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High Pressure Synthesis of New Hydrogen Storage Materials

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Introduction

The goal of the project was to synthesize new and inexpensive lightweight metal hydrides by exploring very high-pressure techniques. A useful benchmark is the complex metal hydride Mg_2FeH_6 that can be obtained by application of ordinary hydrogen gas pressure (≈ 50 bar) and by ball milling. The compound has a volume efficiency for hydrogen storage (150 g H/liter) that exceeds that of liquid hydrogen (71 g H/liter) by a factor of two, has a weight efficiency of 5.5 wt.%, and is cheap to fabricate. It has been shown to be useful for thermal energy storage at high temperature ($\approx 450^\circ\text{C}$), but it is thermally too stable for reversible hydrogen storage applications at room temperature (decomposition temperature at 1 bar hydrogen pressure 320°C). The question was whether thermally less stable complex (or saline) metal hydrides could be stabilized by application of very high-pressure techniques (≈ 50 kbar).

Summary of Results

During this project, over thirty new complex and saline metal hydrides have been discovered. Most have been synthesized in a multi-anvil pressure cell under quasi-hydrostatic pressure, in particular the saline hydrides, but some have also been obtained in autoclaves under normal hydrogen gas pressure. The compositions and hydrogen storage properties of the various compounds are summarized in Table I (complex metal hydrides) and Table II (saline metal hydrides). Most contain magnesium as the primary constituent.

Among the newly found complex metal hydrides, the most interesting is manganese based Mg_3MnH_7 [1]. The compound has been prepared in collaboration with V. Verbetzky at Lomonosov University in Moscow by application of a hydrostatic pressure of ~ 20 kbar at $\sim 700^\circ\text{C}$. It has a reddish color and contains the first known hexahydridomanganese(I) complex $[\text{MnH}_6]^{5-}$ (see Figure 1). The $[\text{MnH}_6]^{5-}$ complex is iso-electronic with the 18 electron $[\text{FeH}_6]^{4-}$ complex in Mg_2FeH_6 and is the first such example known for manganese. The hydrogen storage efficiencies of Mg_3MnH_7 are promising: 5.2 wt.% and 119 g H/liter (i.e. twice as much as liquid hydrogen). The compound is presumably cheap to fabricate and thermally less stable than Mg_2FeH_6 . It decomposes at $\sim 250^\circ\text{C}$ under 1 bar hydrogen pressure into elemental manganese and magnesium. Attempts to decrease the decomposition temperature further by suitable catalysts and/or preparation methods (ball milling) have so far not been successful.

Attempts to substitute magnesium partially by other alkaline earth elements such as calcium resulted in the discovery of the first quaternary metal hydrides. Although the hydrogen storage efficiencies of compounds such as $\text{Ca}_4\text{Mg}_4\text{Fe}_3\text{H}_{22}$ are comparable to those of Mg_2FeH_6 , their thermal stability is still too high for reversible hydrogen storage applications near room temperature.

Attempts to synthesize hydrides containing other cheap 3d transition metals such as copper resulted in the discovery of $\text{Ba}_7\text{Cu}_3\text{H}_{17}$. The compound is the first copper based complex metal hydride. Its trigonal structure contains tetrahedral 18-electron $[\text{Cu(I)H}_4]^{3-}$ anions and desorbs hydrogen at room temperature. However, its hydrogen storage efficiency is relatively low (1.5 wt.%, 63 g H/liter). New complex 3d transition metal hydrides were also found with zinc. The orthorhombic compound K_2ZnH_4 , for example, contains tetrahedral $[\text{ZnH}_4]^{2-}$ complexes. Its hydrogen storage efficiency is 2.7 wt.% (57 g H/liter) and it desorbs hydrogen at 310°C .

