

The European Marie Curie Research Training Network COSY “Complex Solid State Reactions for Energy Efficient Hydrogen Storage”

1. Overview

The European Marie Curie Research Training Network COSY “Complex Solid State Reactions for Energy Efficient Hydrogen Storage” ran from November 2006 to October 2010.

It comprised **13 research institutions** from Spain ([Instituto de Ciencia de Materiales de Sevilla](#), Prof. Dr. Asunción María Fernández Camacho; [Universitat Autònoma de Barcelona](#), Prof. Dr. Maria Dolors Baró Mariné), Italy ([Universita di Torino](#), Prof. Marcello Baricco), France ([European Synchrotron Facility, Grenoble](#), Dr. Gavin Vaughan; [Grenoble Institute of Technology](#), Prof. Alain Reza Yavari; [Laboratoire de Réactivité et de Chimie des Solides LRCS, Amiens](#), Dr. Aline Rougier), the United Kingdom ([University of Oxford](#), Prof. John Sykes), Switzerland ([EMPA, Dübendorf](#), Prof. Dr. Andreas Züttel), the Netherlands ([Vrije Universiteit, Amsterdam](#), Prof. Bernard Dam, now with TU Delft; [Universiteit Twente](#), Dr. Geert H.L.A. Brocks) and Germany ([Leibniz-Institute for Solid State and Materials Research Dresden](#), Dr. Oliver Gutfleisch; [Karlsruhe Institute of Technology](#), Dr. Wiebke Lohstroh; [Helmholtz-Zentrum Geesthacht](#), Dr. Martin Dornheim).

Dr. Klaus Taube (GKSS, now [Helmholtz-Zentrum Geesthacht](#)) was the Coordinator of the Network.

These partners worked together with the aim of **characterization and optimization of novel light weight hydride composites**. The results can be the basis for further optimisation of such materials for mobile hydrogen storage applications, e.g. in tanks for emission-free automobiles.

Research topics included the **production** of metal hydride composites by different methods, their **characterization** with respect to the relevant application properties, e.g. hydrogen sorption kinetics and thermodynamics, the influence of additives as well as of the microstructure, as well as **ab initio calculations** of stable and hypothetical structures.

One of the main tasks of COSY was the **education** of early stage researchers (ESR) and young more experienced researchers (ER) in the field of hydrogen storage materials. Therefore COSY offered **ESR and ER positions** to young scientists interested in the development of nanocrystalline lightmetal hydride composites. These gave training and research experience for young researchers by giving them the opportunity to spend three years in another country during their PhD thesis or PostDoc time resp. as part of an international high-quality research project. A detailed career development plan incl. exchange programme between the partners was part of the work contract for each position.

COSY in total trained 13 ESRs and 5 ER. 6 of these were women, i.e. nearly 40% of the fellows. Real progress in the field of hydrogen storage in Reactive Hydride Composites was achieved by breaking traditional academic borders, because the COSY fellows were trained in cross-disciplinary and collaborative work. COSY educated a new category of 'materials science' experts who can work across disciplines. This was achieved by an unprecedented interdisciplinary training programme comprising experimental physicists, chemists and materials scientists, surface chemists and computational materials science experts.

The network not only opened up possibilities for researchers of EU member states, but also for researchers of associated member states and third countries, thus stressing that science acts as a spearhead of internationalisation. This was demonstrated by the nationalities of the various young researchers in COSY. The 11 appointed ESR's are coming from Belgium (1), Brazil (1), France (2), Italy (3), Japan (1), Syria (1), Nigeria (1), Poland (1), the 5 ER's are from Spain (1), Italy (1), Turkey (1), Russia (1) and Ukraine (1).

The young researchers of the COSY network in total participated at 83 different workshops, conferences etc. They presented their work in total with 28 posters at conferences, 15 posters at workshops and 7 posters at other meetings. Furthermore they presented or were co-authors in 23 talks on conferences, 55 on workshops and 5 at other meetings.

7 Training Workshops have taken place at different partners of the network (<http://www.cosy-net.eu/workshops.html>). The COSY Project fellows organized among themselves 3 Young Researchers Workshops in order to discuss their scientific work, to implement their soft skills, e.g. on presentation and discussion techniques, and to improve their knowledge on energy related topics.

The Joint NESSHY-COSY final event (http://www.cosy-net.eu/workshop_final.html) was a special opportunity to meet not only international scientists with an excellent reputation like Prof. Etsuo Akiba

from AIST, Japan, but also representatives from industrial companies like Dr. Scott Jorgensen, from General Motors Research and Development, USA, or Dr. Jörg Wind, from Daimler AG, Germany, as well as representatives from the EU like Dr. Evelyne Weidner from the FCH JU program office.

