Supplementary Information

Reaction Pathways in $Ca(BH_4)_2$-$NaNH_2$ and $Mg(BH_4)_2$-$NaNH_2$ Hydrogen-Rich Systems

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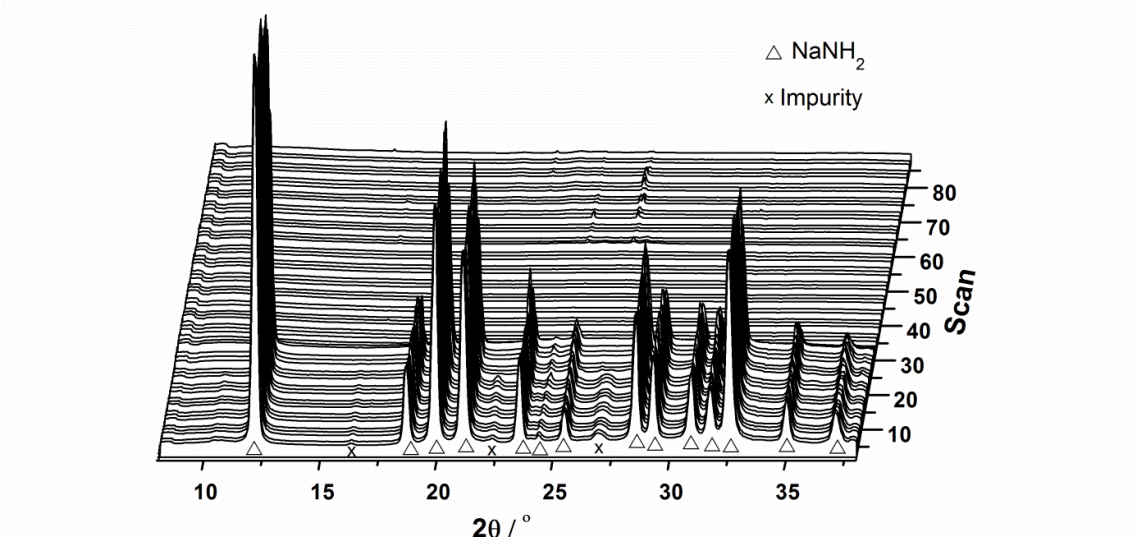

Figure S1. *In situ* SR-PXD on the pristine $NaNH_2$. Na_3N is not observed after the decomposition of $NaNH_2$, contrary the $Ca(BH_4)_2$-$NaNH_2$ samples. The impurity marked with the x sign is NaOH.

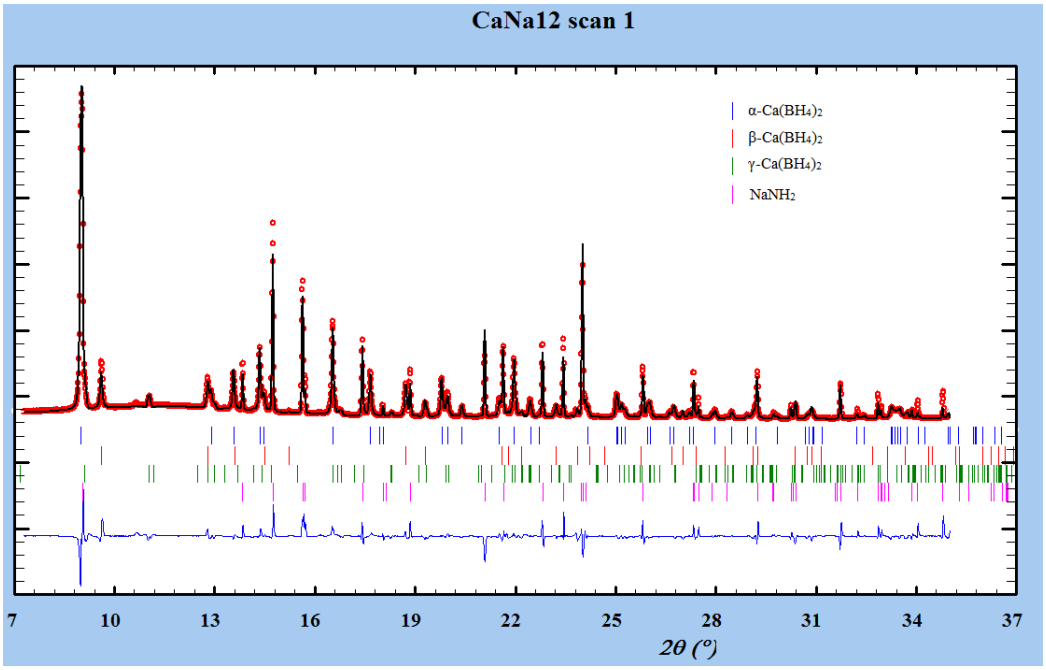

Figure S2: Rietveld fit of the first scan of the *in situ* SR-PXD of CaNa12. $NaNH_2$ could not be fitted very well due to its spottiness. (red circles are the data, black line is the model, blue line shows the residues)

