

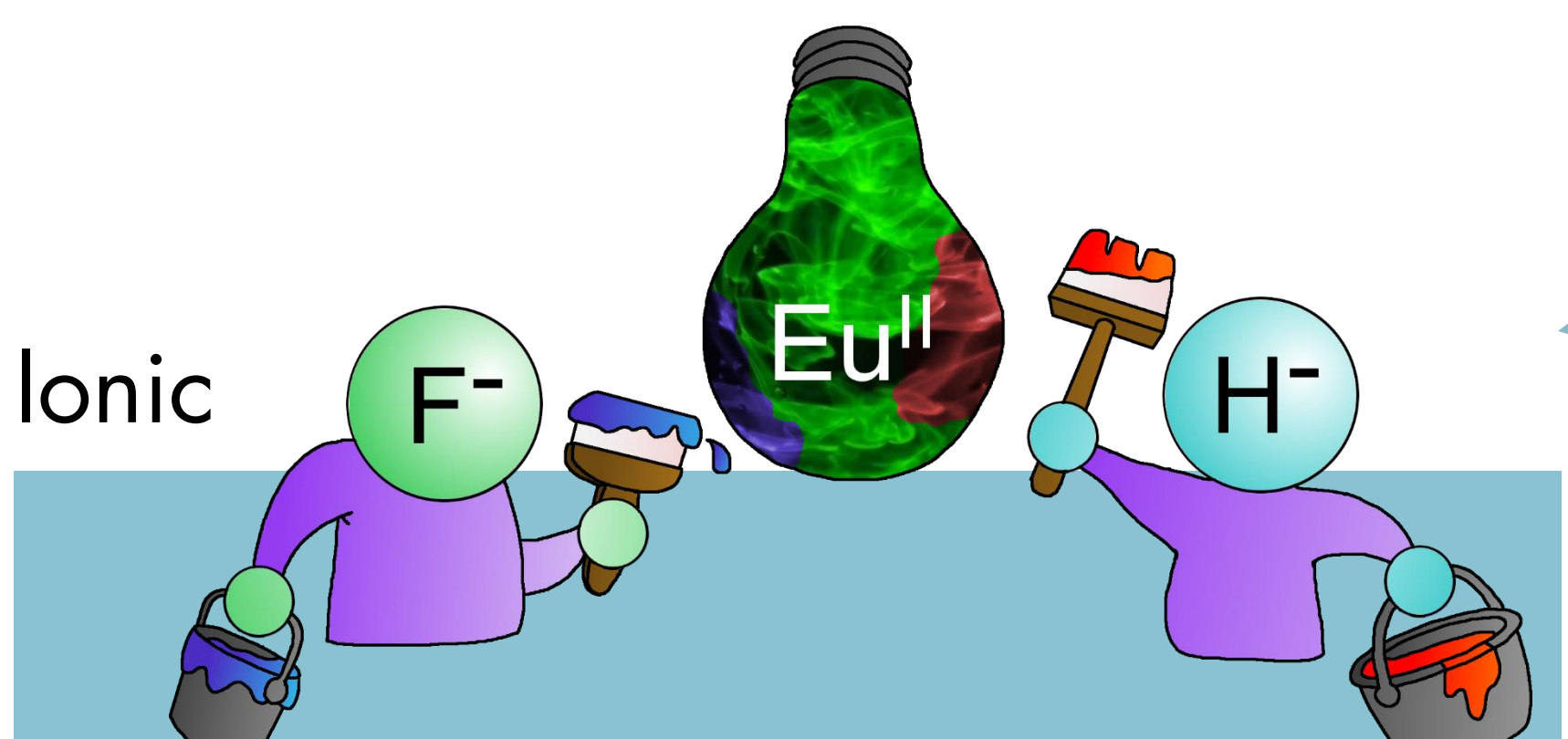
Functional Materials

Team of Prof. Holger Kohlmann


Research topics: Our research is on preparative solid-state chemistry with a focus on metal hydrides, functional materials and reaction pathways of solid-state and solid-gas reactions. Topics range from pure basic research like fundamental questions on bonding in solids or magnetic order in materials (e.g. $\text{SmCo}_5^{[1]}$) to more applied questions like the reduction of metal oxides to pure metals. In the latter, hydrogen acts as reducing agent analogously to its use in organic synthesis. To most elements however, it acts as an oxidizing agent, forming metal hydrides. Metal hydrides can roughly be categorized by their bonding situation into ionic, covalent and metallic. However, the transition between the different bonding types is continuous and some compounds even exhibit different bonding types. The hydrogen atoms in metal hydrides are negatively polarized. The incorporation of hydrogen in metallic hosts can strongly influence chemical and physical properties. To pick a few examples hydrogen can change the emission wavelength in Eu^{II} -doped compounds, oxidize polyanions of Zintl phases or induce rearrangements of the packing of intermetallic compounds.

