Supporting Information for:

Halide Substitution in Magnesium Borohydride

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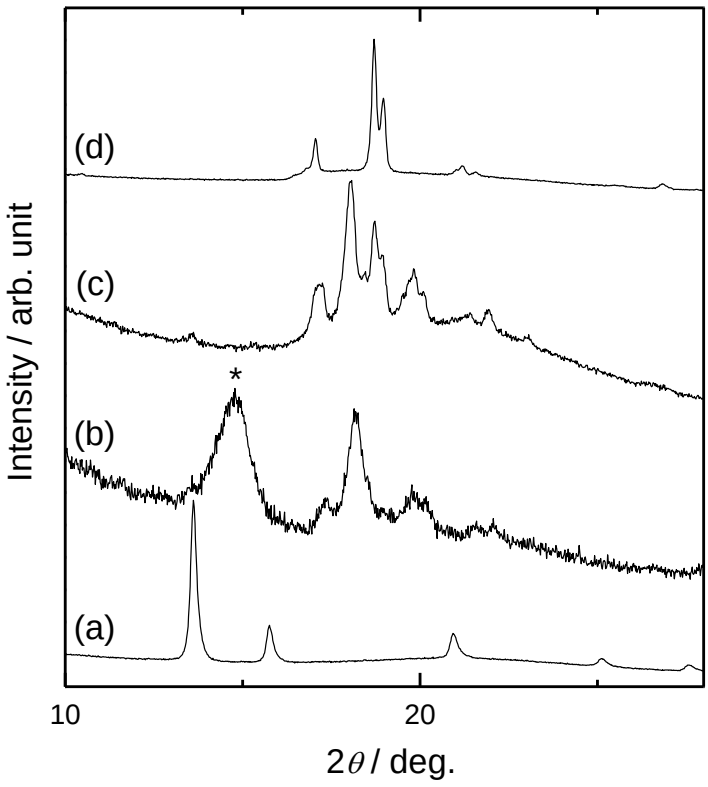


Figure S1. PXD-data (Cu Kα) for (a) as purchased γ-$Mg(BH_4)_2$ from Aldrich, (b) the mixture of as synthesized $Mg(BH_4)_2$ and $MgCl_2$ milled for 12 h at 505 rpm and annealed at 160 °C, (c) $Mg(BH_4)_2$ from Aldrich after heating at 170 °C (ε-polymorph), and (d) at 210 °C (β-polymorph). The peak marked with (*) comes from $MgCl_2$.

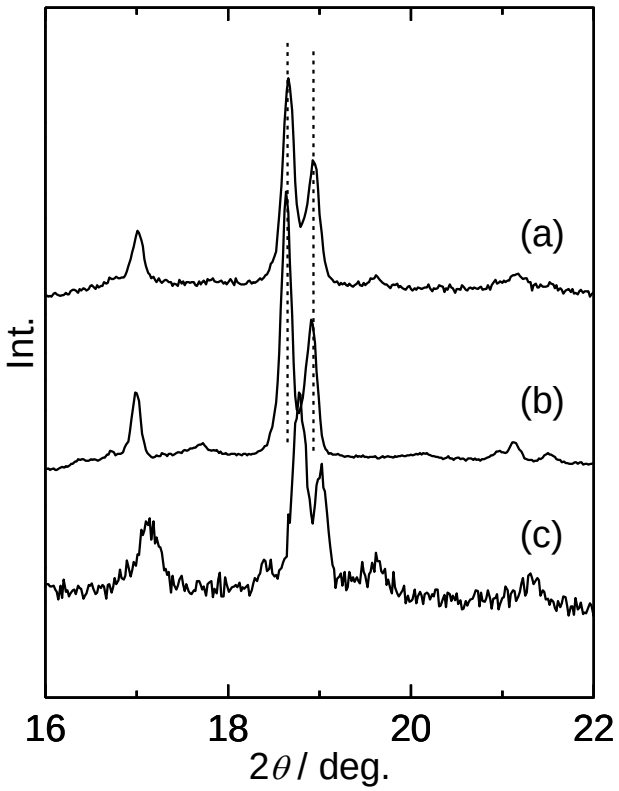


Figure S2. PXD-data (Cu Kα) for (a) $Mg(BH_4)_2$ after heating up to 300 °C, (b) $Mg(BH_4)_2$ milled for 12 h at 280 rpm and annealed for 10h at 200 °C, (c) the mixture of $Mg(BH_4)_2$ and $MgCl_2$ milled and annealed in the same condition.