9 ESR of COSY have pursued a PhD thesis at their host institutions, 3 of them have defended their theses at the time of finalising this report.

14 joint publications of the COSY partners were published during the runtime of the project, and in total 28 publications in high ranked journals resulted from the project (<http://www.cosy-net.eu/publications.html>).

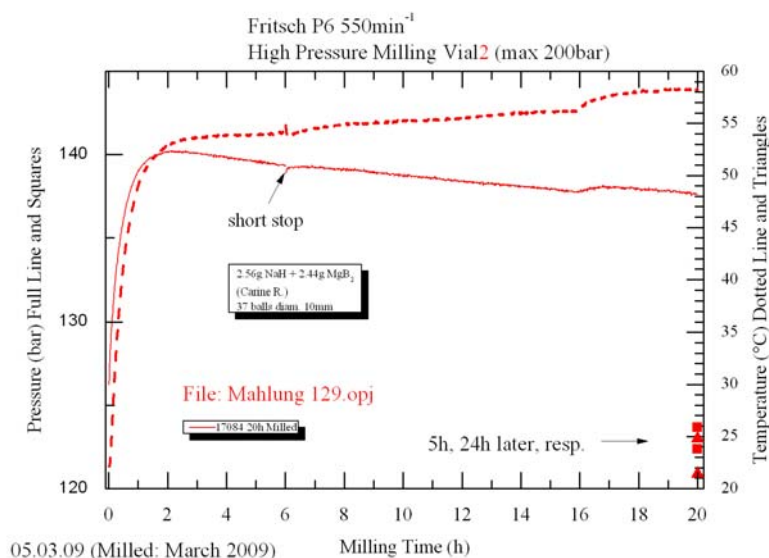
2. Scientific Achievements

High energy ball milling, either at ambient pressure or under high pressures, either under inert gas (e.g. Ar) or H₂ atmosphere, was established as the preferential preparation method for Reactive Hydride Composites (RHC), in order to achieve sufficient mixing of the components of the composites. The microstructural characterisation revealed, that different types of mills yield comparable microstructures, provided that the total energy input into the material was the same.

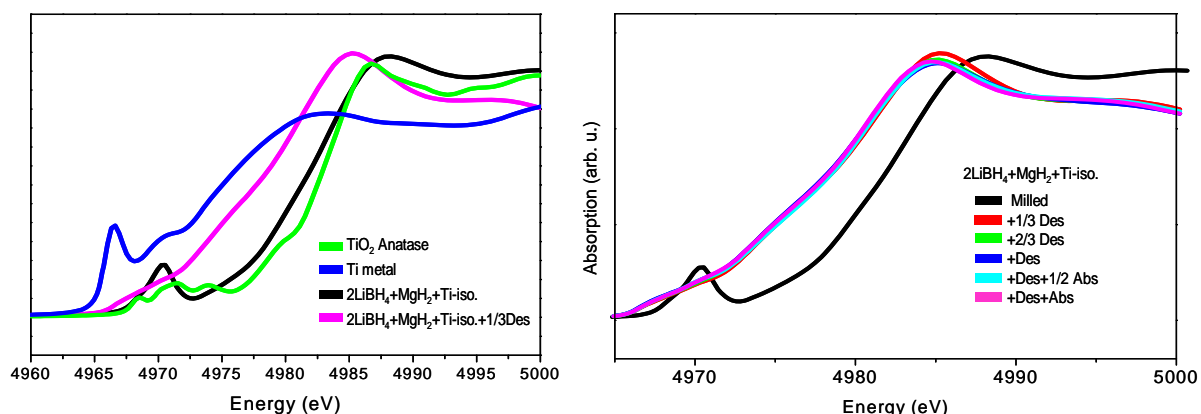
Synthesis of complex hydrides could be obtained at room temperature by using high-pressure reactive milling. The combination of high energy input during milling and the use of high hydrogen pressure allows the synthesis of doped complex hydrides in one step. This preparation method for the first time succeeded to produce to NaBH₄ and Ca(BH₄)₂ at room temperature, which could up to now only obtained using high temperature and pressure. But the yield of borohydrides production has still to be increased significantly to use it as a standard procedure.

The investigations highlighted the importance of grain size and solid state diffusion of reacting species in RHC. Smaller diffusion paths enhance the kinetics of hydrogen sorption in the materials .

