H3	24*g*	1	0.180(8)	0.680(5)	0.680(5)	0.0250
Cl	8*c*	1	0.8927(6)	0.1073(6)	0.8927(6)	0.020(3)
Li	12*d*	0.6667	¼	1/2	0	0.0250

Table S7 Crystallographic data for $Sm(BH_4)_2$ at about 200 °C from *in situ* SR-PXD data. Estimated standard deviations in parenthesis

Phase data						
Compound	$Sm(BH_4)_2$					
Space group	*Pbcn* (60)					
Unit cell parameters	a = 6.9848(1) Å b = 8.4464(1) Å c = 7.5891(1) Å					
Unit cell volume	447.73(1) $Å^3$					
Z	4					
Calculated density	2.672 g/cm^3					
Atomic parameters						
Atom	**Wyck.**	**Occ.**	***x*/a**	***y*/b**	***z*/c**	***U* [$Å^2$]**
Sm	4*c*	1	½	0.1522(1)	¼	0.0352(2)
B	8*d*	1	0.7320(11)	0.1144(11)	0.9206(9)	0.003(2)

H1	8*d*	1	0.6131(11)	0.0423(11)	0.8400(9)	=*U*B1
H2	8*d*	1	0.7989(11)	0.0307(11)	1.0320(9)	=*U*B1
H3	8*d*	1	0.8560(11)	0.1567(11)	0.8222(9)	=*U*B1
H4	8*d*	1	0.6601(11)	0.2277(11)	0.9881(9)	=*U*B1

Table S8. Some selected bond distances (Å) and bond angles (°) in $Sm(BH_4)_2$. Estimated standard deviations in parenthesis.

Sm_B	(2x) 2.996(7)
Sm_B	(2x) 3.011(8)
Sm_B	(2x) 3.061(8)
B_Sm_B	(2x) 81.7(2)
B_Sm_B	85.3(2)
B_Sm_B	(2x) 88.3(2)
B_Sm_B	(2x) 89.3(2)
B_Sm_B	(2x) 92.7(2)
B_Sm_B	(2x) 95.3(2)
B_Sm_B	98.2(2)
B_Sm_B	167.8(2)
B_Sm_B	(2x) 173.0(2)
Sm_B_Sm	98.3(2)
Sm_B_Sm	128.7(2)
Sm_B_Sm	129.0(3)

