



	Experiment title: Evaluation of crystal structure defects in lithium based complex metal hydrides for hydrogen storage	Experiment number: 01-01-784
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Names and affiliations of applicants (* indicates experimentalists):

- *Radovan Černý¹
- *Dhanesh Chandra²
- *Michel Latroche³
- *Junxian Zhang³

¹Laboratoire de Cristallographie, Université de Genève, 24, quai Ernest-Ansermet
CH-1211 Genève 4, Suisse

²Mar. Sci. And Eng., Chem. And Metallurg. Eng. Dpt., University of Nevada, Reno, USA

³CNRS UMR 7182, Thiais, France

$\text{Li}_{3-x}\text{M}_x\text{N}$ ($M = \text{Co}, \text{Ni}$) compounds were prepared using the SPS technique from two precursors: Li_3N (Aldrich) and M metal powders. First the Li_3N and M powders were ball milled together in a Fritsch Pulverisette 7 for 1 hour at a rotation speed of 500 rpm with a ball-to-powder mass ratio 10:1. The mixture was sintered by SPS under 50 MPa of pressure for 15 minutes at 700°C. Then, the samples have been hydrogenated at 255°C by solid gas reaction at two different hydrogen contents. The first one at 0.7 H/ Li_3N where the Li_4NH phase should form and the second one at 1.4 H/ Li_3N where the $\text{Li}_3\text{N}_2\text{H}_3$ phase should occur. The X-ray powder diffraction data were collected using a high resolution powder diffractometer equipped with a multi-crystal analyzer ($\lambda = 0.50195 \text{ \AA}$). Phase analysis and structural determination were done by using the full profile fitting program FULLPROF based on the Rietveld's method.

Fig. 1 shows the powder X-ray diffraction of the purchased Li_3N , and synthesized $\text{Li}_3\text{N}+5\%\text{Ni}$, $\text{Li}_3\text{N}+5\%\text{Co}$ and $\text{Li}_3\text{N}+11\%\text{Co}$ after SPS treatment. The purchased Li_3N powder (Fig 1a) contains two phases: $\alpha\text{-Li}_3\text{N}$ and $\beta\text{-Li}_3\text{N}$. After the SPS treatment, samples contain only the $\alpha\text{-Li}_3\text{N}$ -type phase, a small amount of lithium oxide and in some cases, traces of the metal M . These results indicate that the metal M has entered the Li_3N structure and that the $\beta\text{-Li}_3\text{N}$ phase is metastable. The substitution of lithium by transition metal atoms (Ni or Co) leads to a modification of the cell parameters of $\alpha\text{-Li}_3\text{N}$, a increases and c decreases. The Rietveld refinement shows that Ni or Co replaces partially the Li atoms in the interlayer Li site and additionally creates Li^+ vacancies within the $[\text{Li}_2\text{N}]$ planes.

Typical refined diffraction pattern is shown in Fig. 2 for $\text{Li}_{2.95}\text{Co}_{0.05}\text{N}$ with 0.7H/ Li_3N . It was observed that for the same H concentrations, the hydrogenation reaction leads to different results depending on M . In our study, the Li_4NH phase was observed for Li_3N at H/ $\text{Li}_3\text{N} \sim 0.7$, but not for the transition-metal doped samples $\text{Li}_{3-x}\text{M}_x\text{N}$. The absence of the Li_4NH phase is not yet clearly understood but the reaction path with H_2 for $\text{Li}_{2.95}\text{Ni}_{0.05}\text{N}$ and $\text{Li}_{3-x}\text{Co}_x\text{N}$ ($x=0.05, 0.11$) is obviously not the same.