The role of some "catalysts" (e.g. Ti-isopropoxide) seems to be to prevent grain growth during milling and/or hydrogen sorption. As shown in a parallel investigation by Bösenberg et al. (" Role of additives in LiBH₄-MgH₂ reactive hydride composites for sorption kinetics", Acta Materialia, 58 (9) (2010), 3381-3389, doi:10.1016/j.actamat.2010.02.012), they also enhance the formation of MgB₂ as heterogeneous nucleation agents (in the form of TiB₂, which forms during the first unloading cycle) during hydrogen desorption and thereby enhance reaction kinetics.



High pressure synthesis of a NaBH₄ / MgH₂ Reactive Hydride Composite (University of Barcelona). Hydrogen pressure and temperature monitored during the milling of 2NaH + MgB₂ powders. Significant parameters involved in the reactive ball milling: Hydrogen gas, 125 bar of constant pressure, 37 balls (10 mm), 550 rpm, 5 g of powders. (Milling vial Evico Magnetics, Dresden, Germany, developed by Institute for Solid State and Materials Research IFW, Dresden) .



XANES spectrum of Ti Edge during adsorption and desorption of $\text{LiBH}_4 / \text{MgH}_2$ composites doped with a Ti isopropoxide catalyst. (**Materials Science Institute of Sevilla, GKSS**).

left: comparison of Rutile (TiO_2 Anatase) and Ti metal spectrum with Ti spectrum in $\text{LiBH}_4 / \text{MgH}_2$ RHC before and after MgH_2 desorption (corresponding to 1/3 Des)

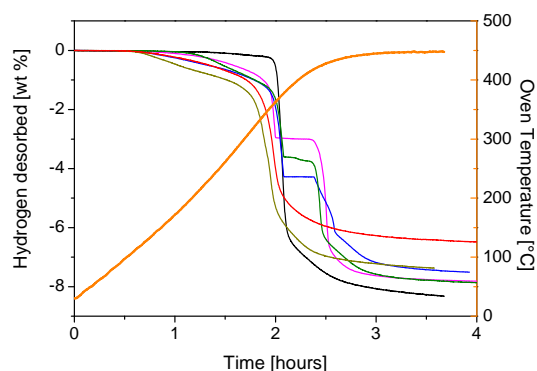
right: Ti spectrum in $\text{LiBH}_4 / \text{MgH}_2$ RHC after milling and further steps in desorption and following reabsorption of hydrogen in the RHC.

1/3 and 2/3 Des: milled, hydrogenated sample after 1/3rd and 2/3rd of total desorption time, respectively; Des: sample after complete desorption; 1/2 Abs and Abs: sample after half of total absorption time and after complete absorption, respectively

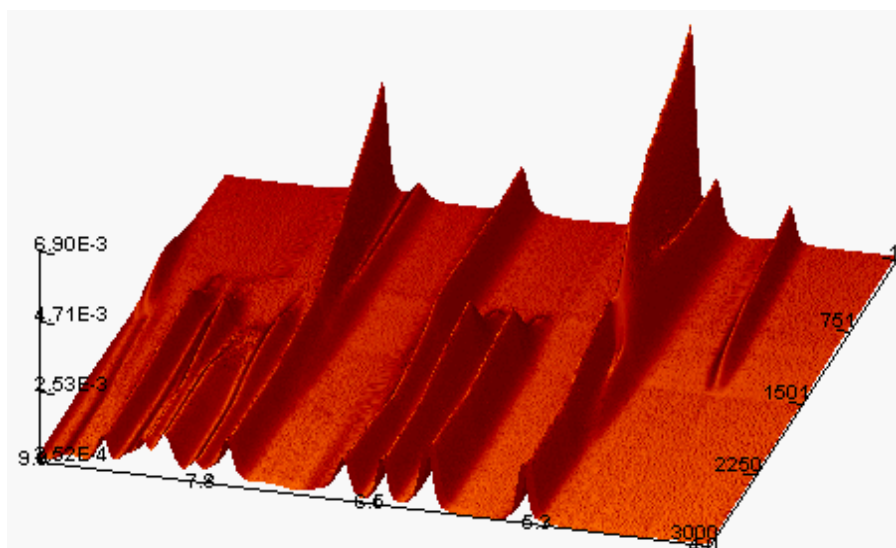
Transition metal fluorides (TiF_4 and NbF_5) were identified as enhancing the reversible hydrogenation of pure $\text{Ca}(\text{BH}_4)_2$ significantly. In the case of the $\text{NaBH}_4 / \text{MgH}_2$ system, also MgF_2 was found to be beneficial for reaction kinetics.

