ESRF	**Experiment title: Nitrides at ultra-high pressures: the Ca-N and Sr-N systems to 240 GPa**	**Experiment number**: HC-4882
Beamline:	**Date of experiment**: from: April 5 2022 to: April 8 2022	**Date of report**: 09.08.2022
Shifts:	**Local contact(s)**: Carlotta Giacobbe	*Received at ESRF:*

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Report:

Objectives

The aims of these experiments were to *i*) synthesize novel Ca_xN_y and Sr_xN_y solids at ultrahigh pressures, *ii*) solve their crystal structure and, *iii*) determine their equation of state and stability domain. This study was expected to lead to more accurate physico-chemical models of alkaline earth-N interactions and, importantly, provide potentially game-changing first insights into the ultrahigh pressure chemistry of nitrogen and ultrahigh energy N-species. The knowledge obtained during these experiments will be key to inspiring new designs of ambient conditions polynitrogen-based materials and potentially unlocking the next generation high energy density material.

Results

BX90-type diamond anvil cells with culets of 40 to 80 μm were prepared. Calcium azide and strontium azide pieces were loaded along with molecular nitrogen, acting as a reagent as well as a pressure transmitting medium. Pressures were measured based on the equation of state of the Re gasket and verified with the first Raman edge of diamond[1,2]. The samples were precompressed to the targeted pressures of 150 and 200 GPa and laser-heated to temperatures above 2000 K at our laboratory in Bayreuth. Preliminary Raman measurements showed new vibrational modes, suggesting the formation of Ca- and Sr-N compounds. These samples were brought to ID11 for single-crystal X-ray diffraction measurements of the synthesized phases.

Upon arrival at the ID11 beamline, it was found that one diamond anvil of the $Sr(N_3)_2+N_2$ cell at about 200 GPa had been broken during transportation, and that pressure had dropped down to 65 GPa. Measurements on the other $Sr(N_3)_2+N_2$, at 150 GPa, revealed the formation of the previously observed SrN_{16} (see experimental report HC-4225), as well as a phase which could not yet be solved due to twinning.

Experiments on $Ca(N_3)_2+N_2$, on the other hand, resulted in the synthesis of four Ca-N phases, CaN_5, α-CaN_6, β-CaN_6 and CaN_8, with all but α-CaN_6 being previously unobserved. Their structures, drawn in Figure 1, were fully solved by single-crystal X-ray diffraction. Remarkably, these four compounds are all comprised of exotic polymeric nitrogen chains. Those found in β-CaN_6 and CaN_8 are especially striking, adopting an arrangement never seen before, which can simplistically be described as chains of N_6 units. These are reminiscent of those found in the hexagonal layered polymeric nitrogen (HLP-N) phase—a phase of pure nitrogen that forms near 250 GPa.[3]

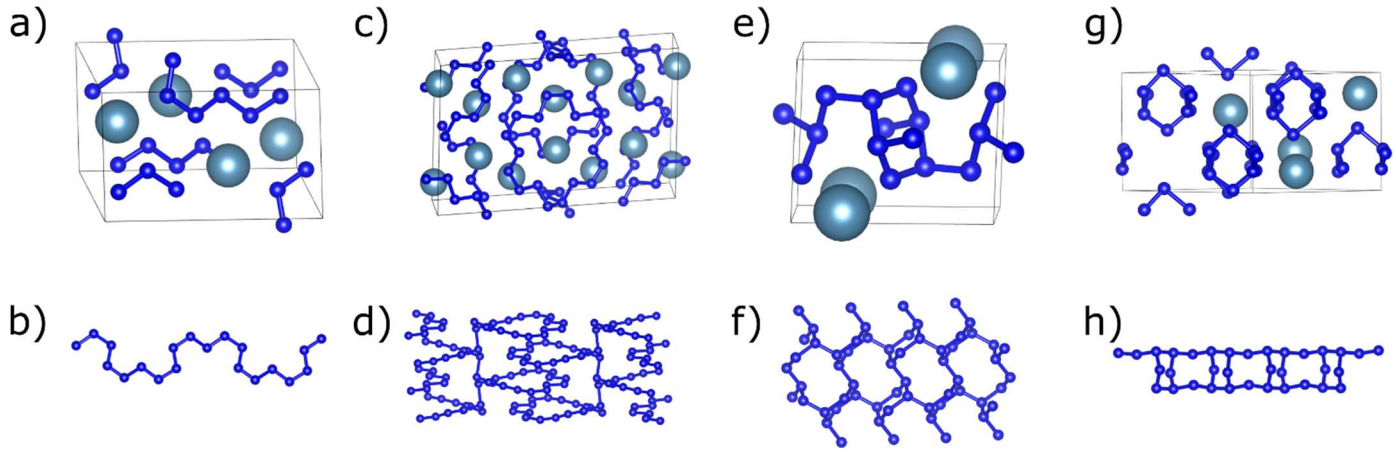

Figure 1: Experimentally determined crystal structures and polynitrogen units of the CaN_5 (a-b), α-CaN_6 (c-d), β-CaN_6 (e-f) and CaN_8 (g-h) compounds.

The comparison of the polynitrogen chains typically formed below 150 GPa and those at greater pressure underpins a clear trend. Polynitrogen chains below 150 GPa typically feature two-fold coordinated nitrogen atoms with shorter N-N distances. On the other hand, the β-CaN_6 and CaN_8 solids produced at higher pressures feature significantly more three-fold coordinated nitrogen atoms with longer N-N distances.

The decompression of these phases was initiated, but could not be completed within the allocated beamtime.

With the synthesis of four phases, including three new, the beamtime was undoubtedly a great success. Future experiments will again attempt the investigation of the Sr-N system at very high pressures and complete the decompression of the CaN_5, α-CaN_6, β-CaN_6 and CaN_8 compounds. This beamtime will result in at least one scientific publication.

References

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2. Akahama, Y. & Kawamura, H. Pressure calibration of diamond anvil Raman gauge to 410 GPa. *J. Phys. Conf. Ser.* **215**, 012195 (2010).
3. Laniel, D., Geneste, G., Weck, G., Mezouar, M. & Loubeyre, P. Hexagonal Layered Polymeric Nitrogen Phase Synthesized near 250 GPa. *Phys. Rev. Lett.* **122**, 066001 (2019).