Supplementary information

Synthesis, structure and properties of bimetallic sodium rare earth (RE) borohydrides, $NaRE(BH_4)_4$, RE = Ce, Pr, Er or Gd.

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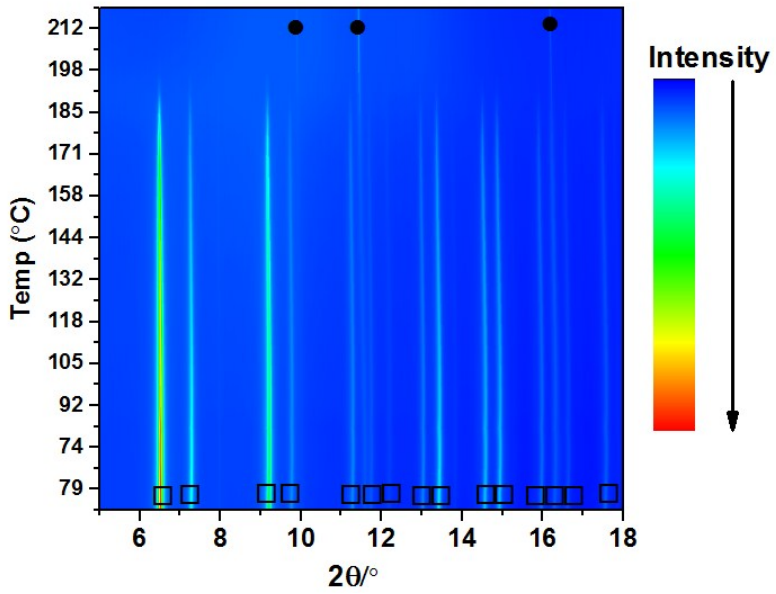

Figure S1 *In-situ* SR-XRPD data for $Gd(BH_4)_3$–$NaBH_4$ (1:1, s5). $\Delta T/\Delta t$ = 5 °C min^{-1} (SLS, λ = 0.62177 Å)