Reaction steps during hydrogen absorption and desorption of RHC could be identified by *in situ* neutron and x-ray diffraction experiments. These are strongly dependent on conditions like hydrogen pressure and temperature as well as exact composition of the RHC.

Thermodynamic and kinetic properties of NaBH_4 and the $\text{NaBH}_4 / \text{MgH}_2$ were determined in detail and could be connected with reaction mechanisms, as determined by careful thermodynamic measurements and *in situ* PXD. It could be shown, that unfavourable reaction conditions lead to a side reaction, producing the unwanted product NaMgH_3 reducing the capacity of the materials. This result could also be modelled by the CALPHAD method, using experimental data from COSY partners. Reaction kinetics could be enhanced as well as a MgF_2 additive as also stoichiometry of the composite, a $\text{NaBH}_4 / 2 \text{MgH}_2$ mixture showing a doubling of reaction speed upon desorption. Theoretical calculation (**Fehler! Verweisquelle konnte nicht gefunden werden.**) indicate a favourable effect Mg in the surrounding of NaBH_4 on decomposition kinetics.

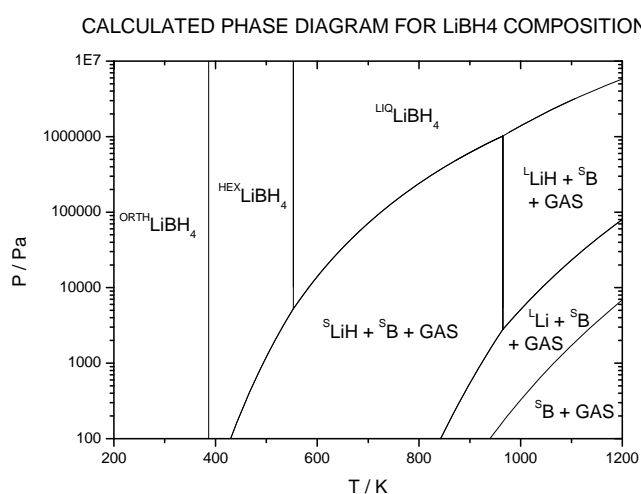


Desorption curves obtained by volumetric measurements of as dried $\text{Ca}(\text{BH}_4)_2$ and milled with fluorides additives (**GKSS, now Helmholtz Zentrum Geesthacht**). Experiments carried out heating from room temperature to 450°C in static vacuum. $\text{Ca}(\text{BH}_4)_2$ (black), $\text{Ca}(\text{BH}_4)_2 + \text{NbF}_5$ (red), $\text{Ca}(\text{BH}_4)_2 + \text{TiF}_3$ (green), $\text{Ca}(\text{BH}_4)_2 + \text{TiF}_4$ (dark yellow), $\text{Ca}(\text{BH}_4)_2 + \text{VF}_3$ (magenta), $\text{Ca}(\text{BH}_4)_2 + \text{VF}_4$ (blue).

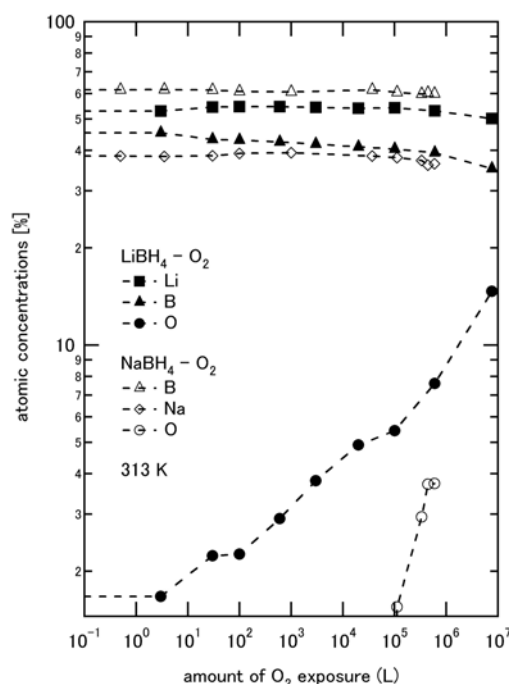


3D plot of temperature evolution of $\text{NaBH}_4 / \text{MgH}_2$ RHC (in situ Synchrotron Radiation Powder X-ray Diffraction (PXRD) at ESRF, Gr noble, France)

The $\text{LiBH}_4 / \text{MgH}_2$ was studied in detail with respect to stability of LiBH_4 at different stoichiometries, phase development during reactions and effects of additives. Using the CALPHAD approach, a pressure vs. temperature phase diagram of the LiBH_4 compound was constructed. Reaction kinetics of the composite were determined in detail and a corresponding kinetic model was set up, which shall be used in the design of hydrogen storage tanks based on this RHC.