Bonding situation in metal hydrides

Ionic

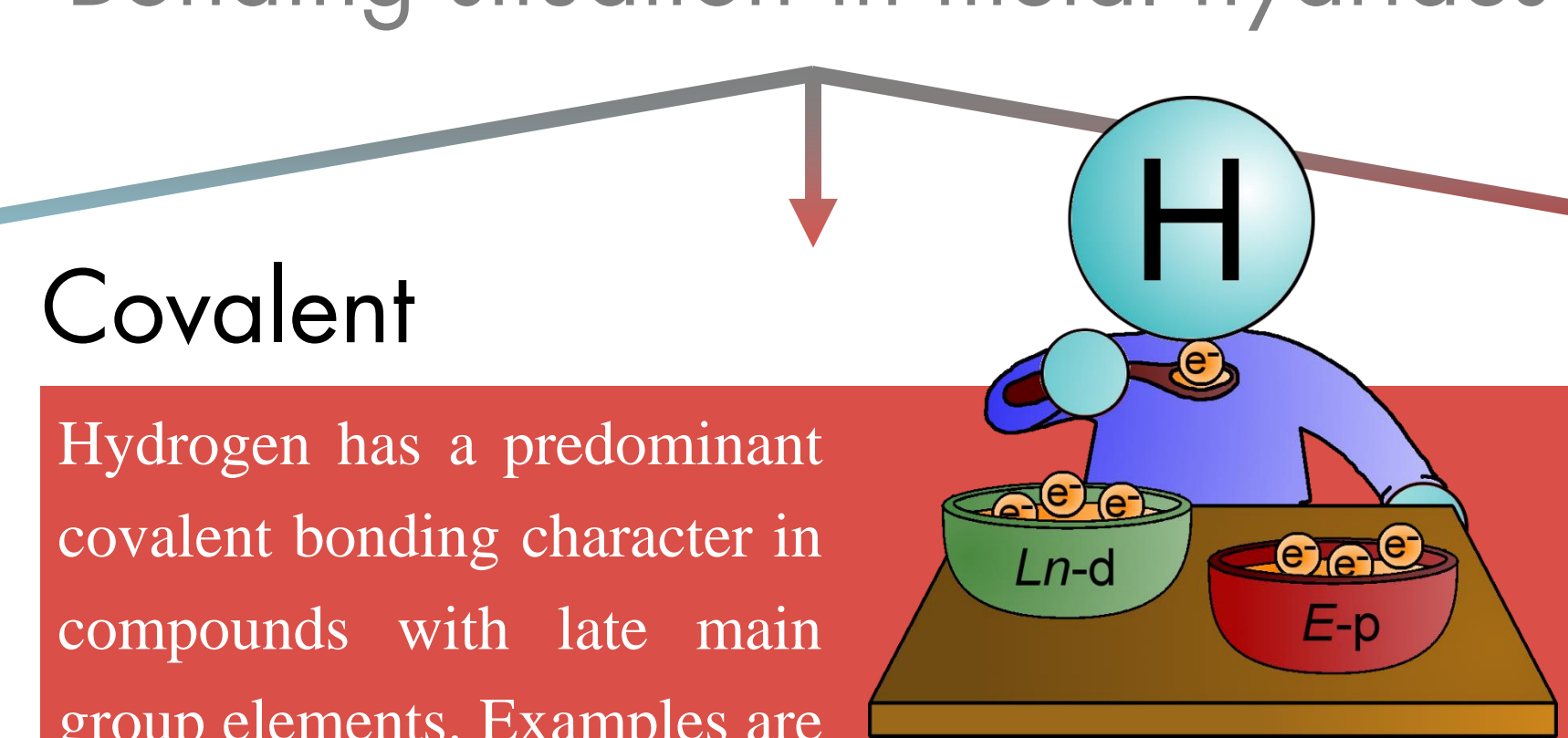


Hydrogen forms salt-like hydrides with alkali and alkaline-earth metals. The ionic radius of the hydride anion, H^- , depends strongly on the polarizing effect of the metal cation, but is comparable to those of fluoride, F^- . Thus, mixed-anionic hydride-fluorides (e.g. $\text{NaMgH}_{3-x}\text{F}_x^{[2]}$) or hydride-oxides (e.g. $\text{HoHO}^{[3]}$) are