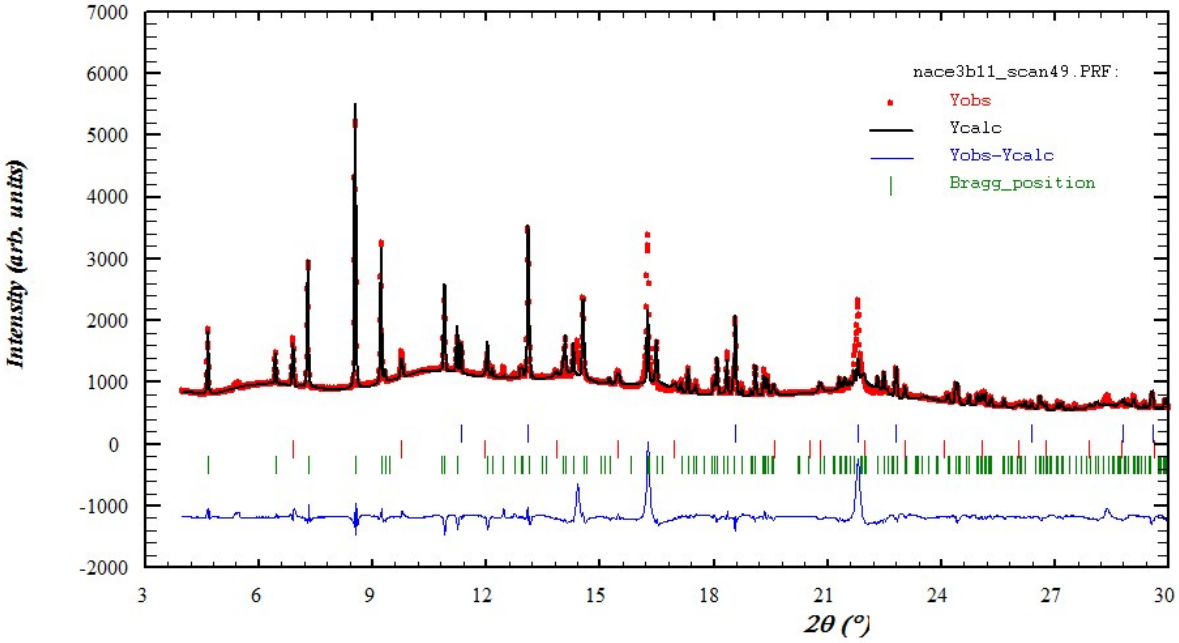

Figure S2 XRPD pattern and refinement for $Ce(BH_4)_3$–$NaBH_4$ (1:1, **s1**, λ = 0.7129) recorded at 181 °C. Red line: experimental data; black line: calculated pattern, blue line: difference pattern. Sample composition: 1. Top, blue tick: $NaBH_4$ (58.31 wt%). 2. Middle red ticks: $Ce(BH_4)_3$ ($Fm\bar{3}c$, 3.08wt%) and 3. Bottom green ticks, $NaCe(BH_4)_4$ (38.61 wt%). R_{wp} = 7.59% (not corrected for background), χ^2 =359**.** The Bragg reflections that aren't refined are for the U2 phase.

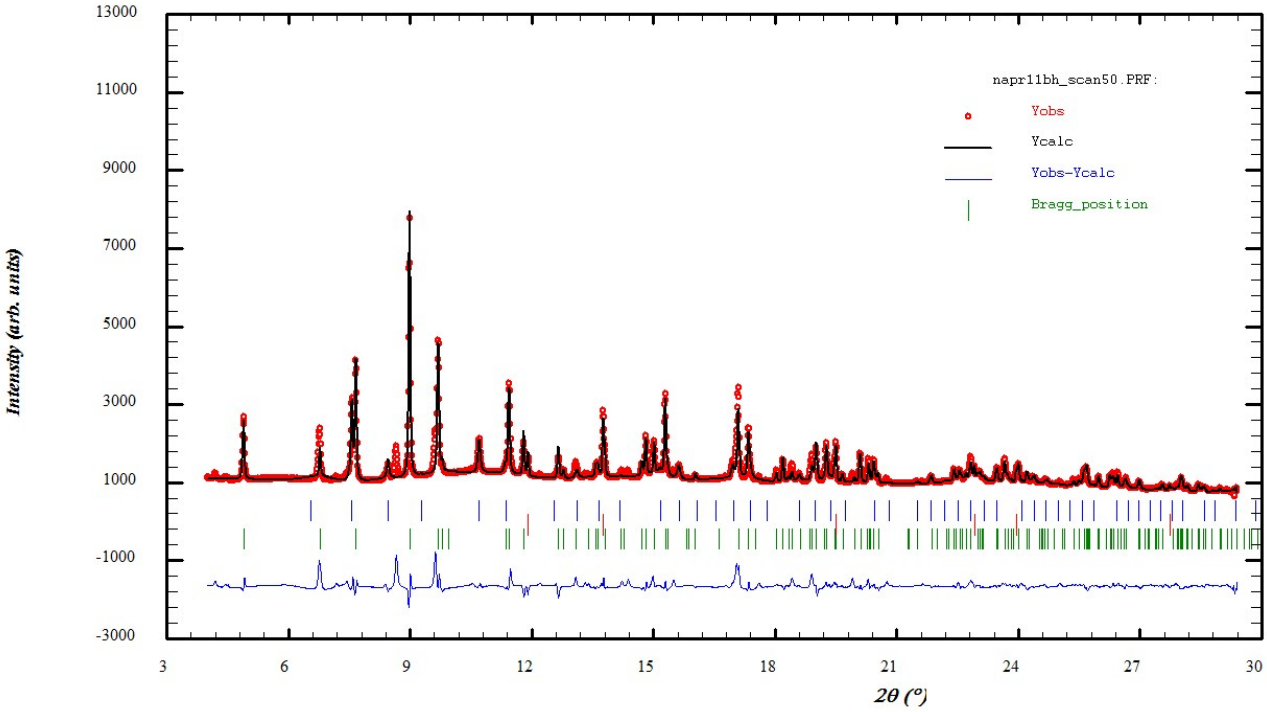

Figure S3 XRPD pattern and refinement for $Pr(BH_4)_3$–$NaBH_4$ (1:1, **s4**, λ = 0.7458) recorded at 134 °C. Red line: experimental data; black line: calculated pattern, blue line: difference pattern. Sample composition: 1. Top, blue tick: $Pr(BH_4)_3$ (16.48 wt%,). 2. Middle red Ticks: $NaBH_4$ (25.35 wt%,) and 3. Bottom green ticks, $NaPr(BH_4)_4$ (58.17 wt%). R_{wp} = 5.85% (not corrected for background), χ^2 =319.