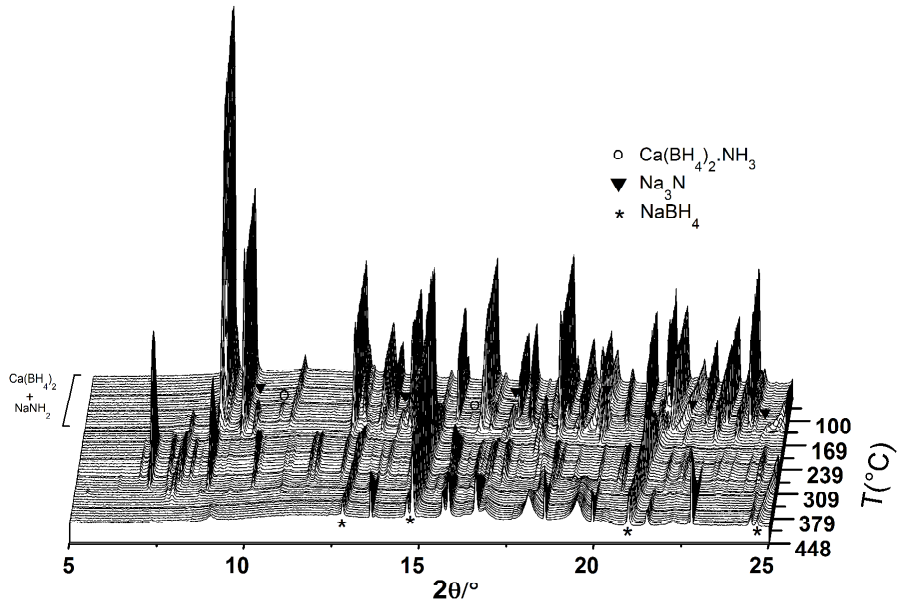

Figure S3. *In situ* SR-PXD on the CaNa11 sample.

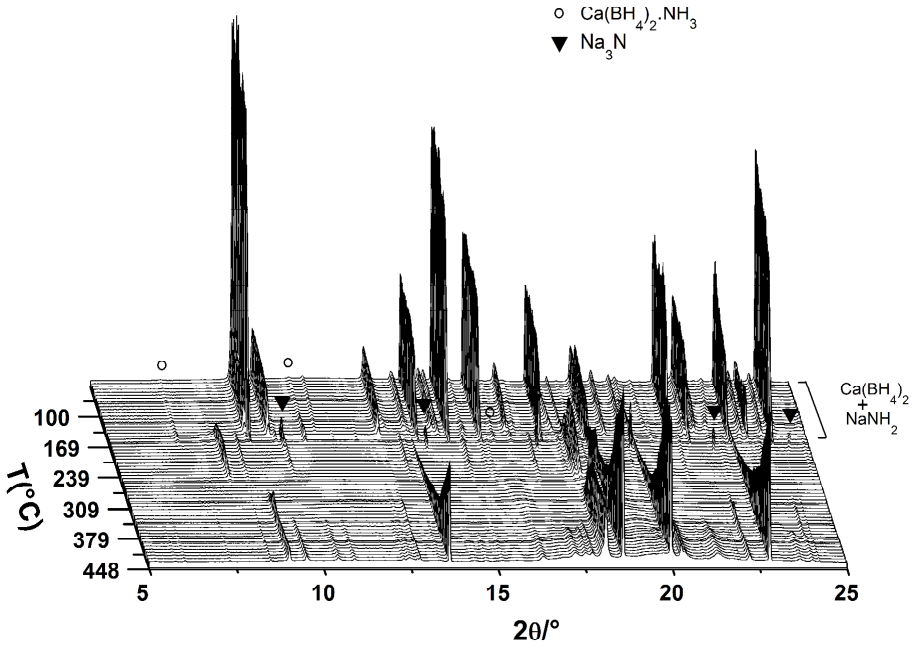

Figure S4. *In situ* SR-PXD on the CaNa13 sample.

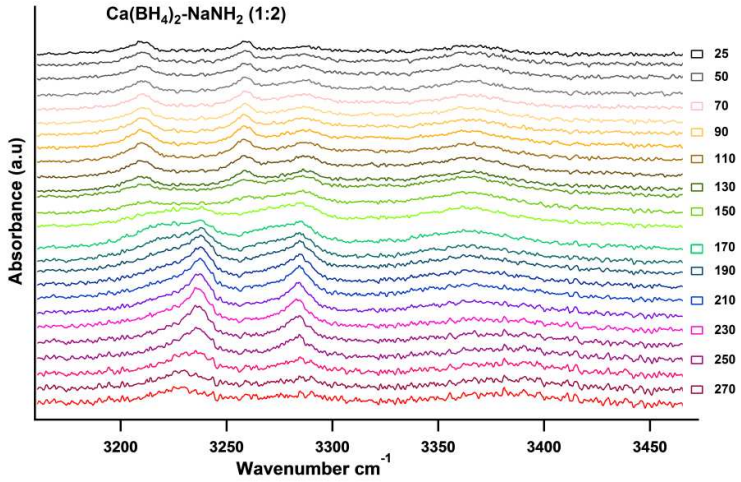

Figure S5. Expansion of the N-H stretching region of the *in situ* FT-IR data on CaNa12.