accessible and can be doped by Eu^{II} to produce luminescence materials. The substitution of fluoride with hydride ions results in a redshift of the emitted radiation (nephelauxetic effect). Thus, the emission wavelength can be tuned.

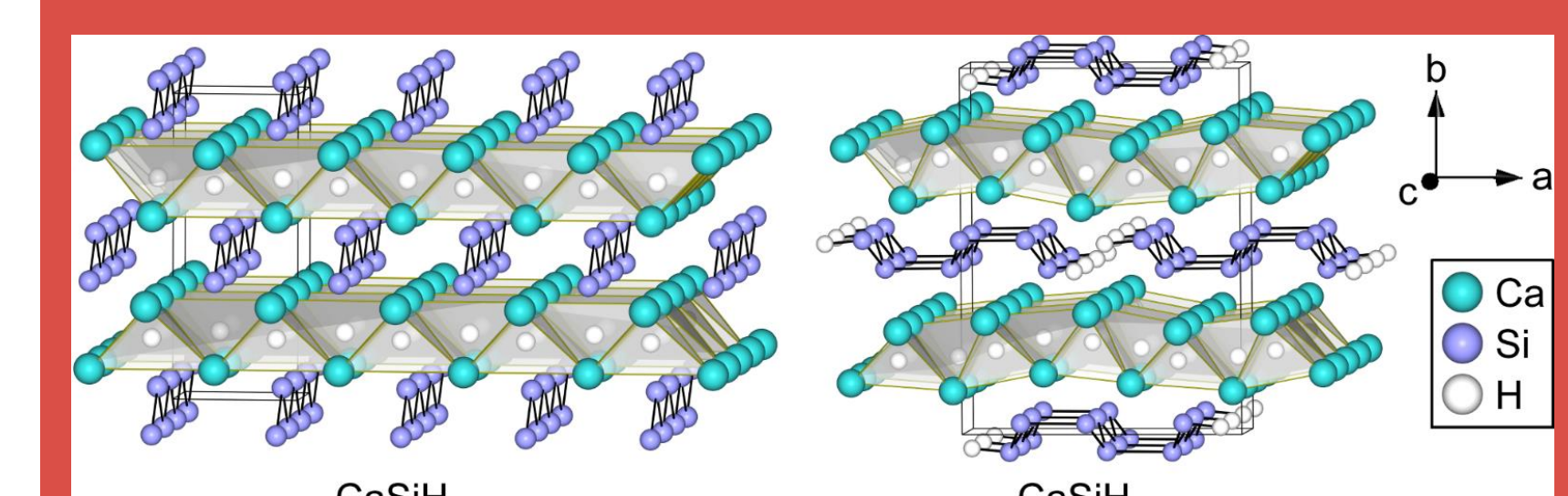


Eu^{II} luminescence (from left to right) of NaMgF_3 (372 nm), NaMgH_2F (665 nm) and NaMgH_3 (680 nm) excited by UV radiation (365 nm).^[2]