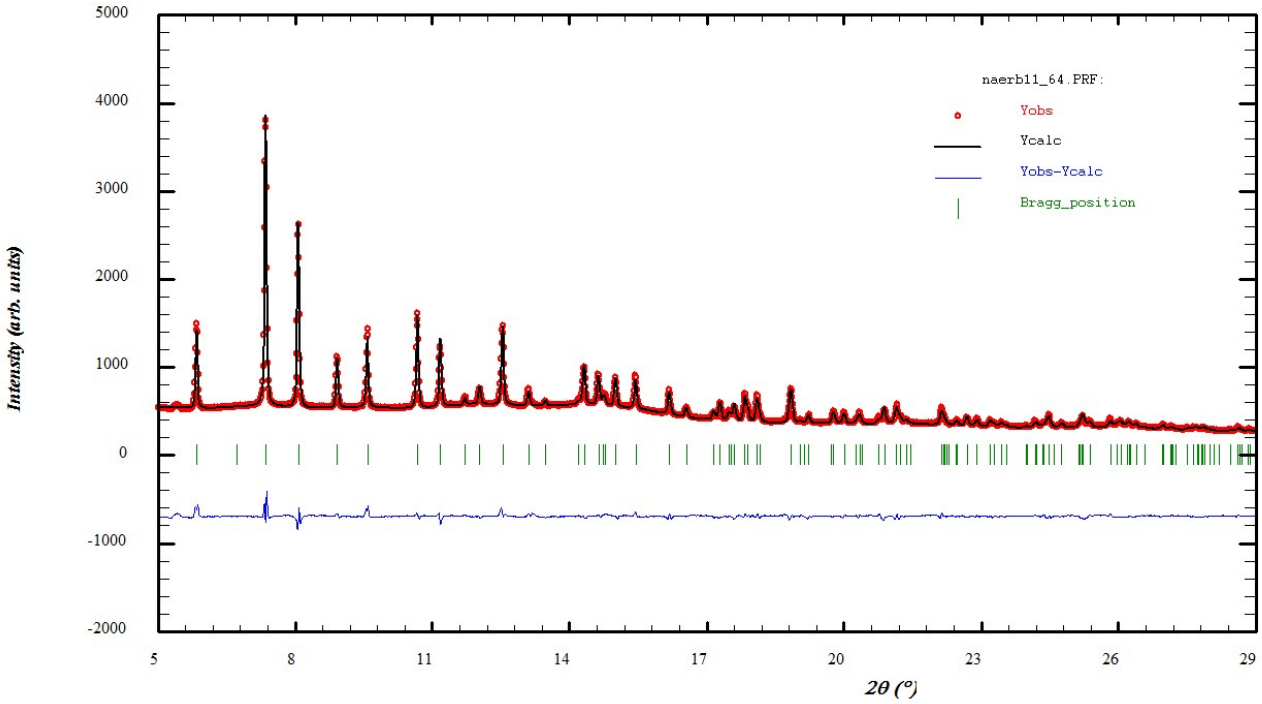

Figure S4 XRPD pattern and refinement of $NaEr(BH_4)_4$ (**s7**, λ = 0.7129) recorded at 122 °C (correct). Red line: experimental data; black line: calculated pattern, blue line: difference pattern. R_{wp} = 2.35% (not corrected for background), χ^2 = 190.