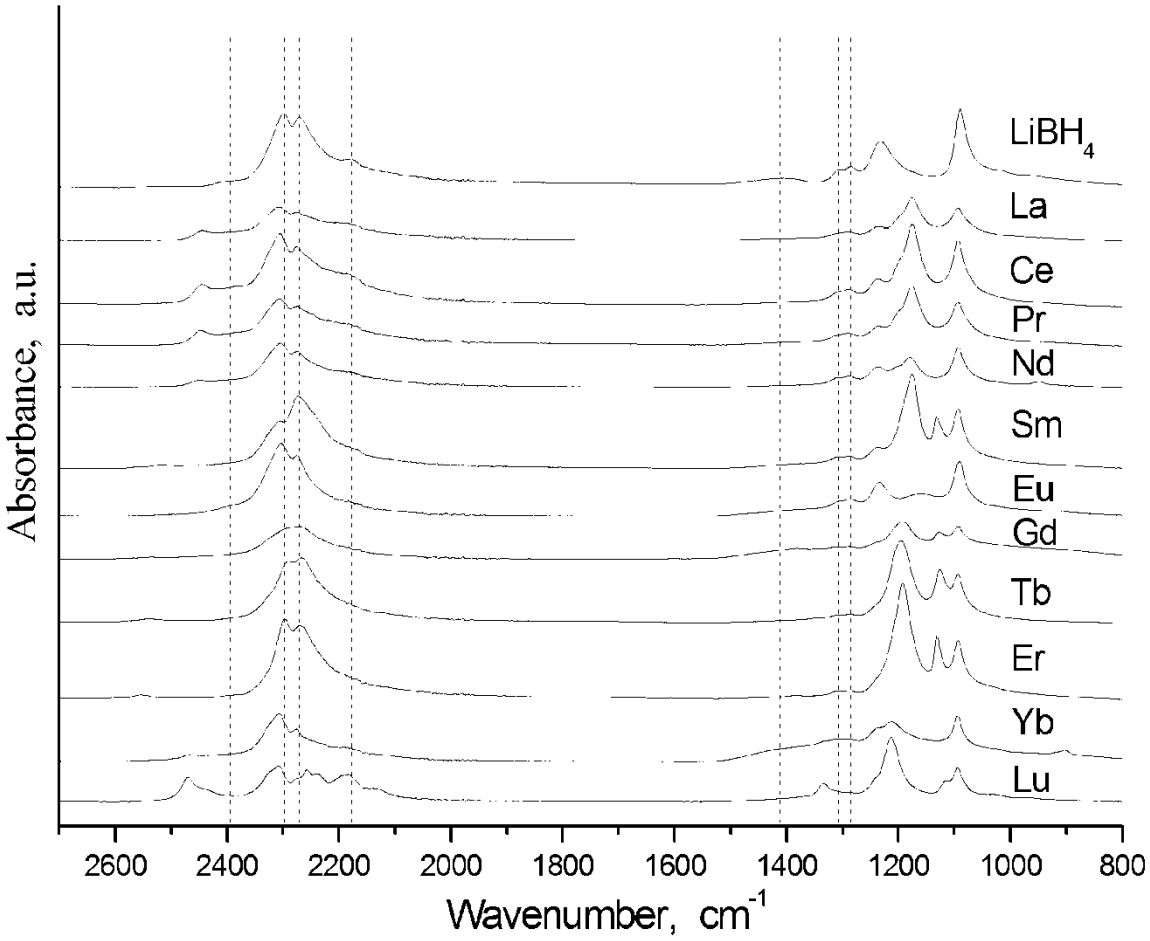

Fig. S1 IR spectra of all samples compared to $LiBH_4$

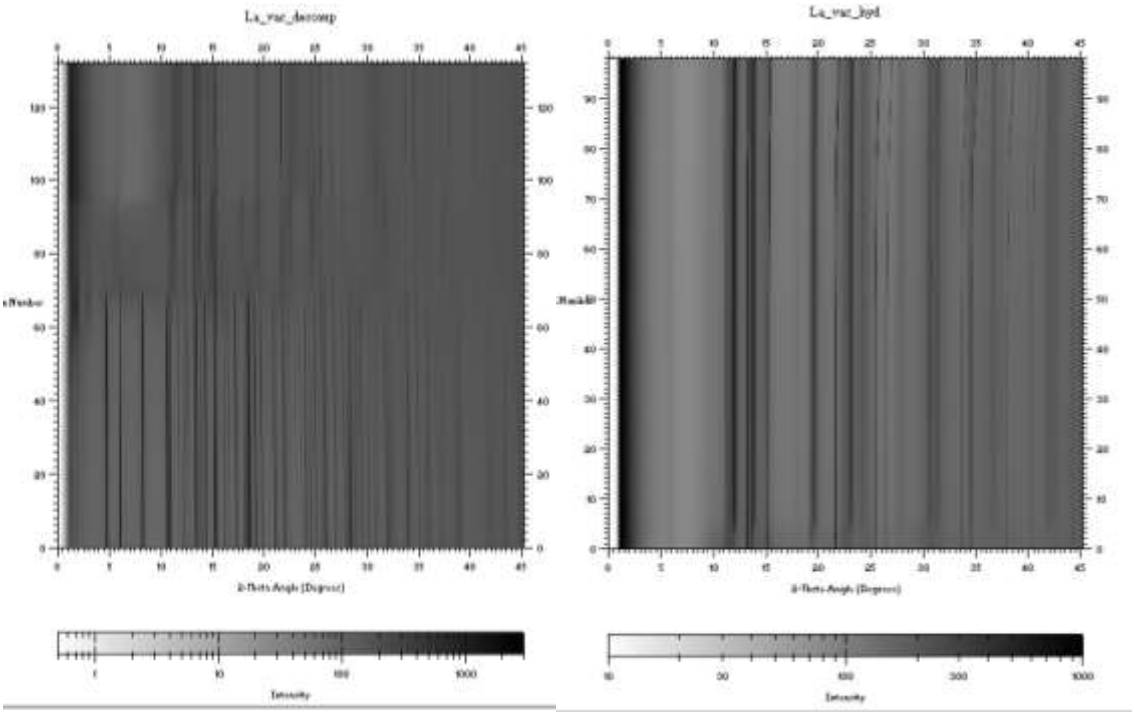

Figure S1 – *In situ* SR-PXD measurement of the ball milled composite of $LaCl_3$ + 6 $LiBH_4$. Decomposition in vacuum (left) and subsequent hydrogenation in 10 MPa H_2(right).