Covalent

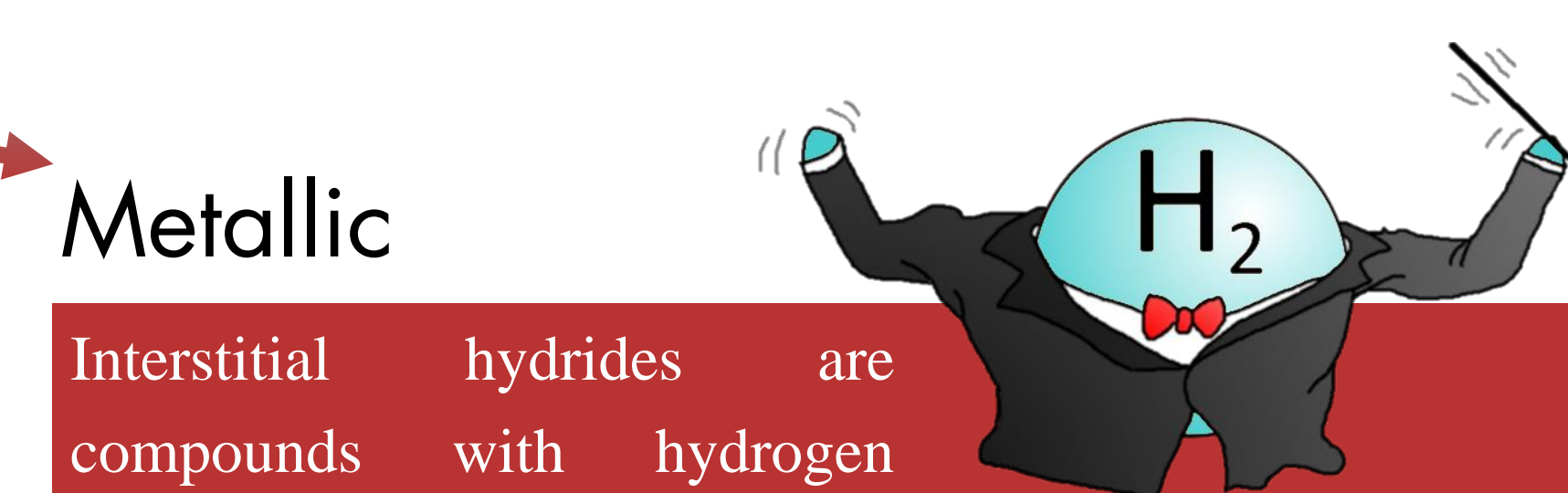


Hydrogen has a predominant covalent bonding character in compounds with late main group elements. Examples are boranates, alanates and Zintl phase hydrides. Hydrogen “eats” Ln-d electrons (Ln : lanthanides) of lanthanide-containing Zintl phases and occupies tetrahedral $[\text{Ln}_4]$ voids.^[4] However, hydrogen is also able to “eat” $E-p$ electrons (E : Al, Ga, Si, Ge) of alkaline-earth containing Zintl phases inducing the condensation of E -chains.