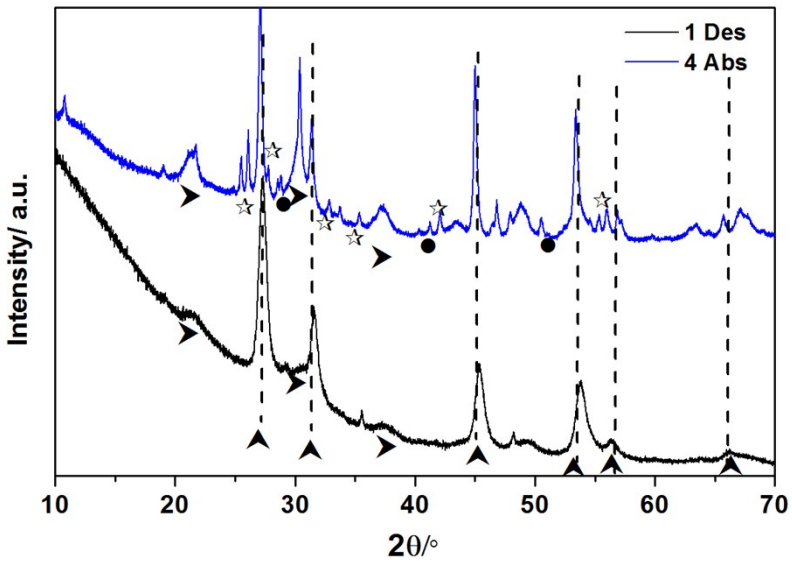

Figure S5 XRPD patterns (λ = 1.54056 Å) of $Ce(BH_4)_3$–$NaBH_4$ (1 : 1, **s1**) after first decomposition (black curve) and fourth absorption (blue curve). Symbols: ⑥, CeB_6; ⑦, CeH_{2+x}; ●; $NaBH_4$ and ☆ for U5.

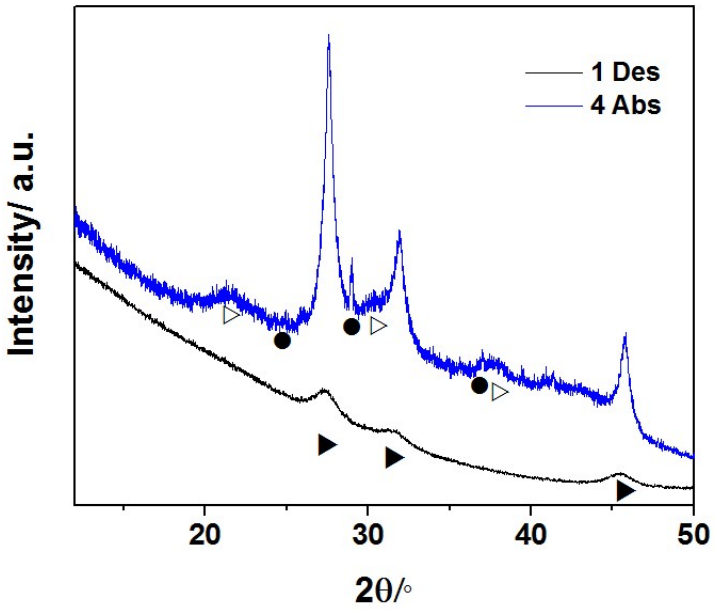

Figure S6 XRPD patterns (λ = 1.54056 Å) of $Pr(BH_4)_3$–$NaBH_4$ (1 : 1, **s3**) after first decomposition (black curve) and fourth absorption (blue curve). Symbols: ⬥, PrB_6; ◆, PrH_2 and ℘ for $NaBH_4$.

