<table>
<tr><td>ESRF</td><td>Experiment title:<br><br>Synthesis of novel highly energetic Li-N compounds under extreme conditions</td><td>Experiment number:<br>HC 3387</td></tr>
<tr><td>Beamline:<br>ID27</td><td>Date of experiment:<br>from: November 25th 2017<br>to: November 28th 2017</td><td>Date of report:<br>26/02/2020</td></tr>
<tr><td>Shifts:<br>9</td><td>Local contact(s): Gaston Garbarino</td><td>Received at ESRF:</td></tr>
<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):<br>Dominique Laniel* – CEA, Bruyères-le-Châtel, DPTA/SPMC, LHPS<br>Gunnar Weck* – CEA, Bruyères-le-Châtel, DPTA/SPMC, LHPS</td></tr>
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The work performed during this beamtime lead to two articles.

1. D. Laniel, G. Weck, G. Gaiffe, G. Garbarino, and P. Loubeyre, High-Pressure Synthesized Lithium Pentazolate Compound Metastable under Ambient Conditions, *The Journal of Physical Chemistry Letters* **9**, 2018.

Abstract: Polynitrogen compounds have been actively pursued driven by their potential as ultra-high-performing propellants or explosives. Despite remarkable breakthroughs over the past two decades, the two figures of merit for a compelling material, namely a large fraction of nitrogen by weight and a bulk stability under ambient conditions, have not yet been achieved. We report the synthesis of a lithium pentazolate solid by compressing and laser-heating lithium embedded in molecular $N_2$ around 45 GPa along with its recovery under ambient conditions. The observation by Raman spectroscopy of vibrational modes unique to the cyclo-$N_5^-$ anion is the signature of the formation of $LiN_5$. Mass spectroscopy experiments confirm the presence of the pentazolate anion in the recovered compound. A monoclinic lattice is obtained from X- ray diffraction measurements and the volume of the $LiN_5$ compound under pressure is in good agreement with the theoretical calculations.

2. D. Laniel, G. Weck, and P. Loubeyre, Direct Reaction of Nitrogen and Lithium up to 75 GPa: Synthesis of the $Li_3N$, LiN, $LiN_2$, and $LiN_5$ Compounds, *Inorganic Chemistry* **57**, 2018.

Abstract: A wide variety of Li-N compounds are predicted as stable under pressure and associated with various nitrogen anionic moieties. Accordingly, the $LiN_5$ compound was recently synthesized at 45 GPa by the direct reaction of nitrogen and lithium. In this study, we present an experimental investigation of the Li-N binary phase diagram from ambient pressure up to 73.6 GPa. The samples loaded in the diamond anvil cells were constituted of pure lithium pieces embedded in a much greater quantity of molecular nitrogen and, at incremental pressure steps, were laser-heated to produce the thermodynamically favored solid. The following compounds are observed: $Li_3N$, $LiN_2$, LiN as well as $LiN_5$, and their pressure stability domain is disclosed. Two are synthesized for the first time, namely *Cmcm* LiN and $P6_3/mmc$ $LiN_2$. Both are structurally resolved and characterized by X-ray diffraction and Raman spectroscopy measurements. Their high bulk modulus is characteristic of charged $N_2$ dimers.