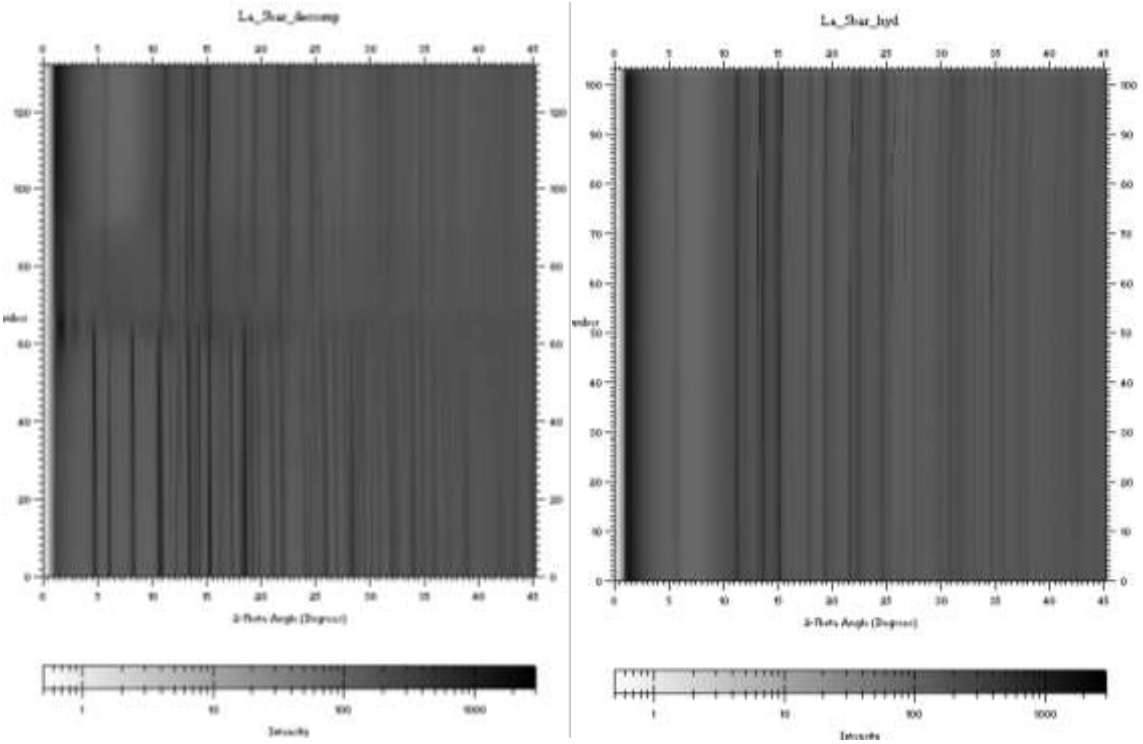

Figure S3 – *In situ* SR-PXD measurement of the ball milled composite of $LaCl_3$ + 6 $LiBH_4$. Decomposition in 0.5 MPa H_2 backpreassure (left) and subsequent hydrogenation in10 MPa H_2(right).