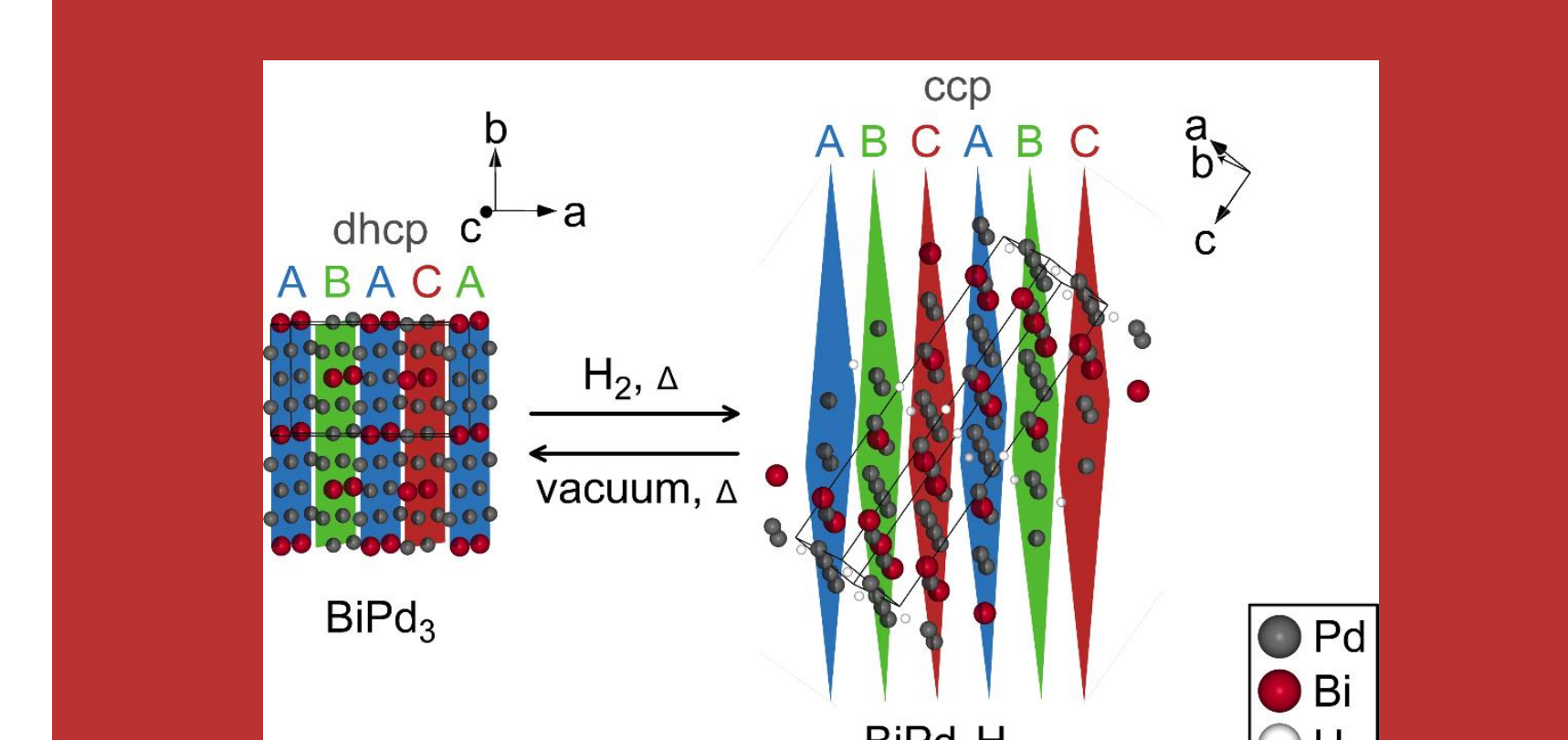


Crystal structures of hydrides of CaSi . Hydrogen occupies $[\text{Ca}_4]$ tetrahedra in the hydrogen poor phase (left) and bonds covalently to Si-chains which condense to Si-H ribbons (right).^[5]

