High pressure reactive ammonia: an innovative route to synthesize new metal hydrides

*The aim of this project is to develop **the high-pressure (HP) synthesis of new metal hydrides by exploiting the high reactivity of ammonia**. These compounds belong to the class of strategic and highly sought materials for applications in energy storage and for their high Tc superconducting properties. Up to now, HP-synthesized hydrides have been mostly obtained by direct reaction of metals with H_2 in diamond anvil cell following "cook and look" methods. Here, we will exploit the stronger reactivity of NH_3 to strengthen the diffusion of H within the metal in order to synthesize innovative metal hydrides MH_x with a high concentration of hydrogen (x>1) at mild pressure conditions (<20 GPa) **compatible with the synthesis in large volume presses**. The mechanism of hydrogen diffusion in the metal will be studied with time-resolved x-ray diffraction experiments at XFEL sources to understand reaction paths and kinetics and determine the optimal (P,T) synthesis parameters. In the meantime, we **will develop a new technology** for their synthesis in large-volume press to fully characterize their physical (e.g. conductivity, hardness) and chemical (e.g. H stoichiometry) properties. This combination of innovative cutting-edge technologies combined with an entirely new collaboration between 2 complementary teams will initiate a promising materials thematic where IMat has many assets to obtain **exceptional and patented metal hydrides**.*

Achieving sustainable growth on a finite planet is a challenge of this century. The needs of societies are changing rapidly and the role of new smart materials in ensuring such transformations is paramount. This challenge requires new kind of materials and, for this, new unexplored dimensions for materials synthesis. That's why **the search for new materials is linked to the development of new synthesis methods**. High-pressure synthesis adds a promising additional dimension for exploration of compounds that are inaccessible to traditional chemical methods, and can lead to new industrially outstanding materials[1]. For example, synthesis ***in large volume presses*** under extreme pressure and temperature conditions is the principal method of diamond synthesis in the industrial field with a world annual production of 3 000 million carats (1 carat = 0.2 g). But, beyond diamond production, high-pressure synthesis is nowadays a vast exciting field of industrial and academic research opening up new frontiers.

History shows that the **successful industrial synthesis of new materials under pressure has always been correlated to technological developments**. It started in 1913 with the synthesis of ammonia from N_2/H_2 mixtures where pressures (P) of a few hundred bars were used to shift a chemical equilibrium. Nowadays, the high pressure (HP) technology allows to generate P in the range of megabars leading to compression energies comparable to the one of the chemical bonds (eV) allowing the access to a whole new chemistry of elements. Indeed, a significant number of new nitride and hydride compounds have been synthesized in the last decade at pressures in the range 50-250 GPa and high temperatures using the laser-heated DAC[2]. Such synthesis exploits the pressure-induced reactivity of elements, such as H_2 but also N_2 and noble metal (e.g. Pt), which are very stable at ambient conditions. This research is mainly motivated by the fact that such materials may present strategic properties such as high hardness, high Tc superconductivity, or remarkable energetic, magnetic, electronic, optical and thermo-electric properties that have great values for technological applications. Nevertheless, **two conceptual locks currently exist in this challenging thematic and prevent further progress**:

1/ A major issue is that the sample volume recovered in DAC-synthesis is tiny (in the order of 10^{-3} mm^3 for a pressure of 10 GPa and 10^{-5} mm^3 for 100 GPa), which prohibits, in principle, any in-depth physical and chemical characterizations. However, to explore the strategic properties of these new materials, it is essential to analyse the samples with a wide range of materials characterizations, often applicable

[1] Y. Le Godec, A. Courac and V. Solozhenko. Journal of Applied Physics, 126 (15), 151102 (2019).