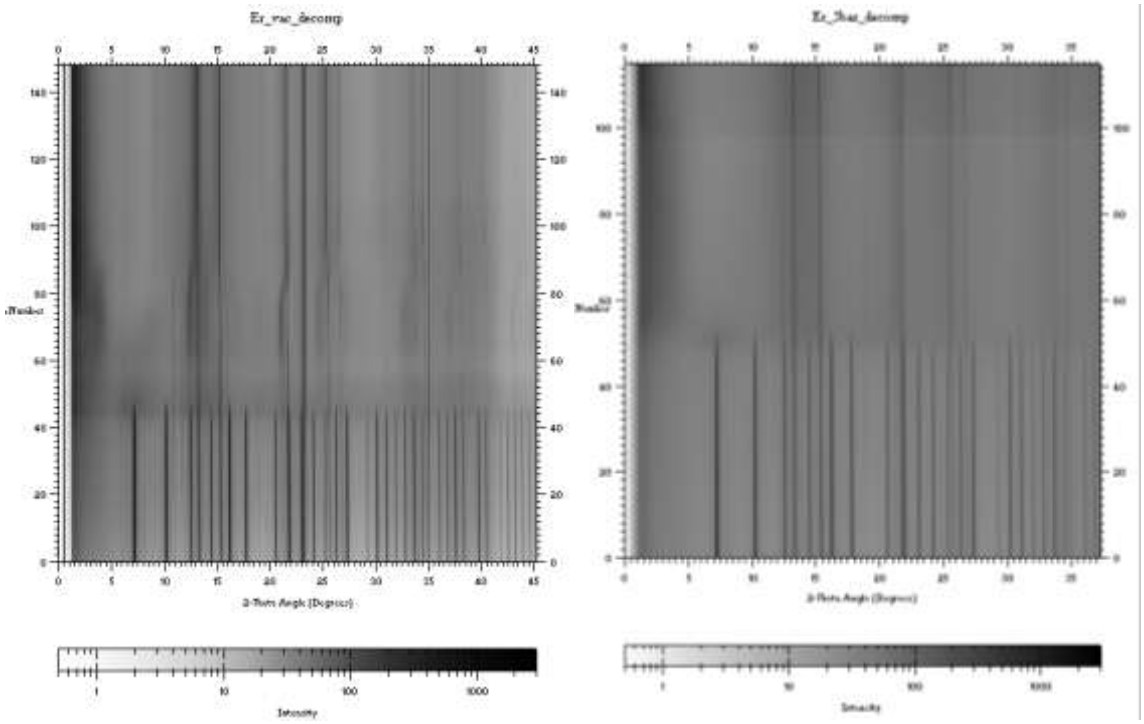

Figure S4. Contour plots from *in situ* SR-PXD during decomposition of the Er-sample, vacuum (left) and 0.5MPa (right). λ = 0.694118 Å

