	Experiment title: Pressure Synthesis of Strontium and Barium Polynitrogen Compounds	**Experiment number**: HC-4225
Beamline: ID15b	**Date of experiment**: from: 03.03.2021 to: 06.03.2021	**Date of report**: 05.09.2021
Shifts: 9	**Local contact(s)**: Tomasz Poreba and Michael Hanfland	*Received at ESRF:*

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Report:

Objectives

The aims of these experiments were to *i*) synthesize novel Sr_xN_y and Ba_xN_y solids, *ii*) determine their crystal structure *in-situ* by employing synchrotron single-crystal X-ray diffraction of the polycrystalline samples (SC-XRDp) and, *iii*) establish the produced compounds' equation of state and find out if they are recoverable to atmospheric pressure. This study is of utmost importance as discovering novel polynitrogen species' geometries stable at ambient conditions is the cornerstone of designing new and improved nitrogen-based technological materials, such as superhard solids and high energy density materials. Moreover, fully completing the high-pressure investigation of nitrogen with AE elements will allow the devising of new crystal-chemical principles regulating the interaction between these elements and provide further insight into the mechanisms promoting the formation of polynitrogen species.

Results

BX90 diamond anvil cells with 120 μm culets were prepared. Strontium azide and barium azide pieces were loaded along with molecular nitrogen, acting as a reagent as well as a pressure transmitting medium. A ruby microsphere was employed as the *in-situ* pressure gauge. The samples were compressed to the targetted pressures and laser-heated to temperatures above 2000 K at our home laboratory in Bayreuth. Preliminary Raman measurements showed new vibrational modes, suggesting the formation of new Sr- and Ba-N

compounds. On account of the sanitary situation, it was only possible for one person in our team to travel to the ESRF, and other team members participated to the beamtime through remote access.

The X-ray diffraction (XRD) mapping of our samples confirmed the Raman measurement as diffraction lines not belonging to any known phases (*i.e.* pure strontium, barium, strontium azide, barium azide or nitrogen) were detected. SC-XRDp was performed on the positions with the highest quality diffraction spots. The structure of the novel strontium-nitrogen compound was fully determined onsite. The solid has the SrN_{16} stoichiometry and comprises both pentazolate rings and triple-bonded molecular nitrogen species, as shown in the background of Figure 1. As shown in the same figure, the compound could be observed between 56 and 94 GPa. Upon decompression to lower pressures, SrN_{16} appeared to decompose as its diffraction lines could no longer be observed.

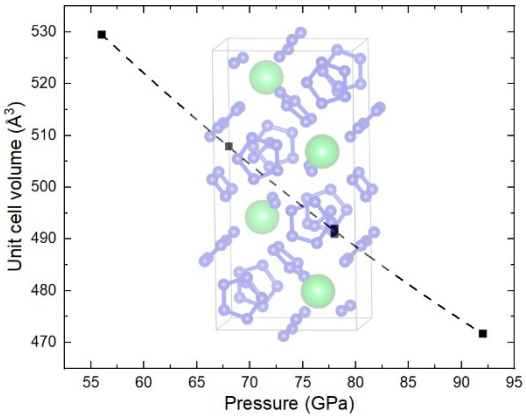

Figure 1: Pressure-volume datapoints of the novel SrN_{16} compound and, in the background, its crystal structure.

In the case of the Ba-N compound, the same new diffraction lines were observed from samples laser-heated at 76.6, 82.0 and 101.3 GPa. The single-crystal data revealed a complicated crystal structure as the obtained phase was unambiguously found to be modulated, making its analysis significantly more challenging. This can be seen from the position of the reflections in the reciprocal space, shown in Figure 2 and described in the figure's caption. A reasonable structural model for the average unit cell was nonetheless obtained. However, to be fully confident in the structure, determining the modulation vector is essential. To accomplish this, a collaboration with experts in modulated crystal structures was initiated. Various combinations of unit cells and modulations vectors are currently being tested. As drawn in Figure 2, a cubic unit cell with a modulation vector q1 = 1/3 1/3 1/3 is one of the most likely possibilities. The probable compound stoichiometry is BaN_6. This behavior is reminiscent of phase IV of barium, found between 12.6 and 45 GPa,[1] which is also modulated.

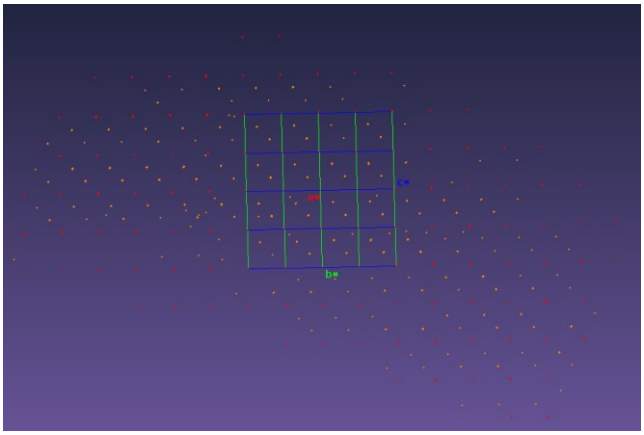
Figure 2: Reflections belonging to a unique crystallite of the new Ba-N compound. The reflections in red form a cubic lattice, while those in orange, of much lower intensity, are the reflections resulting from the modulation.

With the synthesis of two new phases and an equation of state, the beamtime was undoubtedly a great success. An overall greater efficiency, with more data points and samples characterized, could have been achieved if all team members had been allowed onsite. Nonetheless, in the current difficult sanitary situation, we are very pleased with the results obtained. This beamtime should result in at least one scientific publication.

References

// [**1**] Nelmes, R. J. *et al. Phys. Rev. Lett.* **83**, 4081–4084 (1999)