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Electronic Supplementary Information

Hydrides of early transition metals as catalysts and grain growth inhibitors for enhanced reversible hydrogen storage in nanostructured magnesium

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Figure S1 displays the graphical output of the Rietveld analysis of 95MgH_2+*ETM*H_x nanocomposites after RBM synthesis. All patterns can be indexed with main contribution of two MgH_2 polymorphs (rutile-type β-MgH_2 and orthorhombic γ-MgH_2) and one or two hydride phases *ETM*H_x namely δ-ScH_2, ε-YH_3, ε-TiH_2, ε-ZrH_2, β_2-VH, and coexistence of β-NbH and δ-NbH_2 for *ETM* = Sc, Y, Ti, Zr, V, Nb, respectively. Crystallographic data results of the Rietveld analysis are given in Table 2.

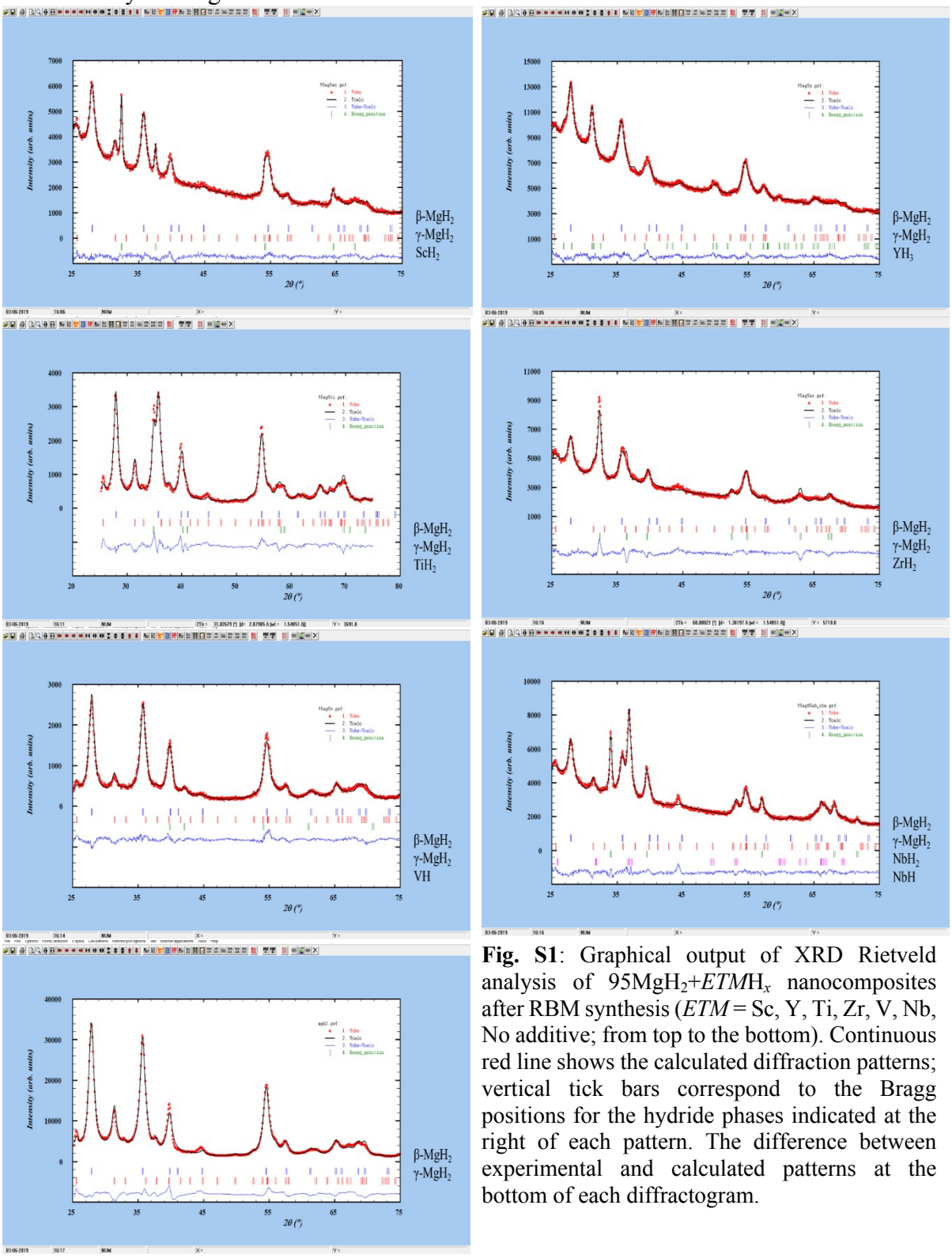

Fig. S1: Graphical output of XRD Rietveld analysis of 95MgH_2+*ETM*H_x nanocomposites after RBM synthesis (*ETM* = Sc, Y, Ti, Zr, V, Nb, No additive; from top to the bottom). Continuous red line shows the calculated diffraction patterns; vertical tick bars correspond to the Bragg positions for the hydride phases indicated at the right of each pattern. The difference between experimental and calculated patterns at the bottom of each diffractogram.

Figure S2 displays the graphical output of the Rietveld analysis of $95MgH_2$+*ETM*H_x nanocomposites after 20th absorption sweep. All patterns can be indexed with main contribution of rutile-type β-MgH_2 phase, α-Mg and one hydride phase *ETM*H_x namely δ-ScH_2, ε-YH_3, ε-TiH_2, ε-ZrH_2, β_2-VH, and β-NbH for *ETM* = Sc, Y, Ti, Zr, V, Nb, respectively. Crystallographic data results of the Rietveld analysis are given in Table 3.