Assessed pressure vs temperature phase diagram for the LiBH_4 compound (University of Turin and Institut National de Polytechnique, Gr noble).

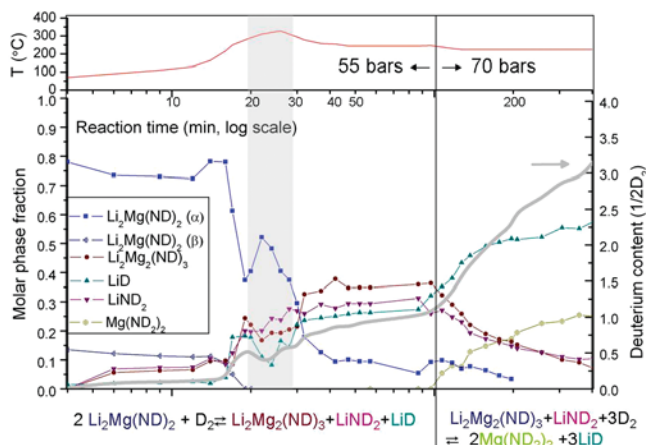


The changes in atomic concentrations of the LiBH_4 and NaBH_4 surfaces under the O_2 exposure at 313 K (EMPA)

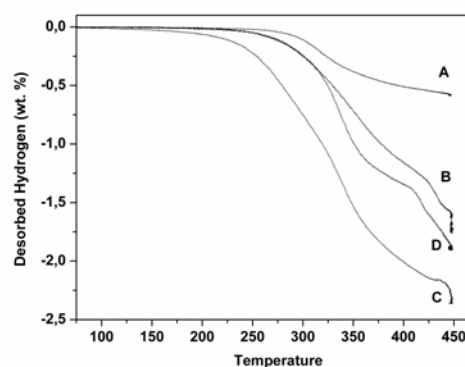
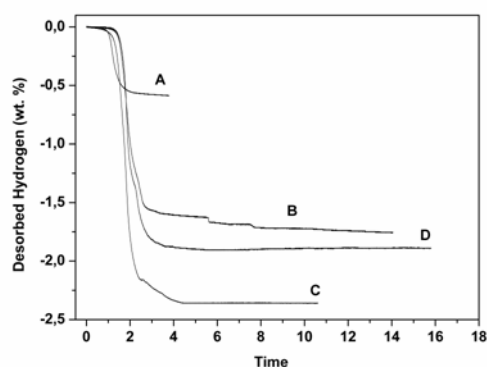
An *in situ* surface composition and desorption analyser has been constructed by the ESR at EMPA, consisting of an X-ray Photoelectron Spectrometer combined with a mass spectrometer. Under practical conditions, surface contamination of the hydrogen storage materials by oxygen has to be taken into account. Therefore, fundamental investigations of the oxidation of hydride surfaces are required in order to clarify the hydrogen sorption mechanisms in reactive hydride composites. The surface oxidation of LiBH_4 and NaBH_4 were studied by means of XPS.

A pronounced effect of D for H substitution in $\text{Mg}(\text{NH}_2)_2 + 2\text{LiH}$ was found, the deuterated samples showing slower hydrogen absorption compared to the hydrided ones. This indicates, that the rate limiting step is connected with the diffusion of a hydrogen containing species. Starting from the mixed imide $\text{Li}_2\text{Mg}(\text{NH})_2$, an intermediate step was identified by *in situ* neutron characterisation of hydrogen uptake in the $\text{Mg}(\text{NH}_2)_2 - 2\text{LiH}$ system. This intermediate comprises LiNH_2 and a mixed imide phase prior to the appearance of $\text{Mg}(\text{NH}_2)_2$ in the neutron spectra. The intermediate phase has been identified as $\text{Li}_2\text{Mg}_2(\text{NH})_3$. The dehydrogenation reaction mechanism of $\text{LiNH}_2\text{-MgH}_2$ systems is suggested to pass through formation of Mg_3N_2 , a highly stable compound, almost independent of compounds ratios and ball milling conditions. Detailed studies of phase formation during dehydrogenation revealed mechanisms, depending on the stoichiometry of the compound. These investigations were accompanied by suitable modelling efforts, confirming partially the measured results.

For the first time worldwide, $\text{Mg}(\text{BH}_4)_2$ was synthesised in a dry reactive ball milling process and the thermodynamic and kinetic properties of the obtained material analysed.