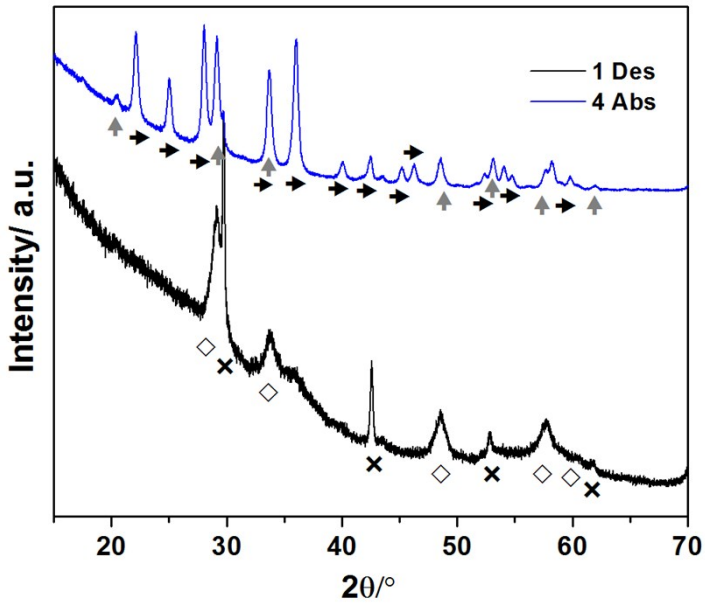

Figure S7 XRPD patterns (λ = 1.54056 Å) of $Er(BH_4)_3$–$NaBH_4$ (1 : 1, s7) after first decomposition (black curve) and fourth absorption (blue curve). Symbols: ❋, ErH_{2+x}; ⌀, Na; ○, ErB_4 and ◎ for Er_2O_3.

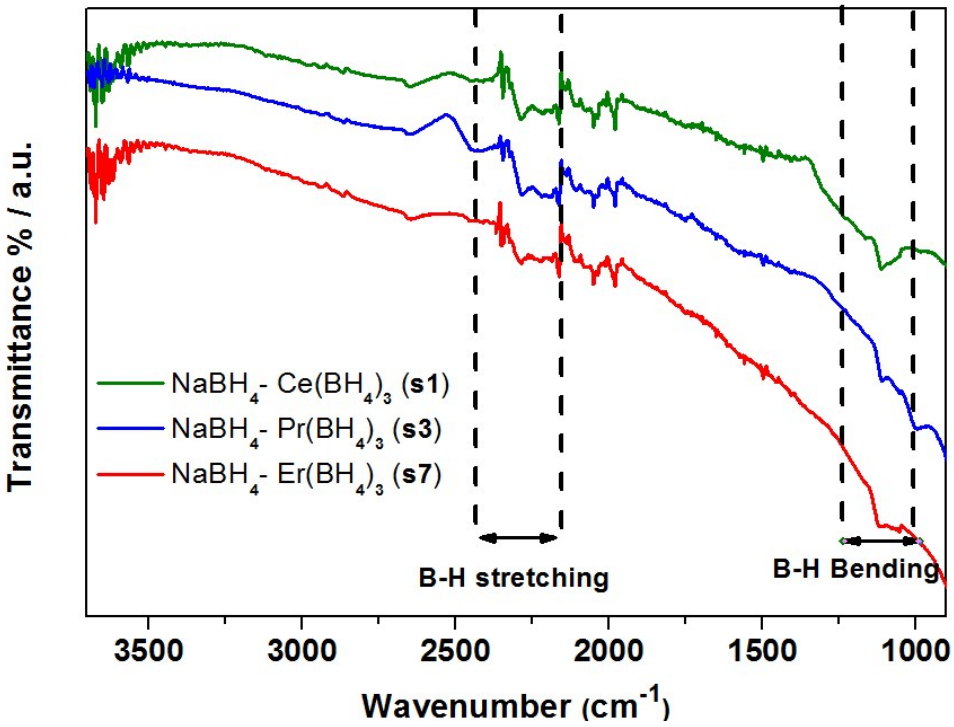

Figure S8 FT-IR spectra of $NaRE(BH_4)_4$, RE = Ce, Pr, Er, after fifth absorption. The FT-IR spectra of $NaBH_4$ is also presented as a reference.

