	Experiment title:	**Experiment**
S N **B L**	In-situ X-ray and Raman studies of phase diagram Li-N-H	**number**: 01-02-854

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A flow *in-situ* cell has been set up in our laboratory in Geneva. This experimental setup allowed us to follow *in-situ* evolution of Li_3N under gas such as hydrogen, deuterium or hydrogen/nitrogen (80/20) mixture. The gas dosing system used is schematized in Fig. 1. All components of the cell are stainless steel (type 316L). Powder samples of Li_3N are introduced inside sapphire capillary tubes (OD = 1.52 mm, ID = 1.07 mm, wall = 0.23 mm, length = 7 cm) which one side is closed with a cap and the other side is mounted on a 'T-piece' with 1/16" Swagelok fittings connected on the goniometric head. Teflon ferrules are used to ensure sealing of the system. The 'T-piece' is then attached to the system *via* two peek capillaries to a stainless steel manifold *via* a second 'T-piece'. The use of peek tubing allows for a certain flexibility allowing rotation of the goniometric head when collecting SR-PXD patterns but also to put this system inside a glove box in order to fill sapphire capillary tubes.

In a typical experiment, the sample placed onto the goniometric head and connected to the dosing system, was outgassed under a vacuum pressure of 10^{-3} mbar at room temperature for few minutes in order to remove the argon gas provided from the glove box. The temperature was controlled with the Oxford Cryostream 700+. The pressure of gas was either adjusted in the manifold, and then added to the sample or a slight gas flow was kept to have a continuously flowing gas on the sample. Typical sequence of powder patterns has been collected 1 min after the gas introduction with an acquisition time of 30 s (rotation rate $1°. s^{-1}$) every 100 s.

The *in-situ* synchrotron powder diffraction experiment concentrates on two objectives: the details of the intermediate phase $Li_{2-x}NH_{1+x}$ including its ordering, and detail of the Li_3N-H phase diagram. We have observed in the *in-situ* experiment the "Li-rich imide" phase $Li_{2+x}NH_{1-x}$. It appears as one cubic imide-like phase with much bigger lattice parameter. We have observed it at the beginning of the hydrogen absorption at 255°C up to 71 mbar of gas pressure, and of the hydrogen/nitrogen mixture at 290°C up to 160 mbar.
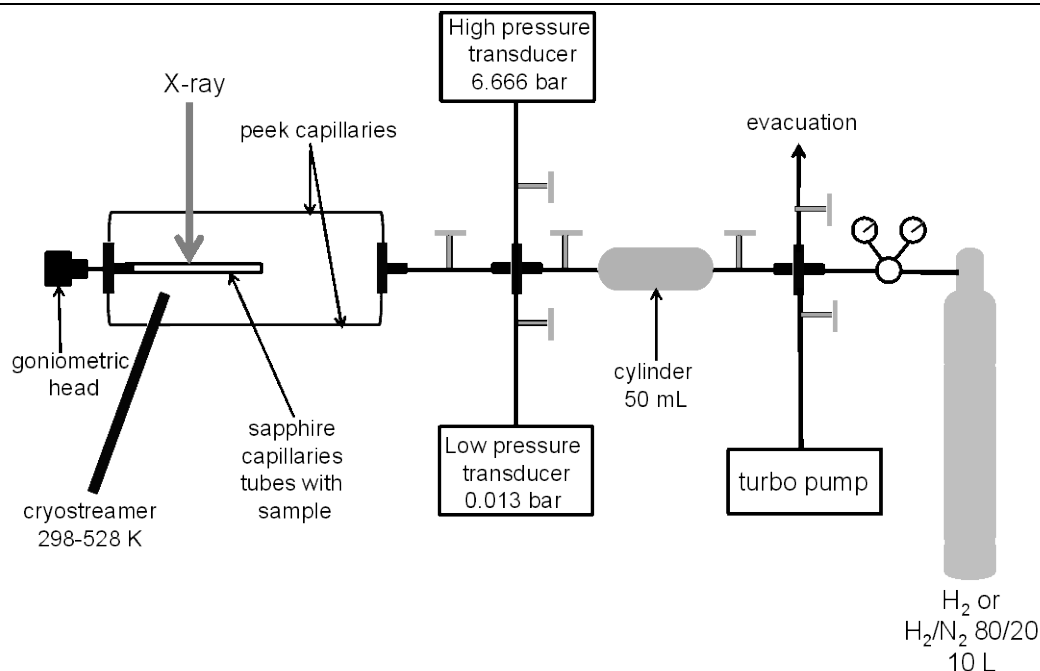
Figure 1. : Schematic diagram of the dosing manifold.

