Supplementary Materials

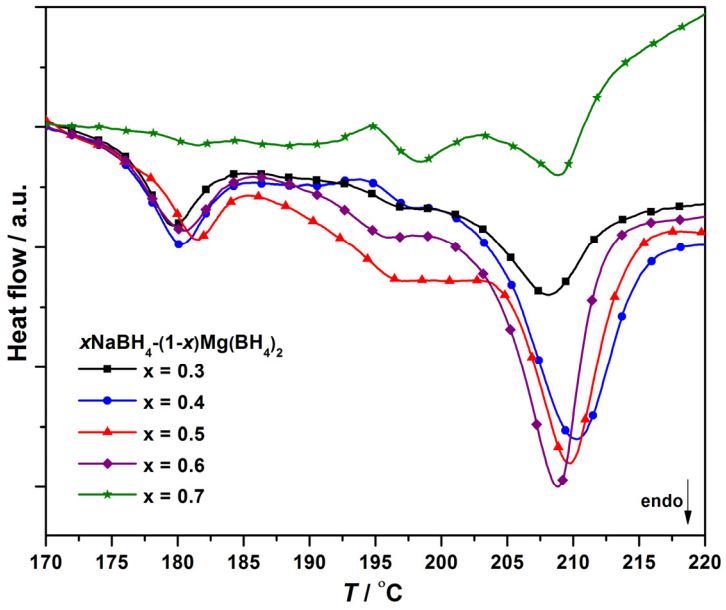

Figure S1. DSC data for selected samples of xNaBH4–(1 − x)Mg(BH4)2 showing the thermal events at 178 and 205 °C.

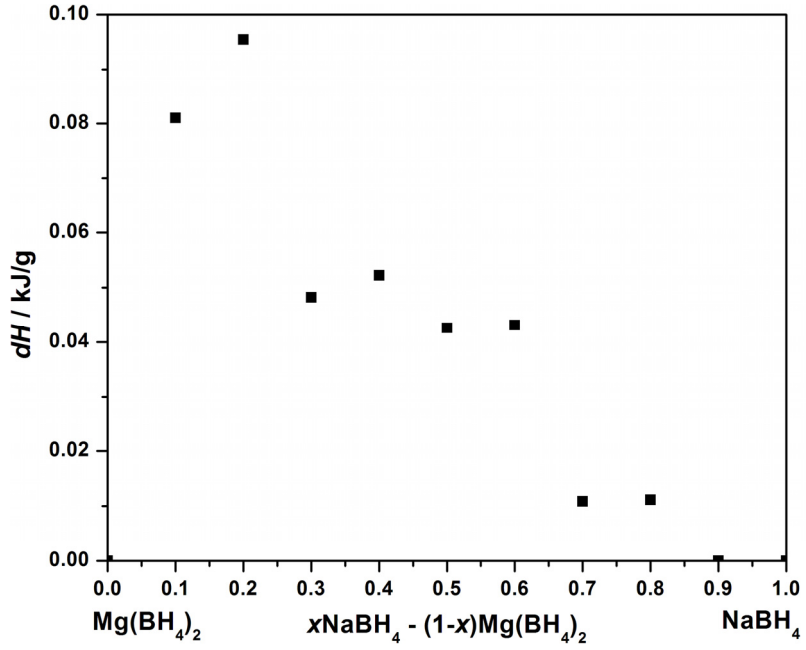

Figure S2. Integrated DSC signal in the temperature range of 175 to 186 °C of the endothermic event per sample mass for xNaBH4–(1 − x)Mg(BH4)2, x = 0 to 1.