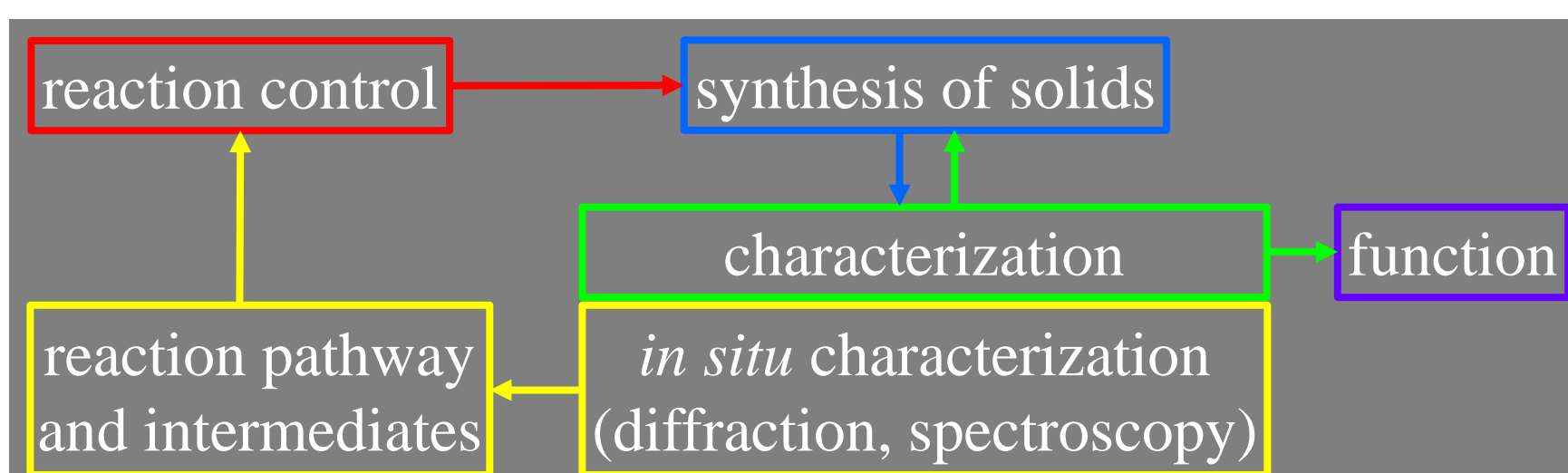
Metallic



Interstitial hydrides are compounds with hydrogen incorporated preferably in tetrahedral or octahedral voids and often exhibit metallic bonding character. Hydrogen has a structure-“directing” influence on intermetallics. In close packed structures, metal layers may shift to generate new suitable voids for hydrogen occupation. As a result, the stacking sequence of close packings is altered and can thus be influenced by hydrogenation reactions.