Temperature programmed photographic analysis

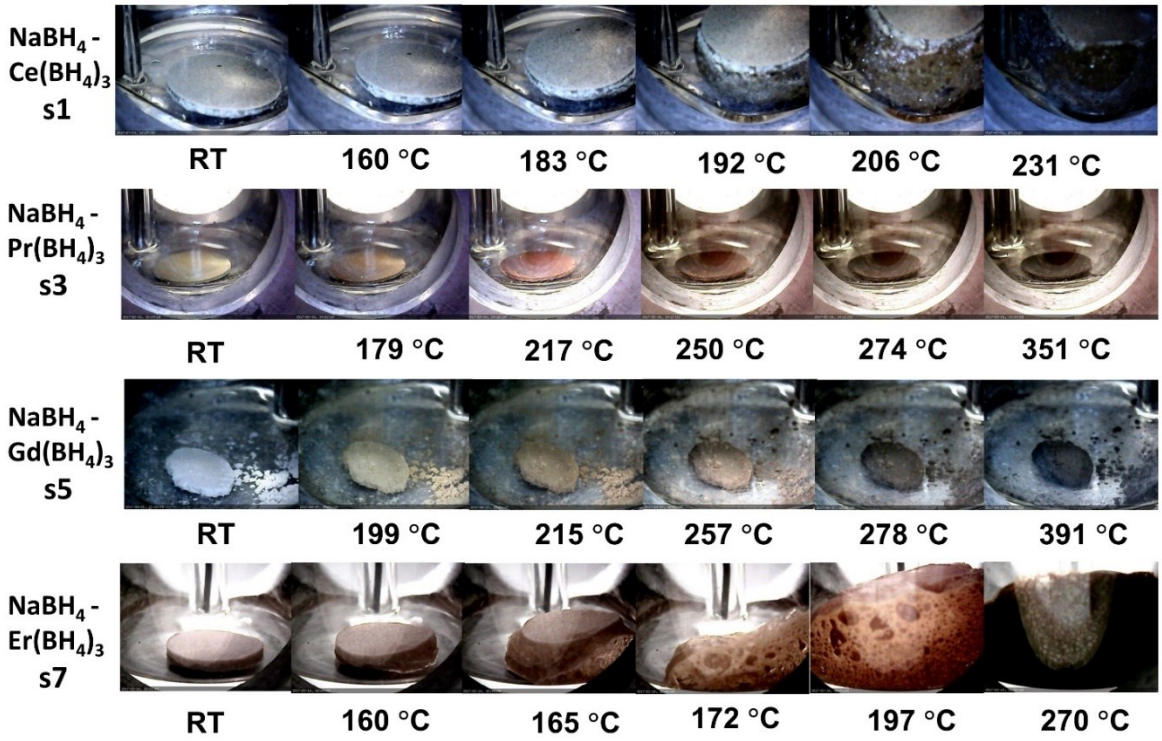

Figure S9 Temperature programmed photographic analysis of samples **s1**, **s3**, **s5** and **s7** ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

The behaviors of the samples **s1**, **s3**, **s5**, and **s7** during heat treatment are investigated by temperature programmed photographic analysis (TPPA) and are displayed in Figure S10. $NaBH_4$ - $Ce(BH_4)_3$ (1:1, **s1**) is a white powder at RT. At T ~ 170 °C the sample starts to melt and foam, which corresponds to the maximum diffracted intensity of $NaCe(BH_4)_4$ observed by *in-situ* XRPD. Foaming continues to T ~ 212 °C and further heating of the sample leads to decomposition at ~230 °C and the color change to black. The disappearance of the Bragg reflections at T = 187 °C in the *in-situ* XRPD is associated with the melting/foaming of the sample.

$NaBH_4$ - $Pr(BH_4)_3$ (1:1, **s3**) sample is light yellow at RT but changes to dark yellow at $T \sim 170$ °C associated with the formation of $NaPr(BH_4)_4$. At $T \sim 211$ °C, the pellet's color turns red, which corresponds to the formation of U4. At $T > 250$ °C, the sample obtain a black color due to decomposition. $NaBH_4$ - $Gd(BH_4)_3$ (1:1, **s5**) sample is white at RT. The pellet shrinks and the sample's color changes to yellow at $T \sim 199$ °C, which matches the formation of humps in the XRPD background data by quenching the sample at $T \sim 205$ °C and suggests the formation of a new unstable compound, see Figure 1.b. At $T > 270$ °C the sample turns black due to decomposition. TPPA shows that $NaBH_4$ - $Er(BH_4)_3$ (1:1, **s7**) is pink at RT and starts to melt/froth at $T \sim 165$ °C and significant volume expansion occurs at ~190 °C. At $T > 216$ °C, the sample starts to decompose and obtain a black color.