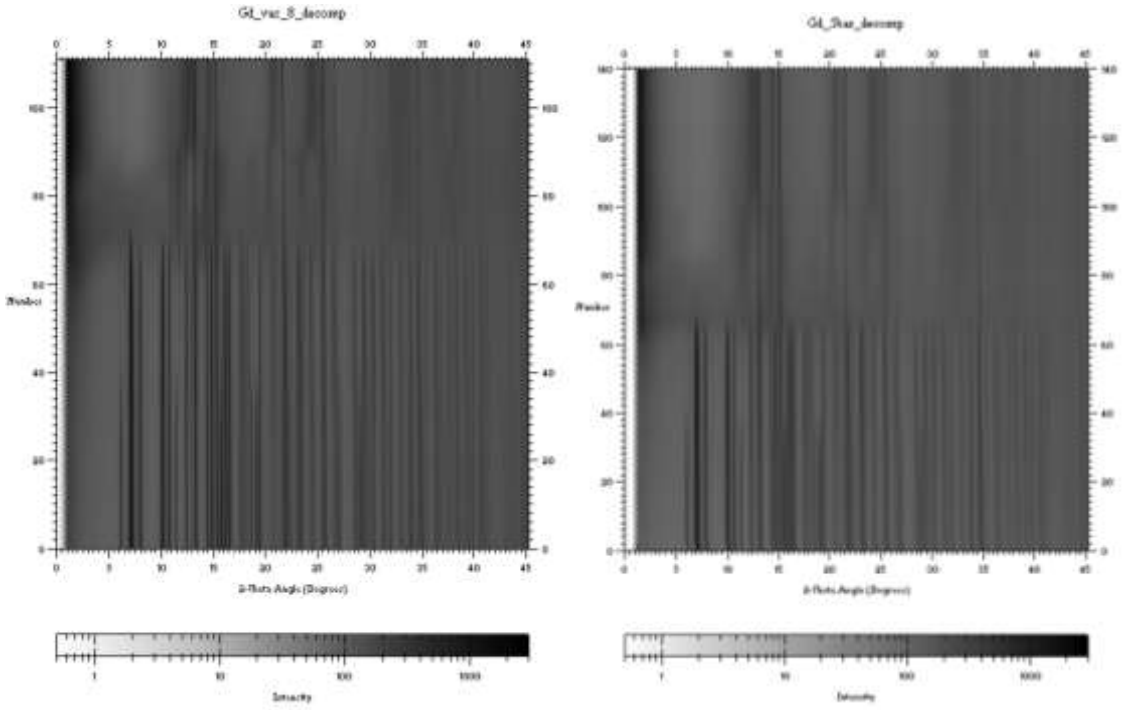

Figure S5. Contour plots from in situ SR-PXD during decomposition of the Gd-sample, vacuum (left) and 0.5MPa (right). λ = 0.694118 Å