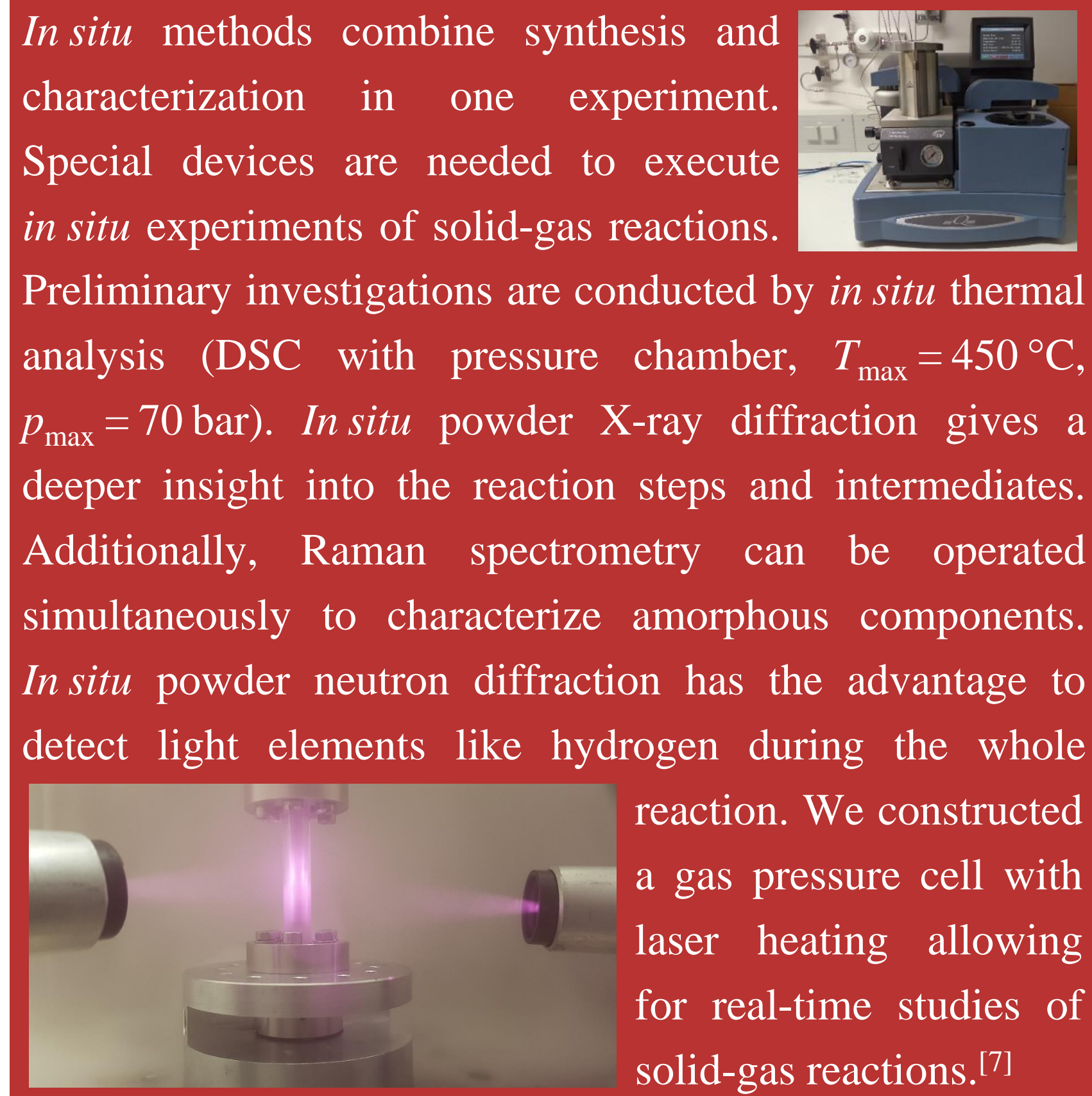
Hydrogen induced rearrangement of BiPd_3 from double hexagonal closed packing (dhcp) to cubic closed packing (ccp).^[6]



Preparation: Classic solid state reactions often require harsh conditions as for temperature and pressure and thus are usually thermodynamically controlled. *Chimie douce* at ambient conditions may be an alternative, especially for metastable compounds, where kinetic control is required. *In situ* studies shed more light on reaction pathways and enable a systematic optimization of syntheses. We use both explorative approaches to synthesize new solid compounds by classical methods and try to get an understanding of the reaction pathway by *in situ* methods. The latter aims at reaction control and rational synthesis planning in solid state chemistry.

