ESRF	**Experiment title:** Synthesis and single-crystal X-ray diffraction characterization of novel scandium nitrides under high pressures up to 175 GPa	**Experiment number**: CH-6542
Beamline: ID11	**Date of experiment**: from: 12.04.2023 to: 17.04.2023	**Date of report**: 04.09.2023
Shifts: 15	**Local contact(s)**: Eleanor Lawrence Bright	*Received at ESRF:*

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Report:

The aims of the proposed experiments were the synthesis of new Sc-N compounds at multimegabar pressure, characterization of their crystal chemistry and compressional behavior, tests of theoretical predictions, and search for regularities in polynitrogen chemistry.

The diamond anvil cells, containing a sample composed of scandium pieces embedded into molecular nitrogen, were compressed to 78, 96, and 125 GPa and laser-heated to 2500 K. The precise 2D X-ray diffraction map, collected with a step of 0.75 µm at ID11 ESRF beamline from the heated area, revealed the crystallization of novel phases and allowed to pinpoint the location of crystallites most appropriate for single-crystal X-ray diffraction measurements (Fig. 1a). High-quality synchrotron single-crystal X-ray diffraction data were then collected from the sample. The subsequent crystal structure solution and refinement revealed the formation of four novel Sc-N phases — Sc_2N_6, Sc_2N_8, ScN_5, and Sc_4N_3 — at pressures between 78 and 125 GPa. Nitrogen-rich scandium polynitrides Sc_2N_6, Sc_2N_8, and ScN_5 demonstrate a unique nitrogen catenation: they feature N_6 units, N_8 units, and 2D polynitrogen ${}^{2}_{\infty}(N_5^{3-})$ layers consisting of N_{12} fused rings, respectively (Fig. 2).

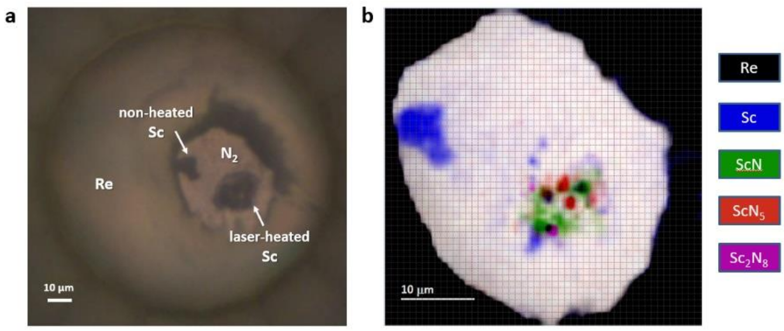

Figure 1. (a) Microphotograph of the sample chamber at 96 GPa. (b) 2D X-ray diffraction map showing the distribution of the scandium nitrides phases within the heated sample.

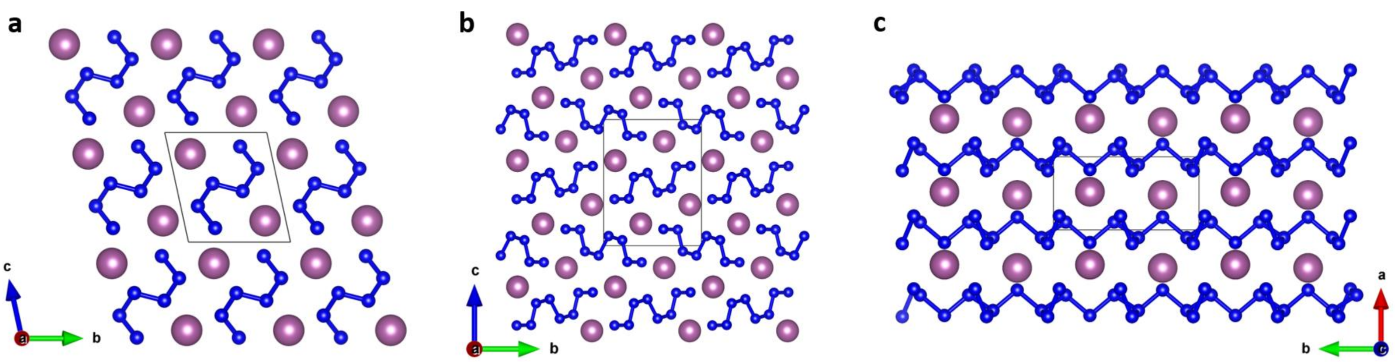

Figure 2. Crystal structure of (a) Sc_2N_6, (b) Sc_2N_8, and (c) ScN_5. All Sc atoms are purple and N atoms are blue.

The discovery of such catenated nitrogen units gives an insight into the possible ways of nitrogen catenation depending on the pressure, significantly extends the chemistry of polynitrides, and may have an impact on general organic and inorganic chemistry. One can expect that the N_6 and N_8 units will be stabilized at ambient conditions in the future, considering a positive example of the N_5^- anion. It may not only open access to novel high-energy density materials but also to analogues of Li- and Mg- metalorganic compounds that are currently widely used in organic synthesis. N_6 and N_8 units, if used as building blocks in organic chemistry, may provide new routes for the targeted synthesis of novel N-heteroatomic organic, metalorganic, and coordination compounds.

The fruitful results of this experiment have been submitted to *Nature Chemistry* and the manuscript is under review now:

A. Aslandukov, A. Aslandukova, D. Laniel, S. Khandarkhaeva, Y. Yin, F. I. Akbar, S. Chariton, V. Prakapenka, **E. L. Bright, C. Giacobbe, J. Wright**, D. Comboni, M. Hanfland, N. Dubrovinskaia, L. Dubrovinsky (2023). Stabilization of N_6 and N_8 anionic units and 2D polynitrogen layers in high-pressure scandium polynitrides, *Nature Chemistry*, under review.