[2] E. Gregoryanz et al., Nat. Mat., 3, 294 (2006) ; T. Scheler et al., Phys. Rev. Lett., 111, 215503 (2013),; A. P. Drozdov et al. Nature, 525, 73 (2015) ; C. Pepin et al., Science, 357, 382 (2017) ; M. Bikov et al., Nat. Mat. 10, 2994 (2019) ; A. P. Drozdov et al., Nature, 569, 528 (2019).

only to much larger volumes. Moreover, these very low synthesis volumes are prohibitive for any future applications. That's why any commercial perspective of these DAC syntheses is difficult to conceive and hence, right now, these researches remain mainly of fundamental interest.
2/ Furthermore, most studies so far were performed with a "cook and look" method, which has proven successful in some cases but is not sufficient to determine the key parameters of synthesis. Actually, **the opportunity of observing *in situ* and in real time the structural evolution of the reactants, the chemical reactions and the possible intermediate phases under extreme conditions is essential**. It allows to tackle these syntheses in all their complexities and to establish (or minimize) their lower (P,T) conditions required by understanding the mechanisms and the kinetics of the transformations at these extreme conditions.

Our project intends to provide answers to these two locks by combining the expertise of the two project leaders.
Firstly, Yann Le Godec (YLG), chemist in the DEMARE group at IMPMC, has a large expertise in HP synthesis under mild P-T range (below 20 GPa) using large volume presses (Paris-Edinburgh or multi-anvil press). This has led to recent successful synthesis of new patented ultrahard materials (some of them are under industrial licence)[3] and some solar optoelectronic and infra-red photonics materials[4] which are recoverable under ambient conditions. He has been also leading in the development of high pressure-high temperature large-volume techniques (some are patented[5]) and has also undertaken many collaborations with European industrial groups. **He already developed in the past an ammonia loading technique for high pressure high temperature large-volume experiments** where he demonstrated that HP-HT reaction of NH_3 (used as solvent) with amorphous boron reduce (by a factor 3!) the pressure conditions for synthesis of c-BN[6], a strategic ultrahard compound synthesized usually at 6 GPa industrially with another solvent. During this thesis project, **this first ammonia loading technique will be greatly improved** to allow the study of high-pressure large-volume synthesis of new metal hydrides with NH_3. Obtaining macroscopic samples will allow us to characterize the full physical and chemical properties of these new compounds and finally consider patenting them for applications.
Secondly, Sandra Ninet (SN), physicist in the PHYSIX group at IMPMC, is an expert in DAC experiments on molecular systems and has a large expertise in *in situ* study of ammonia under high P-T range (up to 200 GPa and 3000 K) using DAC combined with synchrotron radiation. Recently, **Sandra Ninet engaged in this new experimental field by studying the reaction between ammonia and metals in DAC using time-resolved XRD experiments at the European XFEL**. Actually, as mentioned below, these syntheses should be studied *in situ* through the use of synchrotron x-ray diffraction in order to determine the relevant P-T conditions and understand the formation path of the products. However this can be made difficult if the time scale of the reactions are shorter than that of the experiment (typically, seconds to minutes). Today, X-ray free electron lasers (XFEL) can generate ultrashort (of the order of femtosecond) X-ray pulses with a repetition rate in the Hz to MHz range depending on the source, and with a brightness several orders of magnitude higher than those of synchrotrons. These **new sources open up revolutionary perspectives for the HP synthesis** as they give access **to reaction paths and kinetics**, even under extreme conditions as recently shown in the synthesis into a DAC of H_2S from H_2+S_8[7], and of iron nitride[8]. Hence, Sandra Ninet has recently demonstrated that the heating of the metal and the monitoring of the reaction can both be ensured by irradiation with a pulsed hard X-ray beam generated by the free electron lasers of the new XFEL sources thanks to time-resolved diffraction measurements. Two XFEL runs (Nov. 2021 and June 2022, the next run is already planned in 2023) have already led to the successful synthesis of **original iron and platinum hydrides** with **rich**