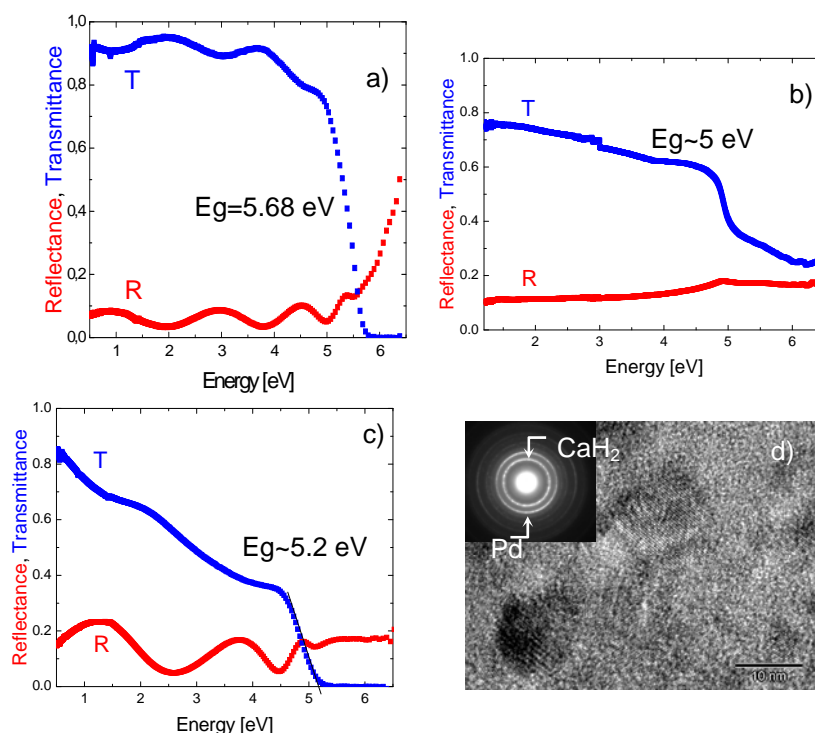


Evolution of molar phase fractions until the end of the reaction time at 400 min (log scale for clarity) (**Karlsruhe Institute of Technology KIT**). The deuterium content was calculated from Rietveld analysis. The two pressure regimes have been separated with a line.



Desorption kinetics of as milled MgB_2 measured in a Sievert's -Type apparatus (**GKSS, KIT**). The samples milled for 50, 100, 200, 300 hours were heated under vacuum condition (10^{-2} bar starting pressure) from RT to 400°C (curve A, B, C and D) using a heating rate of 3°C/min. (left) desorbed hydrogen against time, (right) desorbed hydrogen against temperature.

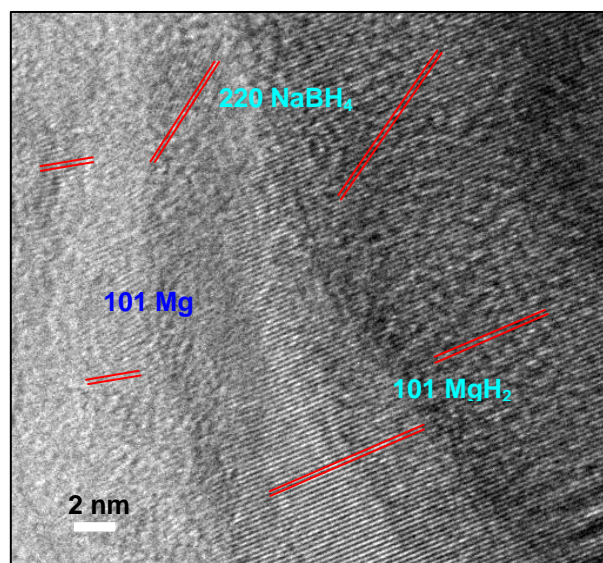
As model materials, various kinds of thin films were prepared by reactive sputtering from Na, Li, Ca and MgB_2 targets, partly in a hydrogen atmosphere. Hydride films exhibit an optical band gap, fitting quite well with theoretical calculations. DSC on a $\text{CaH}_2 - \text{MgB}_2$ co-sputtered film yielded a peak comparable with one from DSC on bulk material onset, which might correspond to the formation of the borohydrides. The formation of this phase still needs further confirmation. In order to simulate absorption spectra of the films and determine their composition, the dielectric function of the materials was simulated.



Experimental optical reflection and transmission for a) NaH, b) LiH and c) CaH₂. (Vrije Universiteit) d) Shows a plan view TEM image of CaH₂ with a Pd capping layer measured in LRCS (Amiens). Crystalline CaH₂ grains of around 10-20 nm were observed. The inset shows the electron diffraction profile, with the diffraction rings of Pd and CaH₂.