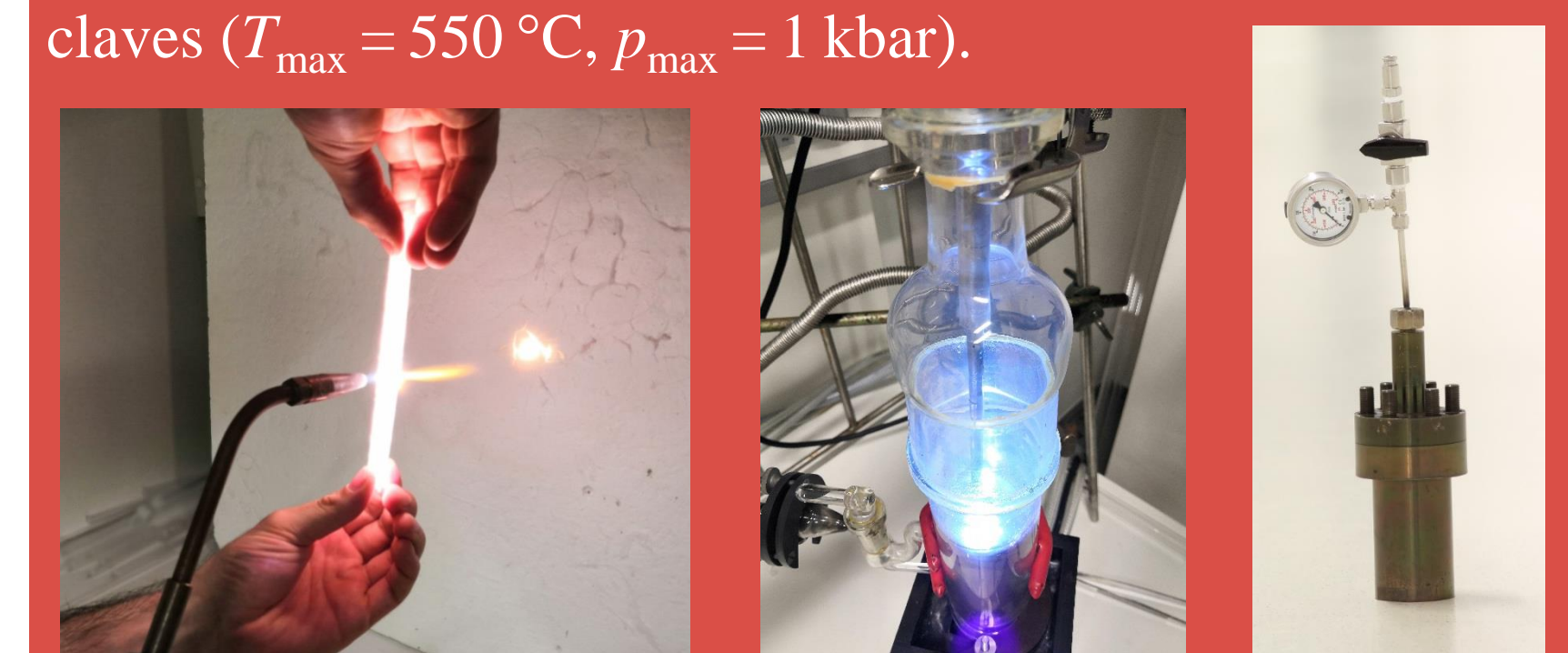
In situ methods

In situ methods combine synthesis and characterization in one experiment. Special devices are needed to execute *in situ* experiments of solid-gas reactions. Preliminary investigations are conducted by *in situ* thermal analysis (DSC with pressure chamber, $T_{\text{max}} = 450\text{ °C}$, $p_{\text{max}} = 70\text{ bar}$). *In situ* powder X-ray diffraction gives a deeper insight into the reaction steps and intermediates. Additionally, Raman spectrometry can be operated simultaneously to characterize amorphous components. *In situ* powder neutron diffraction has the advantage to detect light elements like hydrogen during the whole reaction. We constructed a gas pressure cell with laser heating allowing for real-time studies of solid-gas reactions.^[7]



Solid-state synthesis

Solid-state syntheses are often executed in sealed silica quartz or metal based (steel, niobium, tantalum) ampoules. The reaction mixtures are annealed for several hours up to days at high temperatures. Additives can enable shorter reaction times and milder conditions. Intermetallic compounds are often prepared by arc-melting. Solid-gas reactions like hydrogenations are executed in special autoclaves ($T_{\text{max}} = 550\text{ °C}$, $p_{\text{max}} = 1\text{ kbar}$).



Characterization of solids

Diffraction is the most important method for structure determination of crystalline samples. X-ray, synchrotron, electron and neutron radiation are diffracted at powder samples or single crystals. The characterization can be complemented by spectroscopic methods like Raman, EDX or fluorescence.

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- [2] C. Pflug, A. Franz, H. Kohlmann, *J. Solid State Chem.* **2018**, *258*, 391-396.
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Reviews

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