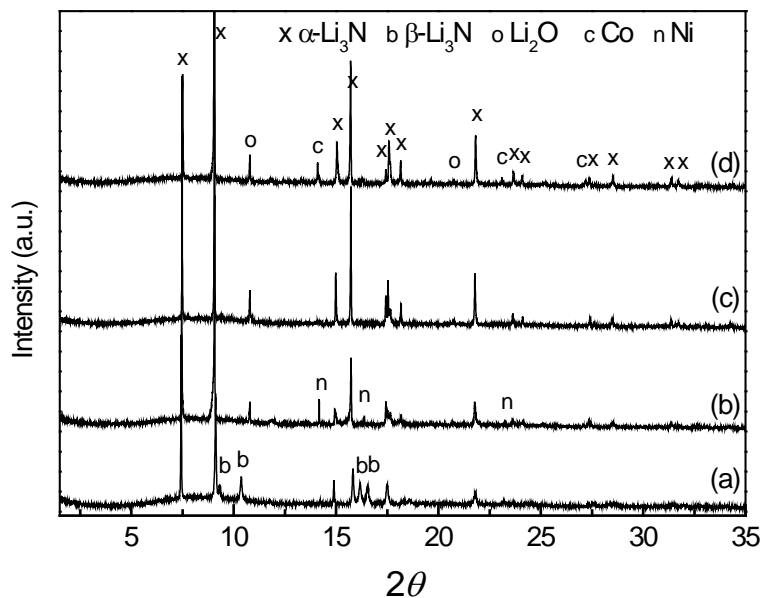


Fig. 1 Synchrotron powder X-ray diffraction patterns of commercial Li_3N (a) and SPS synthesized $\text{Li}_{2.95}\text{Ni}_{0.05}\text{N}$ (b), $\text{Li}_{2.95}\text{Co}_{0.05}\text{N}$ (c) and $\text{Li}_{2.89}\text{Co}_{0.11}\text{N}$ (d) compounds.

For $M=\text{Ni}$, with increasing H concentrations, the observed molar fraction of pure Ni metal increases from 0.2 to 2.0 and 3.1 at.% for 0, 0.7 and 1.4H/ Li_3N respectively. The Ni precipitates may play a catalytic effect in the conversion of the compound. Furthermore, a new phase $\text{Li}_5\text{Ni}_3\text{N}_3$ is formed. It suggests that the Ni-substituted Li_2NH imide phase is less stable than Ni metal and the $\text{Li}_5\text{Ni}_3\text{N}_3$ phase.

For $M=\text{Co}$, the $\text{Li}_{3-x}\text{Co}_x\text{N}$ compound does not show Co metal decomposition upon hydrogenation since metallic Co rate keeps constant to the amount observed just after the SPS treatment. Upon hydrogenation, $\text{Li}_{2.95}\text{Co}_{0.05}\text{N}$ and $\text{Li}_{2.89}\text{Co}_{0.11}\text{N}$ compounds transform into imide and LiH. The intermediate phase $\text{Li}_3\text{N}_2\text{H}_3$, which should be observed for $\text{H}/\text{Li}_3\text{N} \sim 1.4$, was not observed for the commercial sample Li_3N and $\text{Li}_{2.89}\text{Co}_{0.11}\text{N}$. In contrast, it is present at $\text{H}=0.7$ and 1.4 for $\text{Li}_{2.95}\text{Ni}_{0.05}\text{N}$ and at $\text{H}=0.7$ for $\text{Li}_{2.95}\text{Co}_{0.05}\text{N}$. Finally, for all samples, the quantity of LiH phase is well correlated to the Li_2NH phase amount.

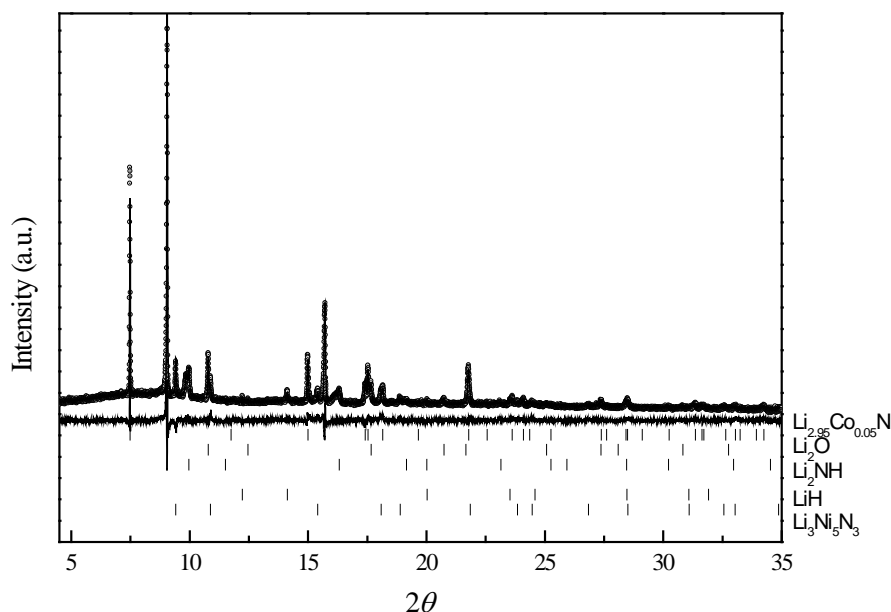


Fig.2 Refined X-ray pattern of $\text{Li}_{2.95}\text{Co}_{0.05}\text{N}$ with 0.7H/ Li_3N . obtained from synchrotron diffraction analysis (measured (dots), calculated (solid line), and difference curves (below)); Vertical bars correspond to diffraction line positions of the phases).