The investigations performed by UAB, ICMSE and UOXFDJ and the achieved results demonstrate that serious investigations are possible by electron microscopy – the investigated materials have been shown to be relatively stable in the electron beam. Samples at different stages in the absorb/desorb process were studied and confirmed the crucial role of MgB₂ and intermediate formation during desorption of hydrogen e.g. from Na-Mg-B-H based Reactive Hydride Composites.

Using the results from first-principles calculations, a simple model for the formation enthalpy of purely ionic borohydrides, such as LiBH₄ and NaBH₄, has been established. First-principles calculations of the formation enthalpy and the dehydrogenation enthalpy of Mg(BH₄)₂ have been carried out. Calculated thermodynamic properties indicate promising values for this material, which have to be confirmed by thermodynamic and kinetic characterisation. It was possible to calculate structure, enthalpy and free energy of Mg(BH₄).

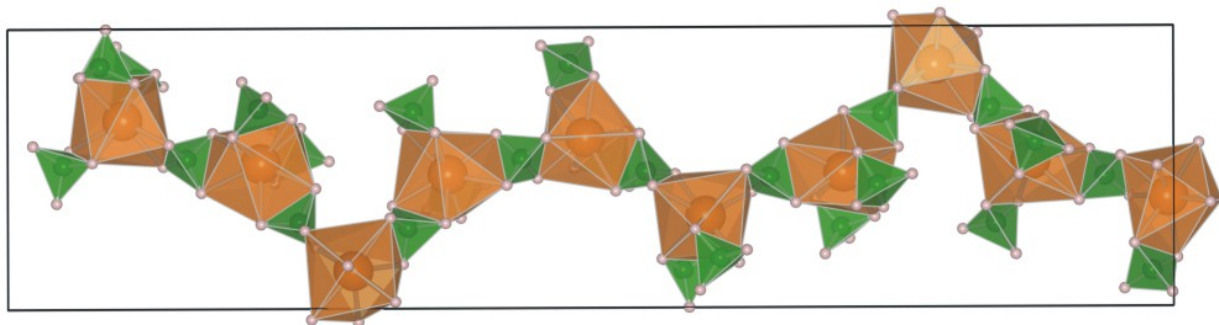


HREM image of as-milled 2NaBH₄+MgH₂ reactive hydride composite. (Oxford University, GKSS)

A Database of thermodynamic properties of a range of materials of value for the project has been set up, to be used in calculations following the CALPHAD method. They yielded thermodynamic properties of different composites and could to be confirmed by thermodynamic and structural characterisation.

1 patent was filed and granted, resulting from the work of one of the fellows (DE 10 2008 063 895, „Verfahren zur Aktivierung oder Regeneration eines Wasserstoffspeichermaterials“, ("Method for Activation or Regeneration of a Hydrogen Storage Material") Inventors: Gagik Barkhordarian, **Claudio**

Pistidda, Martin Dornheim, Rüdiger Bormann, granted 10.6.2010, US 12/635,315., applied for 10.12.2009, CA 2 688 774 A1, applied for 17.12.2009, EP 2 199 256 A1, applied for 09.12.2009, JP 2010 142804A, applied for 07.01.2010). The patent is applicable to a wide range of on board and stationary applications. In the application of a solid state hydrogen storage tank it is impossible to access the storage material without opening the material container. The methodology described in this patent is the only tool to activate and/or regenerate in situ the storage material in the tank. It might have wide use at future times, when complex hydride based tanks are established in industrial and user applications for stationary and mobile hydrogen storage.



*A substructure in the $Mg(BH_4)_2$ crystal illustrating MgH_8 dodecahedra (orange) linked by BH_4 tetrahedra (green) along the c-axis of the unit cell. Each dodecahedron is linked to other substructures by two more tetrahedra, thus forming a tetrahedral network. Results from calculations performed at **University of Utrecht in collaboration with KIT**.*