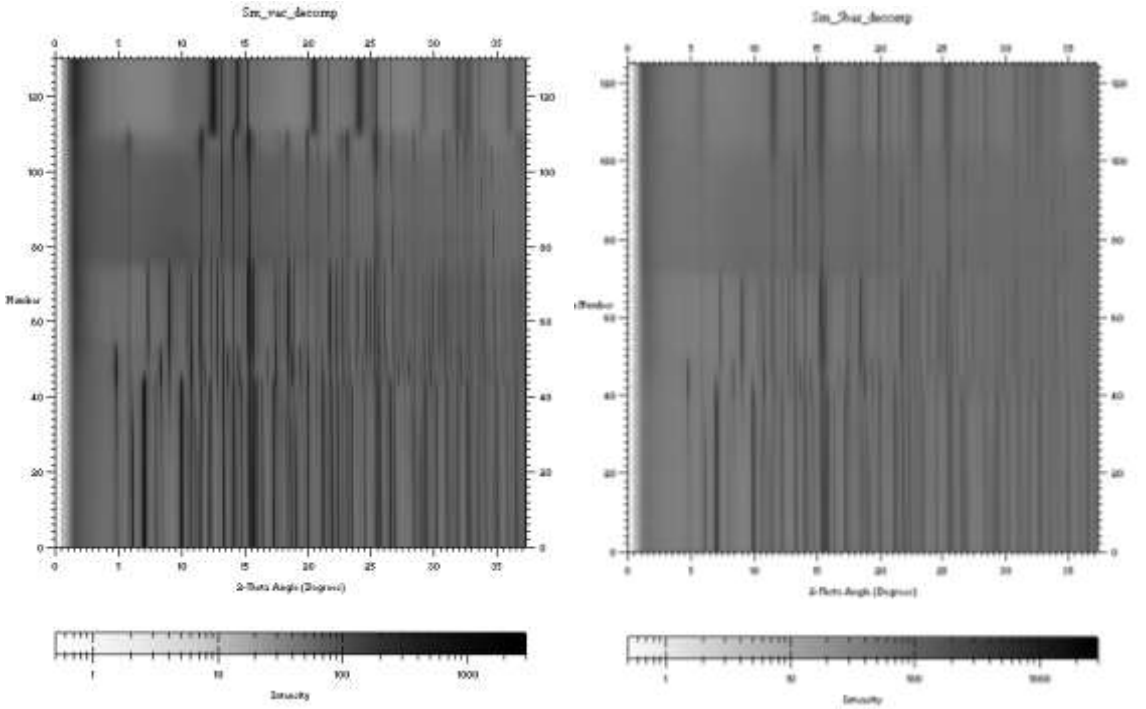

Figure S6. Contour plots from in situ SR-PXD during decomposition of the Sm-sample, vacuum (left) and 0.5MPa (right). λ = 0.694118 Å

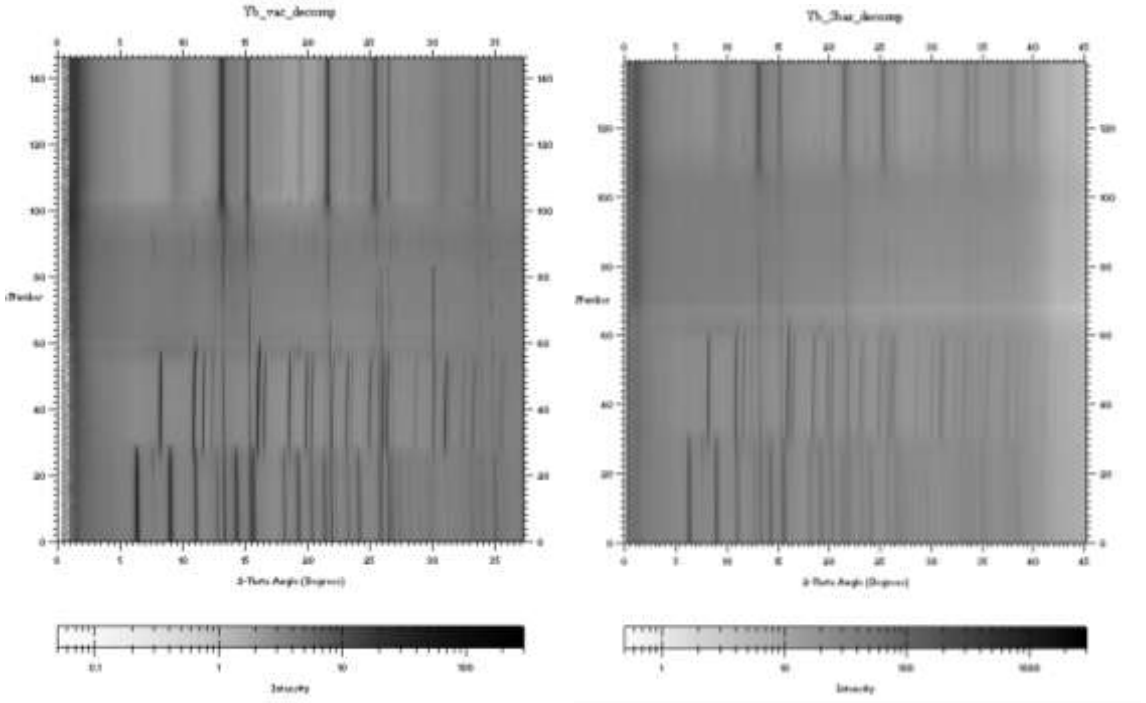

Figure S7. Contour plots from in situ SR-PXD during decomposition of the Yb-sample, vacuum (left) and 0.5MPa (right). λ = 0.694118 Å