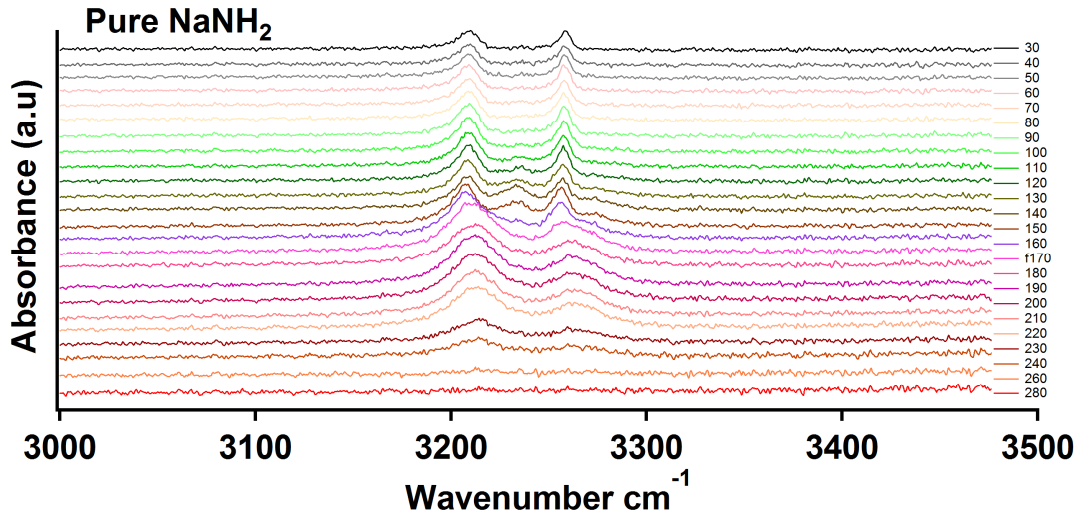

Figure S6: Temperature dependent FT-IR spectra of pure $NaNH_2$, focus on the N-H stretching bands. To the contrary of what happens in the CaNa12 sample, the bands remain centered at the same frequency up to the decomposition of the compound.

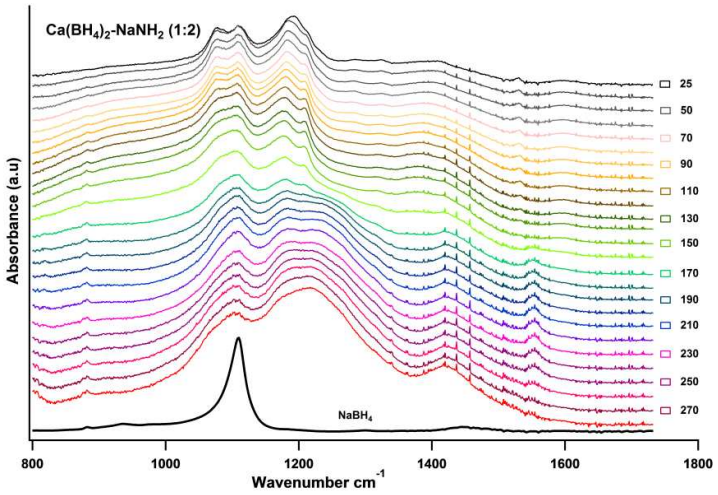

Figure S7. Expansion of the B-H bending region of the *in situ* FT-IR data on CaNa12.

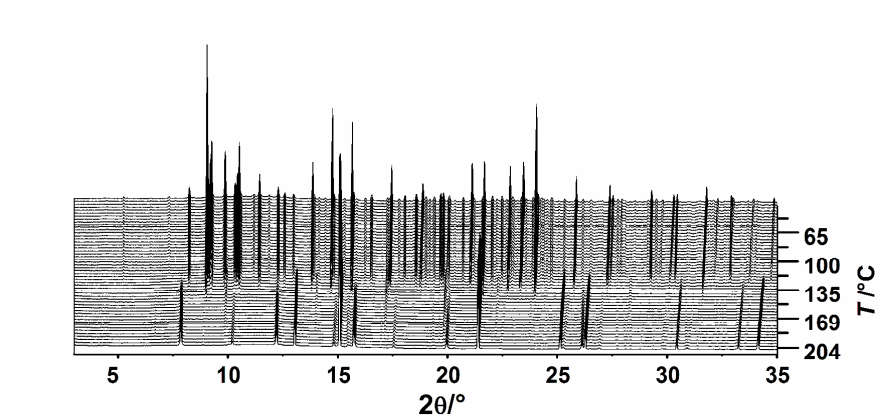

Figure S8. *In situ* SR-PXD on the MgNa12 sample. The starting materials disappear from the diffraction pattern around 135 °C, forming $NaBH_4$ and some other unknown material, similarly to the other samples.