COSY Joint Publications

1. "Hydrogen desorption mechanism of $2NaBH_4 + MgH_2$ composite prepared by high-energy ball milling", **S. Garroni, C. Pistidda**, M. Brunelli, G.B.M. Vaughan, S. Suriñach and M.D. Baró, Scripta Materialia 60 (2009) 1129–1132.
2. "Oxidation State and Local Structure of Ti-Based Additives in the Reactive Hydride Composite $2LiBH_4 + MgH_2$ ", **E. Deprez**, Miguel A. Muñoz-Marquez, Manuel A. Roldan, C. Prestipino, F. Javier Palomares, **C. Bonatto Minella**, U. Bösenberg, M. Dornheim, R. Bormann, and A. Fernandez, J. Phys. Chem. C 114 (2010) 3309.
3. "Microstructural study of the $LiBH_4$ – MgH_2 reactive hydride composite with and without Ti-isopropoxide additive"; **E. Deprez**, A. Justo, T.C. Rojas, C. Lopez-Cartes, **C. Bonatto Minella**, U. Bösenberg, M. Dornheim, R. Bormann, A. Fernandez, Acta Materialia 58 (2010) 5683-5694.
4. "Combined XPS and SEM-EDX studies of the $LiBH_4$ - MgH_2 reactive hydride composite with and without a Ti-based additive", **E. Deprez**, M. A. Muñoz-Márquez, M. C. Jimenez de Haro, F. J. Palomares, F. Soria, M. Dornheim, R. Bormann, A. Fernández, J. Appl. Phys., accepted.
5. "Sorption properties of $NaBH_4/MH_2$ ($M = Mg, Ti$) powder systems", **S. Garroni**, C. Milanese, A. Girella, A. Marini, G. Mulas, E. Menéndez, **C. Pistidda**, M. Dornheim, S. Suriñach, M.D. Baró, International Journal of Hydrogen Energy, Volume 35, Issue 11, June 2010, Pages 5434-5441.
6. The In-Situ Deposition of Alkali and Alkaline Earth Hydride Thin Films to Investigate the Formation of Reactive Hydride Composites", **M. Gonzalez-Silveira**, R. Gremaud, H. Schreuders, E. Batyrev, L. Dupont, B. Dam, M. van Setten, A. Rougier, W. Lohstroh, Journal of Physical Chemistry C 114 (2010) 13895-13901
7. "Microstructural analysis of hydrogen absorption in $2NaH+MgB_2$ "; **C. C. Nwakwuo**, **C. Pistidda**, M. Dornheim, J. L. Hutchison, J. M. Sykes; Scripta Materialia (accepted)
8. "Synthesis of amorphous $Mg(BH_4)_2$ from MgB_2 and H_2 at room temperature" **C. Pistidda**, **S. Garroni**, **F. Dolci**, E. G. Bardají, A. Khandelwal, P. Nolis, M. Dornheim, R. Gosalawit, T. Jensen, Y. Cerenius, S. Suriñach, M. D. Baró, W. Lohstroh, M. Fichtner, Journal of Alloys and Compounds, 508, (1), (2010) pp. 212-215.
9. "Pressure effect on the $2NaH+MgB_2$ hydrogen absorption reaction" **C. Pistidda**, **S. Garroni**, G. Barkhordarian, **C. Bonatto Minella**, **F. Dolci**, T. R. Jensen, P. Nolis, U. Bösenberg, Y.

- Cerenius, W. Lohstroh, M. Fichtner, Maria D. Baró, R. Bormann, M. Dornheim J. Phys. Chem. C (accepted)
10. "Hydrogen release and structural transformations in LiNH₂-MgH₂ systems"; **D. Pottmaier, F. Dolci, M. Orlova**, G. Vaughan, M. Fichtner, W. Lohstroh, M. Baricco, Journal of Alloys and Compounds, In Press, Accepted Manuscript, Available online 4 November 2010
 11. "Hydrogen desorption reactions of the Na-Mg-B-H system", **D. Pottmaier, S. Garroni**, M. D. Baró and M. Baricco, Advances in Science and Technology Vol. 72 (2010) pp 164-169.
 12. "Effect of additives on the synthesis and reversibility of Ca(BH₄)₂"; **C. Rongeat**, D'Anna V., Hagemann H., Borgschulte A., Züttel A., Schultz L., Gutfleisch O. – Journal of Alloys and Compounds – 493 (2010) 281-287
 13. "Effect of the presence of chlorides on the synthesis and decomposition of Ca(BH₄)₂" **C. Rongeat**, Lindemann I., Borgschulte A., Schultz L, Gutfleisch O. – International Journal of Hydrogen Energy, accepted 2 October 2010, available online 4 November 2010.
 14. "NaBX₄-MgX₂ composites (X= D, H) investigated by in situ neutron diffraction", **D. Pottmaier, S. Garroni**, M. Brunelli, G. B. M. Vaughan, A. Castellero, E. Menendez, M.D. Baró and M. Baricco, Mat. Res. Soc. Symp. Proc., Vol. 1262, Accepted Manuscript.