Absorption of hydrogen at 290°C has been started immediately at 54 mbar, and the "Li-rich imide" phase has not been observed in this experiment. We have observed the "Li-poor imide" intermediate imide-amide phase $Li_{2-x}NH_{1+x}$. The structural model of the $Li_{2-x}NH_{1+x}$ phase was refined in the same model as for Li_2NH (F-43m) with the site 4a mixed occupied by NH^{2-} and NH_2^- anions. It has been modeled by the variable occupancy of H on 16e site with the composition constrain according to the charge balance $Li^+_{(2-x)}(NH)^{2-}_{(1-x)}(NH_2)^-_x$. This model has been later confirmed by the DFT calculations [1]. Refinement of the Li-site occupation constrained negatively to the H-site occupation produce nice agreement with the powder diffraction data, and correlates well with the $Li_{2-x}NH_{1+x}$ lattice parameter. The upper composition limit of $Li_{2-x}NH_{1+x}$ at 290°C and 1.243 bar of hydrogen or 4.3 bar of hydrogen/nitrogen (80/20) mixture is $Li_{1.08}NH_{1.92}$ which is close to the stoichiometric amide $LiNH_2$. This upper limit is close to the thermodynamic equilibrium as it is observed at the end of the time dependent gas absorption. The lattice parameter at 290°C of $Li_{1.08}NH_{1.92}$ is for both gases $a = 5.10$ Å, giving the volume/f.u. = 33.2 Å^3. It compares better with the volume/f.u. = 33.2 Å^3 for stoichiometric amide $LiNH_2$, than with the volume/f.u. = 32.3 Å^3 for stoichiometric imide Li_2NH as observed at the end of hydrogen absorption at 290°C.

At 255°C, the Li_4NH phase forms since beginning (6.5 mbar of hydrogen) in parallel with Li_2NH and without production of LiH. The two-phase region Li_4NH and Li_2NH have been identified between 6.5 mbar and 71 mbar at 255°C. At 290°C, the upper limit of the two-phase region is shifted to 104 mbar of hydrogen. At higher pressures, above the two-phase region Li_4NH - Li_2NH, the phase Li_4NH disappears: At 255°C, the Li_4NH phase disappears above 71 mbar when Li_2NH splits into two cubic phases: Li_2NH and $Li_{2-x}NH_{1+x}$ and LiH starts to form at the same time. At 290°C, the LiH starts to appear and simultaneously Li_4NH starts to disappear at 104 mbar but Li_2NH splits into Li_2NH and $Li_{2-x}NH_{1+x}$ only at 818 mbar of hydrogen. Disappearing of Li_4NH can be explained like reaction of Li_4NH with hydrogen. When all Li_4NH disappears, Li_3N continues to react with hydrogen showing very slow kinetics of that reaction. In the hydrogen/nitrogen mixture, we observe the same formation and decomposition of Li_4NH but at higher total pressure (~4 bar of the mixture).

For 80/20 H_2/N_2 mixtures we observe a significant enhancement of the reversible capacity (from ~ 3 wt.% H to ~ 10 wt.% H after 516 cycles at 528 K), as compared to cycling without nitrogen additives. We attribute this enhancement to the reaction of nitrogen with liquid lithium during cycling as the Gibbs free energies of formation of Li_3N (ΔG^o=-98.7 kJ/mol) are more negative than that of LiH (ΔG^o=-50.3 kJ/mol). We propose that there occurs a continuous accumulation of the Li_2NH phase as these materials are subjected to cycling in H_2/N_2 atmospheres.

[1] J.C. Crivello, M. Gupta, R. Cerny, M. Latroche, D. Chandra, *Phys. Rev. B*, **2010**, *81*, 104113.