EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: Phase changes and thermal stability investigation of hydrazine borane and derivatives $M(N_2H_3BH_3)_n$ with M = Li, Na, K, Ca, Rb, Cs and n = 1, 2	**Experiment number**: MA-2017
Beamline: BM01A	**Date of experiment**: from: 13.12.2013 to: 18.12.2013	**Date of report**: 11.03.2014
Shifts: 9	**Local contact(s)**: Dr. Dmitry CHERNYSHOV	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

- Dr. Umit B. DEMIRCI,* Institut Européen des Membranes, Université Montpellier 2, Place Eugène Bataillon, CC047, 34090 Montpellier 2
- Mr. Jean-Fabien PETIT,* Institut Européen des Membranes, Université Montpellier 2, Place Eugène Bataillon, CC047, 34090 Montpellier 2
- Dr. Pascal YOT,* Institut Charles Gerhardt Montpellier, Université Montpellier 2, Place Eugène Bataillon, CC1505, 34090 Montpellier 2
- Dr. Fabrice SALLES,* Institut Charles Gerhardt Montpellier, Université Montpellier 2, Place Eugène Bataillon, CC1505, 34090 Montpellier 2

Brief introduction about the experiment. In chemical hydrogen storage, boron- and nitrogen-based materials have shown to be promising solutions for carrying elemental hydrogen (in both protic and hydridic forms) effectively and safely. Since very few years, we have been involved in the development of *novel* boron- and nitrogen-based materials, typically of hydrazine borane $N_2H_4BH_3$ and derivatives (hydrazinidoboranes) $M(N_2H_3BH_3)_n$, but also of hydrazine bisborane $BH_3N_2H_4BH_3$. Our experiment aimed at investigating the phase changes and thermal stability of these materials over a wide temperature range (80 → 500 K). X-ray diffraction and Raman spectroscopy were both used for *in operando* analyses.

Experimental conditions. The powder diffraction patterns were collected using a monochromatic beam with the wavelength of 0.70814 Å and PILATUS 2M detector. The sample-detector distance (343.71 mm) and parameters of the detector were calibrated using NIST standard LaB_6. Two-dimensional diffraction images were integrated using Fit2D software. Samples were loaded into a glass capillary of 0.5 mm diameter. Capillary was cooled from room temperature to 80 K and then heated at 60 K per hour rate up to 500 K, while synchrotron powder-diffraction data were collected in situ. The temperature was controlled with an Oxford Cryostream 700+. During each collection time (60 s per image) the capillary was rotated by 60° in the same angular interval

Hydrazine borane and derivatives. According to our experiment program, we first analyzed hydrazine parent because it is the parent material of the novel hydrazinidoboranes we synthesized.

We collected X-ray diffraction and Raman data over the aforementioned temperature range. These data are of importance as they are references for comparing with those obtained with the derivatives, for which our main results/observations are as follows:

- $LiN_2H_3BH_3$: there is a phase change at ~90°C, revealing the existence of 2 phases (α- and β-$LiN_2H_3BH_3$). The low temperature phase has shown to be less stable.
- $NaN_2H_3BH_3$: no phase change was observed over the temperature range at which it is stable towards dehydrogenation.
- For both of these derivatives, heating at temperatures higher than ~70°C leads to amorphization due to dehydrogenation and subsequent polymerization.
- $Mg(N_2H_3BH_3)_n$ and $Ca(N_2H_3BH_3)_n$: we have defined the temperatures at which the mixture [MgH_2 or CaH_2 + n $N_2H_4BH_3$] (with n = 1 and 2) interacts to give a new material, *i.e.* a new hydrazinidoborane derivative.

Hydrazine bisborane (Figures 1 and 2). This is one of our last materials synthesized. As no data of fundamental importance are available yet, we have analyzed it. For the first time, we have observed that this borane has 2 phases: a low temperature one (<–(~10°C)) and a high temperature one, called respectively α and β phases. The former phase has a orthorhombic crystal structure with a *Pbca* space group. The latter one has a monoclinic crystal structure but defining the space group is somehow difficult due to a strong overlapping of the diffraction peaks.

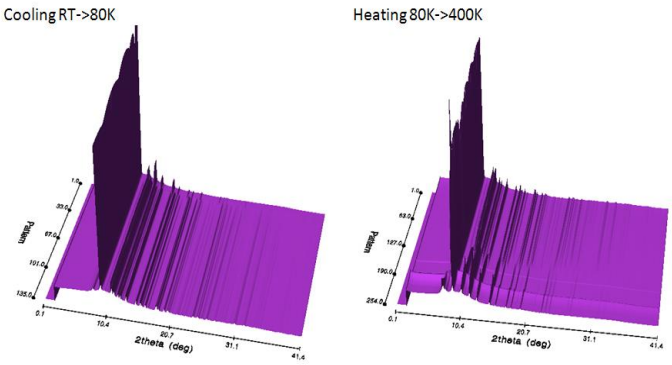

Figure 1. Powder x-ray thermodiffractogram for hydrazine bisborane sample during the cooling (left) anf the heating (right) ramps from 80K up to 400K.

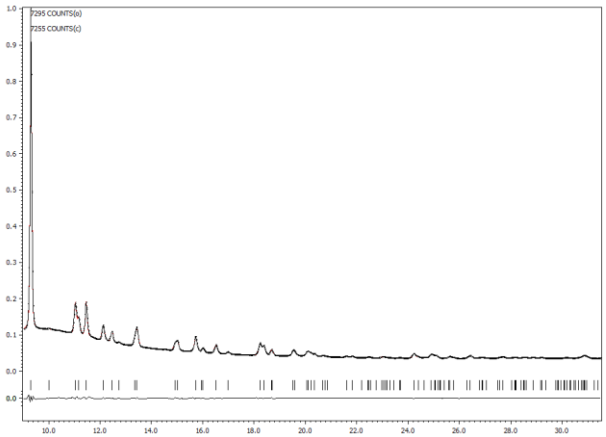

Figure 2. Structure-independent refinements of the unit-cell of the diffraction pattern obtained at 80K (α-hydrazine bisborane). S.G. : Pbca (No 61), Z=4, a=7.2784(2) Å, b=7.3607(2) Å, c=8.1176(3) Å (Vol.=434.9(1) $Å^3$).

Various ammonia boranes NH_3BH_3. Because hydrazine borane and hydrazine bisborane are derivatives of ammonia borane, we have analyzed 3 different ammoniaboranes. These materials are considered different because their thermal behaviour is different in the sense that the dehydrogenation starts at different temperatures (>100°C). Our experiment showed that there is another difference for these boranes. The phase change at low temperatures (between –60 and –40°C) takes place at different temperatures. Each of the borane would have its own intrinsic properties. Such a behaviour is not understood yet but additional experiments are on progress (*e.g.* MAS NMR and XPS) to highlight that.

Outcome. As all of our data are not yet exploited, we have not a precise idea of the final outcome yet. However, we are able to state that:

- A 1st paper on hydrazine bisborane is being written (to be submitted within 2/3 months);
- There is a 2nd one on hydrazinidoboranes; it should be in preparation soon (within 2014).
- There is a third one on ammonia boranes; it should be in preparation soon (within 2014).

Besides, it is important to state that the experiment gave us the experimental conditions to synthesize *novel* hydrazinodiboranes like $Mg(N_2H_3BH_3)_n$ and $Ca(N_2H_3BH_3)_n$.