Table I: Complex transition metal hydrides

Formula	Anions	Hydrogen Density (wt.%)	(g/liter)	Desorption Temperature (1bar)
BaReH ₉	[ReH ₉] ²⁻	2.7	134	<100°C
NaKReH ₉	[ReH ₉] ²⁻	3.5	117	<100°C
Mg ₃ MnH ₇	[MnH ₆] ⁵⁻ , H ⁻	5.2	119	~280°C
Mg ₂ FeH ₆	[FeH ₆] ⁴⁻	5.5	150	320°C
Ca ₄ Mg ₄ Fe ₃ H ₂₂	[FeH ₆] ⁴⁻ , 4H ⁻	5.0	122	395°C
SrMg ₂ FeH ₈	[FeH ₆] ⁴⁻ , 2H ⁻	4.0	115	440°C
LiMg ₂ RuH ₇	[RuH ₆] ⁴⁻ , H ⁻	4.3	113	>400°C
LiMg ₄ Os ₂ H ₁₃	[OsH ₆] ⁴⁻ , H ⁻	2.6	121	>400°C
BaMg ₂ RuH ₈	[RuH ₆] ⁴⁻ , 2H ⁻	2.7	98	>400°C
Mg ₃ RuH ₃	[Ru ₂ H ₆] ¹²⁻	1.7	54	>400°C
Mg ₂ RuH ₄	[RuH ₄] _n ⁴ⁿ⁻	2.6	95	>400°C
Mg ₂ CoH ₅	[CoH ₅] ⁴⁻	4.5	126	280°C
Mg ₆ Co ₂ H ₁₁	[CoH ₄] ⁵⁻ , 3H ⁻	4.0	97	370°C
Ca ₄ Mg ₄ Co ₃ H ₁₉	[CoH ₅] ⁴⁻ , 4H ⁻	4.2	106	>480°C
Mg ₂ NiH ₄	[NiH ₄] ⁴⁻	3.6	98	280°C
CaMgNiH ₄	[NiH ₄] ⁴⁻	3.2	87	405°C
LiSr ₂ PdH ₅	[PdH ₃] ³⁻	1.7	74	>400°C
Ba ₇ Cu ₃ H ₁₇	[CuH ₄] ³⁻ , 5H ⁻	1.5	63	20°C
K ₂ ZnH ₄	[ZnH ₄] ²⁻	2.7	57	310°C
K ₃ ZnH ₅	[ZnH ₄] ²⁻ , H ⁻	2.7	56	360°C
α-MgH ₂		7.7	109	280°C
H ₂ (liquid)		100	71	-253°C

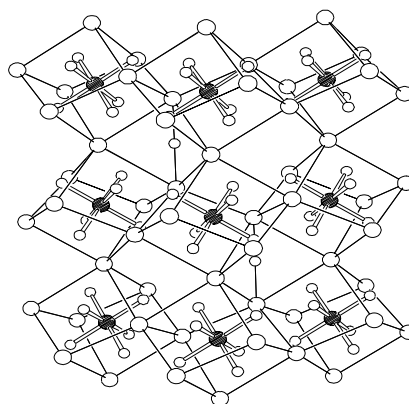


Figure 1 - Structure of Mg₃MnH₇ viewed perpendicular to the hexagonal axis; open circles Mg (large) and H (small), filled circles Mn.

Table II: Saline metal hydrides

Compound	Analogues	Hydrogen Density (wt. %)	(g/liter)	Desorption Temperature (1 bar)
LaMg ₂ H ₇	<i>CeMg₂H₇</i>	3.6	119	220°C
Ca ₄ Mg ₃ H ₁₄	<i>Yb₄Mg₃H₁₄</i>	5.7	99	>400°C
Ca ₁₉ Mg ₈ H ₅₄	<i>Yb₁₉Mg₈H₅₄</i>	5.4	101	~400°C
SrMgH ₄	<i>BaMgH₄, EuMgH₄</i>	3.5	89	>400°C
Sr ₂ Mg ₃ H ₁₀	<i>Ba₂Mg₃H₁₀</i>	3.9	95	>400°C
Ba ₆ Mg ₇ H ₂₆	<i>M₂ZnH₄ (M=K,Rb,Cs)</i>	2.6	84	>400°C
Rb ₂ MgH ₄		2.0	46	320°C
Rb ₃ MgH ₅	<i>M₃ZnH₅ (M=K,Rb,Cs), Cs₃CdH₅</i>	1.8	43	320°C
CsCaH ₃		1.7	51	?
RbMgH ₃		2.7	70?	?
Rb ₄ Mg ₃ H ₁₀		2.4	57	?
Sr ₂ MgH ₆		2.9	91	?
EuMg ₂ H ₆	<i>Eu₂MgH₆, Ba₂MgH₆</i>	2.9	88	?
α-MgH ₂		7.7	109	280°C
H ₂ (liquid)		100	71	-253°C

An overview of the known transition metal complexes in metal hydrides is given in Table III. Clearly, those based on the light (and cheap) 3d elements are the most promising. Most complexes conform to the 18-electron rule and thus help to predict possible compositions of new metal hydrides.