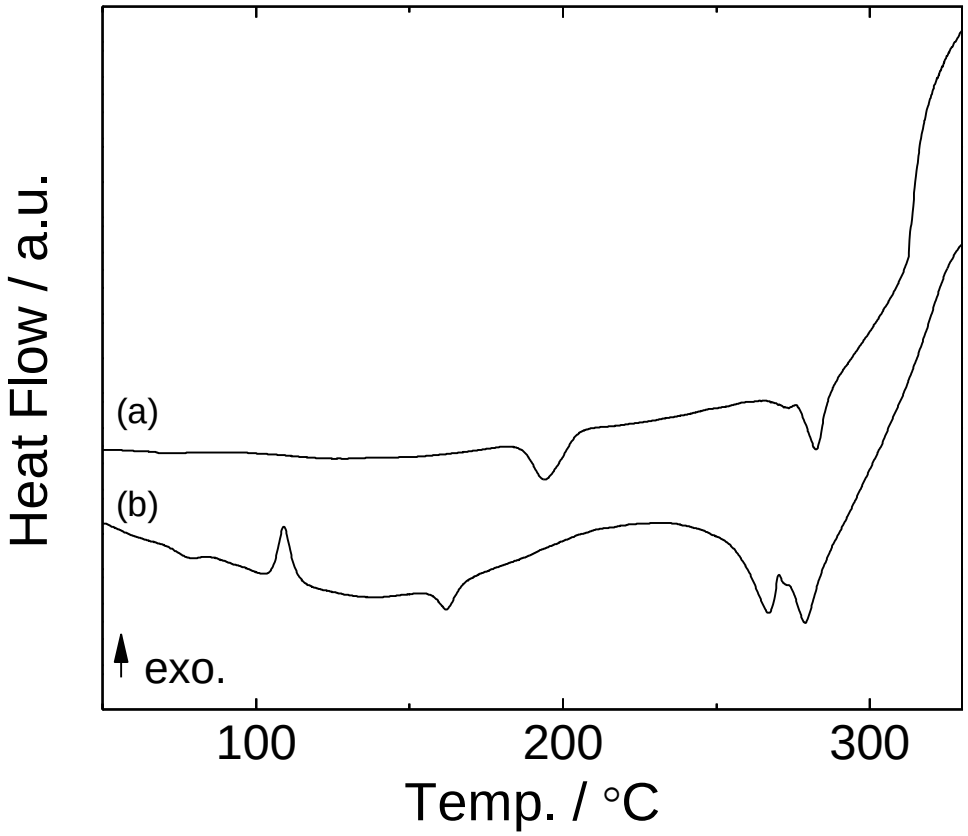


Figure S3. DSC profiles measured under 1 MPa H_2 for $Mg(BH_4)_2$ + $MgBr_2$ milled for 12 h with (a) 280 rpm and (b) 505 rpm. Heating rate is 2 °C/min.

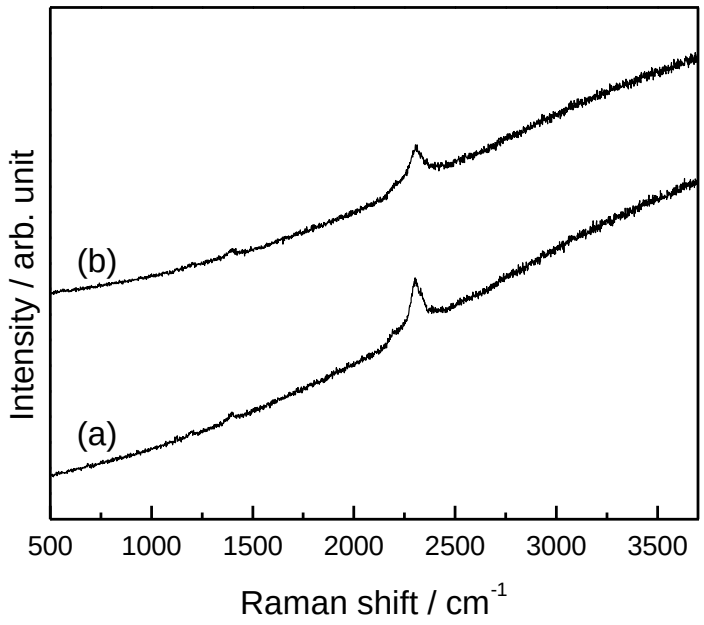


Figure S4. Raman spectra for (a) the mixture of $Mg(BH_4)_2$ and $MgCl_2$ milled for 12 h at 360 rpm and (b) at 505 rpm.

Complete author list:

Ref. 3 Rude, L. H.; Nielsen, T. K.; Ravnsbaek, D. B.; Bosenberg, U.; Ley, M. B.; Richter, B.; Arnbjerg, L. M.; Dornheim, M.; Filinchuk, Y.; Besenbacher, F.; Jensen, T. R. *Physica Status Solidi a-Applications and Materials Science* **2011**, *208*, 1754-1773.

Ref. 16 Rude, L. H.; Zavorotynska, O.; Arnbjerg, L. M.; Ravnsbæk, D. B.; Malmkjær, R. A.; Grove, H.; Hauback, B. C.; Baricco, M.; Filinchuk, Y.; Besenbacher, F.; Jensen, T. R. *Int. J. Hydrogen Energy* **2011**, *36*, 15664-15672.

Ref. 26 Dovesi, R.; Saunders, V. R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Pascale, F.; Civalleri, B.; Doll, K.; Harrison, N. M.; Bush, I. J.; D'Arco, P.; Llunell, M. *CRYSTAL2009 User's Manual*; University of Torino: Torino; 2009.