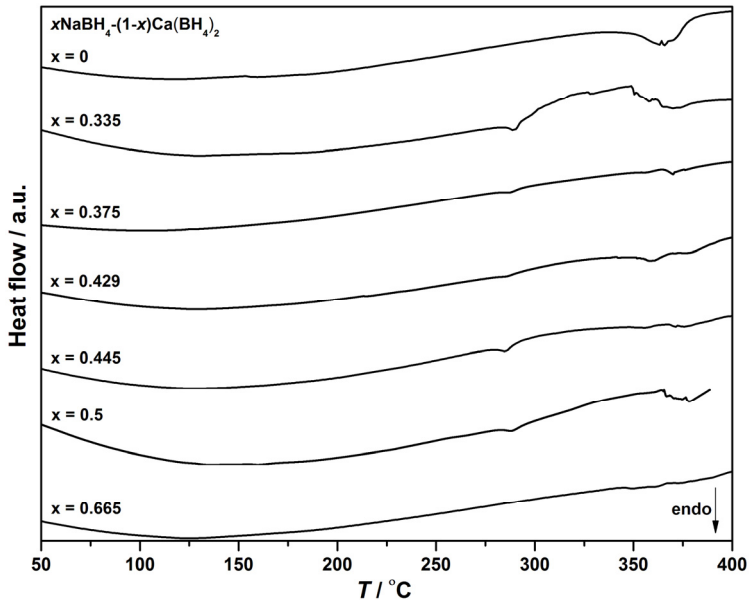

Figure S3. Normalized DSC curves of $Ca(BH_4)_2$ (x = 0) and $x NaBH_4$–$(1 - x)Ca(BH_4)_2$, x = 0.335 to 0.665, in the temperature range of 50 to 400 °C.

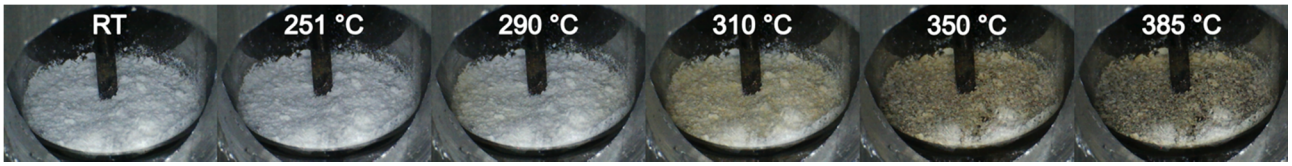

Figure S4. TPPA sequence for $0.5NaBH_4$–$0.5Mg(BH_4)_2$ at six selected temperatures between RT and 400 °C, $\Delta T/\Delta t$ = 5 °C/min, Ar atmosphere.

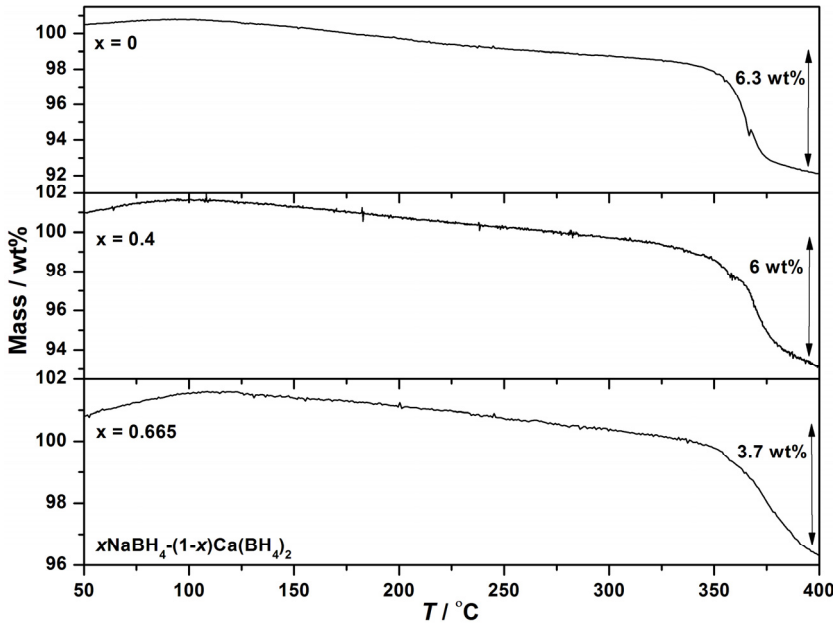

Figure S5. TGA data for selected samples of $x NaBH_4$–$(1 - x)Ca(BH_4)_2$.