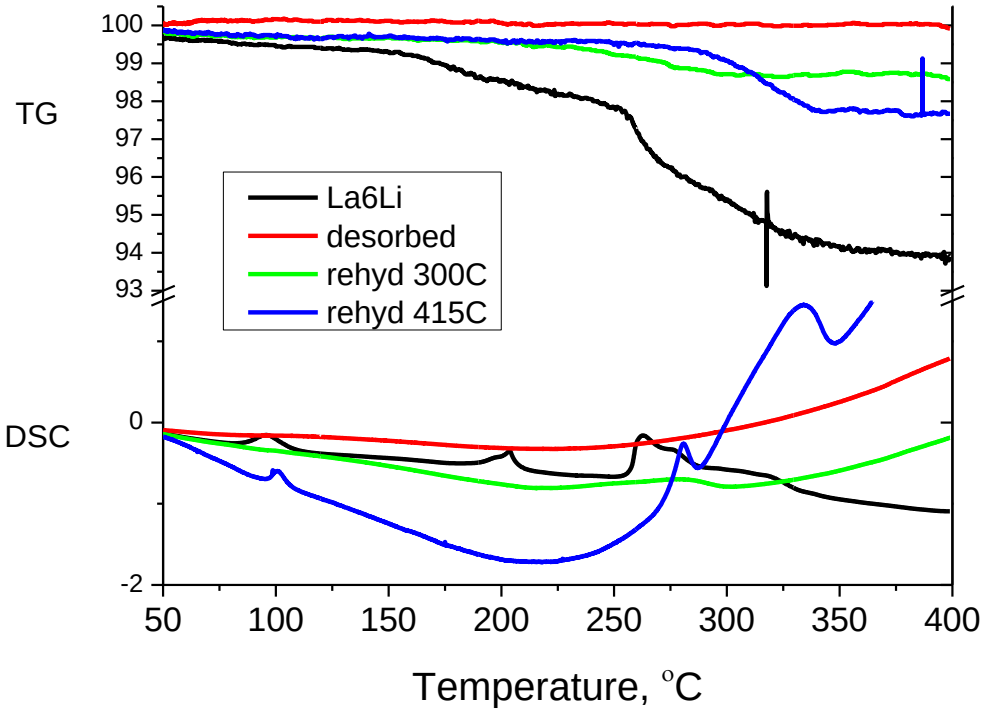

Figure S8 - TG/DSC measurement for the rehydrogenation samples of $LaCl_3$ + 6 $LiBH_4$. The spectra of the ball milled sample (black), the desorbed sample (red), the sample rehydrogenated at 300 °C (green) and the sample rehydrogenated at 415 °C (blue).