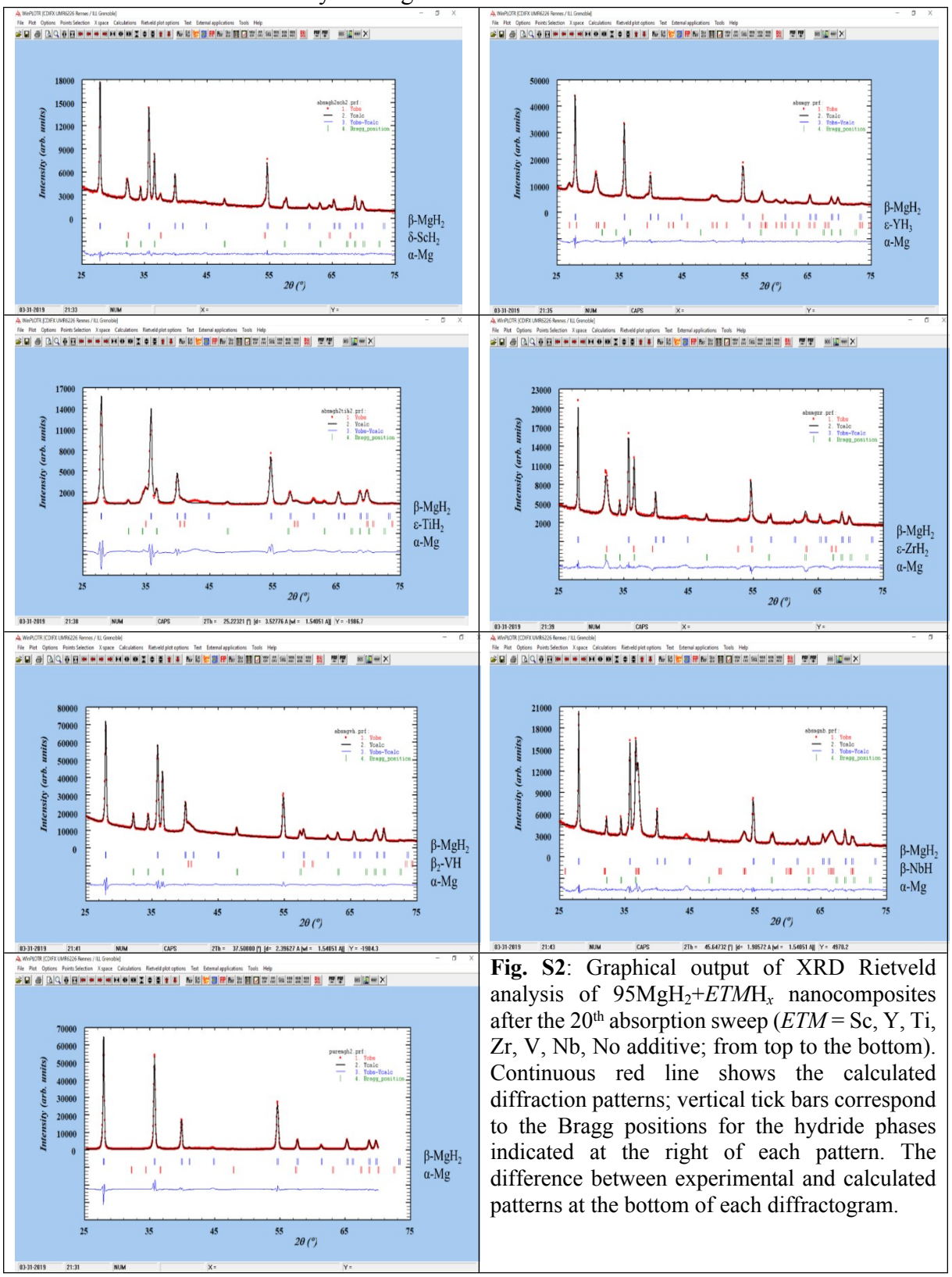

Fig. S2: Graphical output of XRD Rietveld analysis of $95MgH_2$+*ETM*H_x nanocomposites after the 20th absorption sweep (*ETM* = Sc, Y, Ti, Zr, V, Nb, No additive; from top to the bottom). Continuous red line shows the calculated diffraction patterns; vertical tick bars correspond to the Bragg positions for the hydride phases indicated at the right of each pattern. The difference between experimental and calculated patterns at the bottom of each diffractogram.

Table S1 gathers molar volumes, V_m, for all ETMH$_x$ hydride phases involved in this study and their relative difference compared to α-Mg and β-MgH_2. Low relative differences are favorable for interface coupling between phases. Good volume mismatch between α-Mg and ETMH$_x$ hydride phases (*e.g.* Mg/TiH_2) inhibits crystal growth of Mg phase. Good volume mismatch between β-MgH_2 and ETMH$_x$ hydride phases (*e.g.* MgH_2/ZrH_2) lowers the energy barrier for nucleation of β-MgH_2 at Mg/ ETMH$_x$ interfaces.

Table S1. Crystal density*(d), molar weight (W_m), molar volume (V_m), relative volume difference between Mg and ETMH$_x$ hydrides (($V_{m,Mg}$ - V_m)/ V_m) and relative volume difference between MgH_2 and ETMH$_x$ hydrides ((V_{m,MgH_2} - V_m)/ V_m)*.

	D	W_m	V_m	$(V_{m,Mg}-V_m)/V_m$	$(V_{m,MgH_2}-V_m)/V_m$
Compound	g/cm³	g/mol	cm³/mol	%	%
Mg	1.76	24.3	13.8	-	-
β-MgH_2	1.43	26.3	18.4	-	-
δ-ScH_2	2.86	47.0	16.4	-16	12
ε-YH_3	3.96	91.9	23.2	-41	-21
ε-TiH_2	3.77	49.9	13.2	4	39
ε-ZrH_2	5.63	93.2	16.6	-17	11
β_2-VH	5.53	52.6	9.5	45	93
β-NbH	7.56	93.9	12.4	11	48

*Crystal densities extracted from P. Villars, K. Cenzual, Pearson's Crystal Data – Crystal structure database for inorganic compounds (on DVD), Release 2018/19, ASM International, Materials Park, Ohio, USA