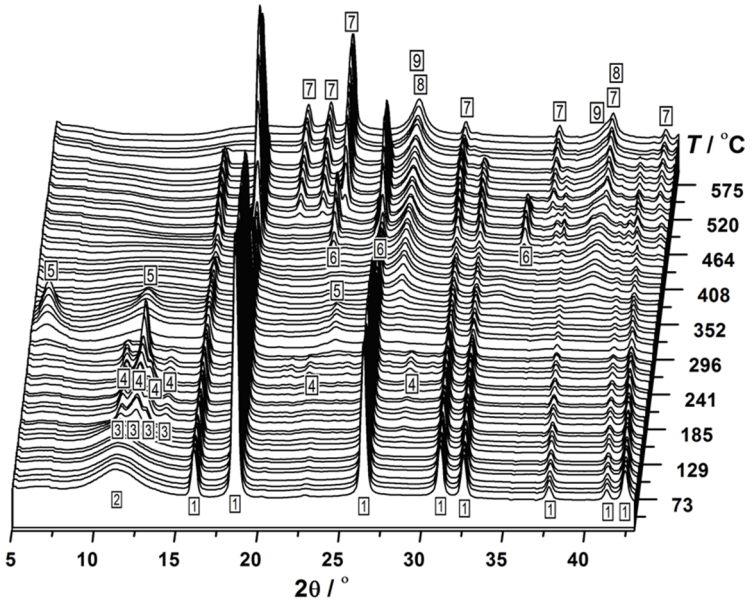

Figure S6. *In situ* SR-PXD data for $0.665NaBH_4–0.335Mg(BH_4)_2$ in the temperature range of RT to 600 °C ($\Delta T/\Delta t$ = 10 °C/min, p(Ar) = 1 bar, λ = 0.999991 Å). Symbols: 1, $NaBH_4$; 2, amorphous $Mg(BH_4)_2$; 3, α-$Mg(BH_4)_2$; 4, β-$Mg(BH_4)_2$; 5, Compound **1**; 6, MgH_2; 7, Mg; 8, MgO; 9, MgB_2.

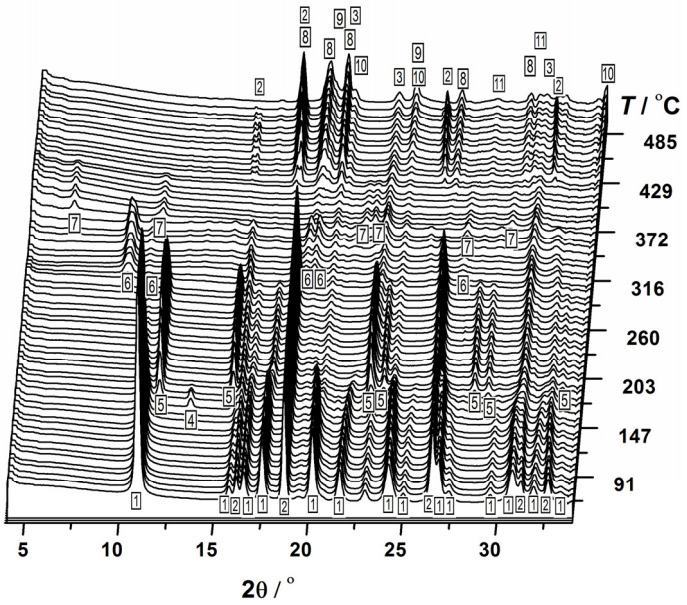

Figure S5. *In situ* SR-PXD data for $0.5NaBH_4–0.5Ca(BH_4)_2$ measured from RT to 500 °C ($\Delta T/\Delta t$ = 5 °C/min, p(Ar) = 1 bar, λ = 1.00355 Å). Symbols: 1, α-$Ca(BH_4)_2$; 2, $NaBH_4$; 3, WC; 4, γ-$Ca(BH_4)_2$; 5, β-$Ca(BH_4)_2$; 6, $Ca_3(BH_4)(BO_3)$; 7, **2**; 8, CaH_2; 9, CaB_6; 10, CaO; 11, $Ca_3(BO_3)_2$.

In situ SR-PXD data obtained for sample $0.5NaBH_4–0.5Ca(BH_4)_2$ are shown in Figure S7. Normalized diffracted intensities of selected Bragg peaks of the compounds are extracted as a function of temperature and displayed in Figure S8. The first SR-PXD pattern measured at RT for $0.5NaBH_4–0.5Ca(BH_4)_2$ reveals Bragg diffraction peaks from α-$Ca(BH_4)_2$ and $NaBH_4$ indicating that