Table III: Transition metal - hydrogen complexes

Mn	Fe	Co	Ni	Cu	Zn
[MnH ₄] ²⁻	[FeH ₆] ⁴⁻	[CoH ₄] _{av} ⁵⁻	[NiH ₄] ⁴⁻	[CuH ₄] ³⁻	
[ZnH ₄] ²⁻	[MnH ₆] ⁵⁻	[CoH ₅] ⁴⁻			
Tc	Ru	Rh	Pd	Ag	Cd
[TcH ₉] ²⁻	[RuH ₃] ⁶⁻	[RhH ₄] ³⁻	[PdH ₂] ²⁻		[CdH ₄] ²⁻
	[RuH ₄] _n ⁴ⁿ⁻	[RhH ₆] ³⁻	[PdH ₃] ³⁻		
	[RuH ₅] _{av} ⁵⁻		[PdH ₄] ²⁻		
	[RuH ₆] ⁴⁻		[PdH ₄] ⁴⁻		
Re	Os	Ir	Pt	Au	Hg
[ReH ₆] ⁵⁻	[OsH ₆] ⁴⁻	[IrH ₅] _{av} ⁴⁻	[PtH ₄] ²⁻		
[ReH ₉] ²⁻		[IrH ₆] ³⁻	[PtH ₆] ²⁻		
			[Pt ₂ H ₉] ⁵⁻		

Among the salt-like metal hydrides emphasis was placed on ternary combinations with magnesium. Magnesium itself forms a dihydride that has favorable hydrogen storage efficiencies (7.7 wt.%, 106 g H/liter), but has low kinetics and is thermally relatively stable. The most interesting ternary hydrides among the newly found compounds are $\text{Ca}_{19}\text{Mg}_8\text{H}_{54}$ [2] and LnMg_2H_7 (Ln = La, Ce) [3]. $\text{Ca}_{19}\text{Mg}_8\text{H}_{54}$ is the second known ternary metal hydride in the Ca-Mg-H system (the other being $\text{Ca}_4\text{Mg}_3\text{H}_{14}$). It crystallizes with a cubic structure and shows hydrogen storage efficiencies (5.4 wt.%, 101 g/liter) that come close to those of MgH_2 . Unfortunately its hydrogen decomposition temperature (380-430°C at 5 bar) is higher than that of MgH_2 (280°C at 1 bar). The tetragonal Laves phase derivatives LnMg_2H_7 (Ln = La, Ce) have the highest known hydrogen-to-metal ratio for this family of compounds. Their hydrogen storage efficiencies reach 3.6 wt.% (116 g H/liter), and the compounds decompose at about 220°C.

Finally, a *Hydride Fluoride Crystal Structure Database (HFD)* has been established [4]. It helps to predict new metal hydrides by making use of the structural analogy between metal hydrides and metal fluorides. The compilation is critical and comprehensive, and contains so far 1150 entries. It is critical as only refined crystal structures are considered and the data are checked for internal consistency, and it is comprehensive as all major scientific journals are covered. This database may be ultimately included in the spectrum of on-line IEA/DOE/SNL hydride databases.

Conclusion and Outlook

High-pressure methods have proven to be a valuable tool for the synthesis of new metal hydrides. Some of the newly discovered compounds have excellent hydrogen storage efficiencies, are cheap to fabricate, but decompose only at relatively high temperature (i.e. Mg_3MnH_7 , $\text{Ca}_{19}\text{Mg}_8\text{H}_{54}$), while others decompose at low temperature, but are too heavy and/or too expensive for commercial applications (i.e. $\text{Ba}_7\text{Cu}_3\text{H}_{17}$, BaReH_9). Clearly future work must concentrate on the search for compounds capable of meeting both requirements. The prospects of finding such compounds are good because the potential of metal hydrides, in particular those containing 3d transition metal complexes, is far from exhausted. Although their thermal stability cannot be predicted, guidelines exist that make their search easier. On the other hand, catalyzed desorption experiments, if successful, will also contribute to opening up the class of complex metal hydrides for reversible hydrogen storage applications at or near room temperature.

References

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