[3] Y. Le Godec et al., brevet EP083802 (2019) ; Y. Le Godec et al., PCT/FR2020/050872 (2020) ; Y. Le Godec et al. EP22211529.7 (2022).
[4] O. Kurakevych et al., Inorg. Chem. 55, 8943 (2016) ; S. Pandolfi et al., Nano Letters 18, 5989 (2018).
[5] Y. Le Godec et al, pct/057337, 1162335 (2014). Y. Le Godec et al, European Patent 17792103.8 (2019).
[6] Yann Le Godec et al., Materials, MDPI, 4 (15), pp.4245 (2021).
[7] E. J. Pace et al., J. Phys. Chem. Lett, 11, 1828 (2020)
[8] H. Hwang et al., J. Phys. Chem. Lett., 12, 3246 (2021)

hydrogen stoichiometry. This work demonstrates that, compared to pure hydrogen, **ammonia as a source of hydrogen favors the high temperature structure of hydrides and increase the hydrogen concentration at low pressure** (20 GPa). New compounds with Mo, Re, Ir have been also synthesized: these new materials can either be new hydrides but also new nitrides with potential ultra-hard properties as ammonia can be also a source of nitrogen. This first successful result opens a new way of synthesis as it shows that the pressure synthesis conditions are **moderate with ammonia** and thus compatible with HP synthesis in large volume press with the ammonia loading technique developed by Yann Le Godec.

Hence, the 2 locks mentioned above can be easily lifted with **this new project** which associates the expertise of a chemist (YLG) and a physicist (SN) **who have never collaborated by now (no joint publication)**. The PhD student will be able to benefit from this double multidisciplinary competence and **many new metal hydrides** should be synthesized, fully characterised (and probably patented) during the 3 years of thesis. The first XFEL experiments have already allow the selection of metals - Fe, Pt, Ir, Mo and Re – which are promising candidate to form high H content metal hydride with ammonia at mild conditions. Moreover, this thematic of research is nowadays the subject of **many *ab initio* studies in the literature** to determine the best Metal-H candidates to obtain remarkable properties and we will be attentive to new published studies to eventually turn out to the most promising systems.

Given the nature of the project combining HP conditions, XFEL experiments and new large volume experiments, and the large and time-consuming experimental work that it requires, **a PhD grant from Imat is essential to boost this innovative challenging materials project**.

Research plan with provisional calendar:

As mentioned below, our recent XFEL runs have already allow the selection of metals - Fe, Pt, Ir, Mo and Re – which are promising candidate to form high H-content metal hydride with ammonia at mild conditions. Our next **XFEL experiment** at Hamburg (***task 1***, in 2023, and more are planned for 2024) will bring additional results to identify the formation of these new promising materials, follow intermediate states and determine the kinetics of the reactions. These results will pave the way for determining the optimal conditions for the synthesis of metal hydrides in larger quantities. Hence, after the **analysis of these XFEL experiments (*task 2)***, we will thus **perform the synthesis of the metal hydrides in large-volume presses (*task 3*).** These 3 tasks can start immediately since (i) a XFEL experiment is already planned in the first year of PhD, (ii) the first two runs (realized in 2022) should be analyzed more attentively and (iii) the ammonia loading system for high pressure high temperature large-volume experiments is already available.
The macroscopic volume of recovered sample will then allow a **complete physical characterization** of the products (***task 4,*** *probably starting in 2024*): we will characterize the new metal hydrides with a large panoply of characterization techniques (spectroscopy, XRD, MEB, TEM, etc.) and measure their mechanical (hardness) and transport (conductivity) properties. We will also studying their thermal stability: at moderate T to analyze their metastability and at high T, with thermic ATD-ATG measurements and/or HT-XRD, to determine their thermal decomposition - H_2 degassing - which is the main parameter for the energy storage application. All these characterizations will be performed at IMPMC which has all the necessary infrastructures. In addition, we also plan to perform neutron diffraction experiments (at ISIS, UK, in 2024 and 2025) to determine the stoichiometry of hydrogen in our new MH_x which is also a key parameter for hydrogen storage application. Also, to define more accurately the structure (and hence stoichiometry) of our new metal hydrides, some internal Sorbonne collaborations (already existing, with many joint papers) will be strengthened with the LCMCP for NMR measurements. The 4 main tasks listed here will be carried out in parallel throughout the doctoral project and should ultimately lead to **obtain exceptional new metal hydrides**.