the compound does not react during ball milling. The polymorphic phase change from α- to β-$Ca(BH_4)_2$ appears to occur via an intermediate, γ-$Ca(BH_4)_2$, which is observed in the temperature range ~125 to 180 °C [1]. The formation of γ-$Ca(BH_4)_2$ is associated with a minor decrease in the peak intensity for $NaBH_4$. At T = 290 °C, diffraction peaks from crystalline β-$Ca(BH_4)_2$ disappear, and $Ca_3(BH_4)_3(BO_3)$ forms instead [2]. Bragg peaks from $NaBH_4$ experience a significant decrease in intensity from 290 to 330 °C. Calcium borohydride borate, $Ca_3(BH_4)_3(BO_3)$, disappears at T ~ 350 °C, followed by the formation of another new compound, denoted **2**. Observation of **2** is characterized by 10 major Bragg reflections with *d*-spacing's 8.99, 5.21, 3.71, 3.39, 3.28, 3.01, 2.64, 2.59, 2.40 and 1.97 Å. It was not possible to obtain a satisfying indexing of the Bragg peaks belonging to unknown **2**. At T ~ 410 °C, diffraction from Compound **2** disappears in 0.5$NaBH_4$–0.5$Ca(BH_4)_2$, and peaks from the decomposition products CaH_2, CaB_6, $Ca_3(BO_3)_2$ and CaO are observed. Interestingly, an increase in diffracted intensity from $NaBH_4$ may be correlated with the decomposition of **2**. Crystalline $NaBH_4$ disappears at T = 480 °C, where also $Ca_3(BO_3)_2$ partly transforms to CaO.

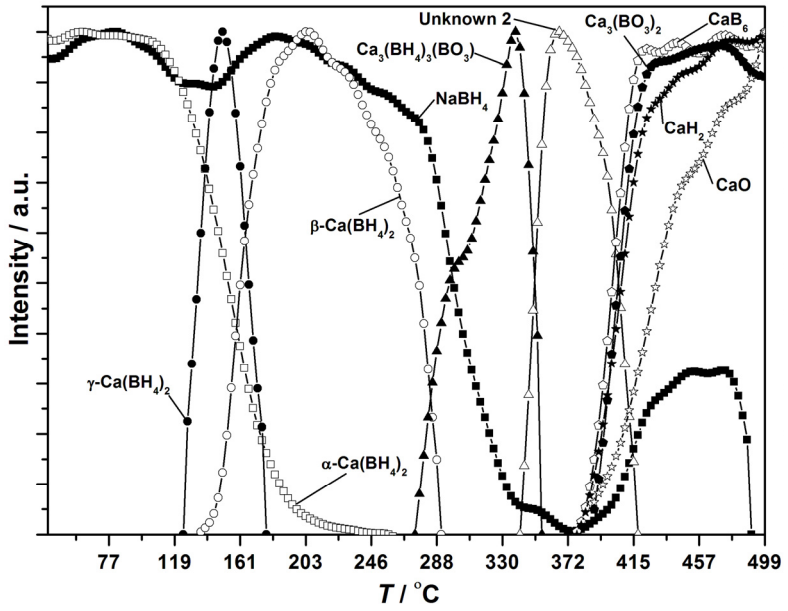

Figure S6. Normalized diffracted intensities of selected Bragg peaks from the compounds observed in the *in situ* SR-PXD study (Figure S7) of $NaBH_4$–α-$Ca(BH_4)_2$ 1:1. Legend: $NaBH_4$ (black square), α-$Ca(BH_4)_2$ (white square), γ-$Ca(BH_4)_2$ (black circle), β-$Ca(BH_4)_2$ (white circle), $Ca_3(BH_4)_3(BO_3)$ (black triangle), Compound **2** (white triangle), $Ca_3(BO_3)_2$ (black pentagon), CaB_6 (white pentagon), CaH_2 (black star), CaO (white star).

References

1. Filinchuk, Y.; Ronnebro, E.; Chandra, D. Crystal structures and phase transformations in $Ca(BH_4)_2$. *Acta Mater.* **2009**, *57*, 732–738.
2. Riktor, M.D.; Filinchuk, Y.; Vajeeston, P.; Bardají, E.G.; Fichtner, M.; Fjellvåg, H.; Sørby, M.H.; Hauback, B.C. The crystal structure of the first borohydride borate, $Ca_3(BD_4)_3(BO_3)$. *J. Mater. Chem.* **2011**, *21*, 7188–7193.