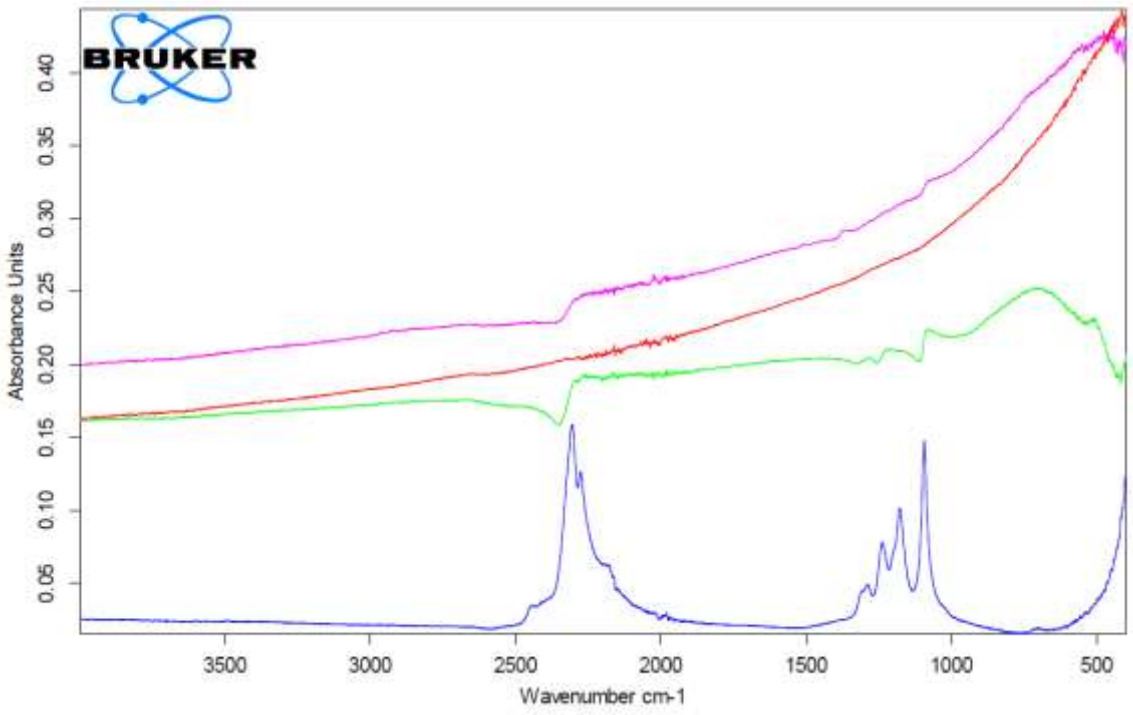

Figure S9 - IR spectra for rehydrogenation samples of $LaCl_3$ + 6 $LiBH_4$. The spectra of the ball milled sample (blue), the desorbed sample (red), the sample rehydrogenated at 300 °C (purple) and the sample rehydrogenated at 415 °C (green).

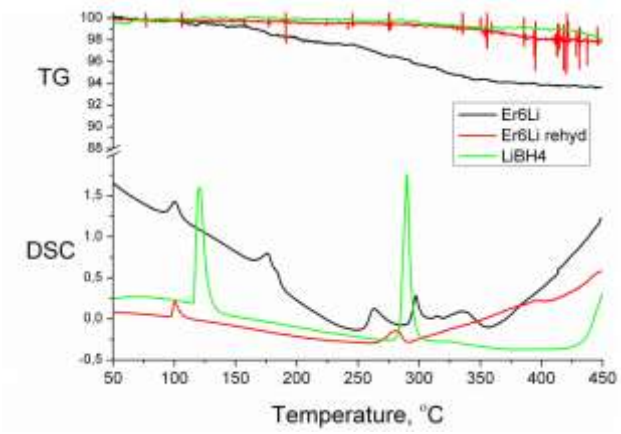

Fig. S10 TG/DSC measurement of $ErCl_3$ + 6 $LiBH_4$ during decomposition (black line) and after first rehydrogenation (red line), TG/DSC data from $LiBH_4$ are added as reference (green line).

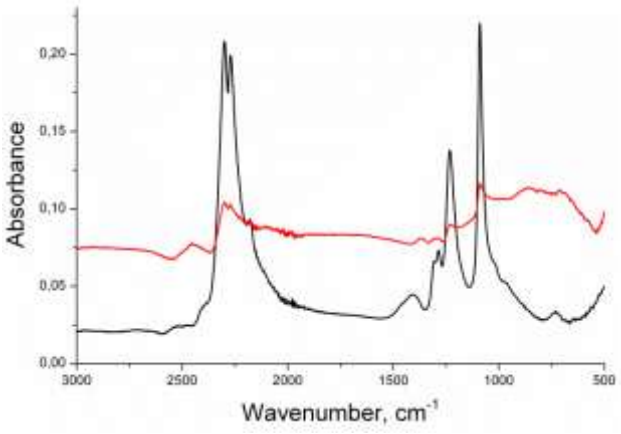

Fig. S11 IR spectra from $LiBH_4$ (black line) and the rehydrogenated Er-sample (red line)