ESRF	**Experiment title:** Synthesis and single-crystal X-ray diffraction characterization of novel gadolinium nitrides under high pressures up to 50GPa	**Experiment number**: CH-6467
Beamline: ID15b	**Date of experiment**: from: 08.09.2022 to: 11.09.2022	**Date of report**: 02.12.2022
Shifts: 9	**Local contact(s)**: Davide Comboni	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists): Andrii Aslandukov*— Bayerisches Geoinstitut, University of Bayreuth		

Report:

This single-crystal X-ray diffraction experiment aimed to determine crystal structures of novel Gd-N compounds synthesized under pressures up to 50 GPa in laser-heated diamond anvil cells and determine the equation of states and existence pressures of all novel yet-to-be-uncovered gadolinium nitrides phases.

BX90 diamond anvil cell with 250 µm culet was prepared. A piece of gadolinium was loaded along with molecular nitrogen, acting as a reagent as well as a pressure-transmitting medium. The sample was compressed to 50 GPa and laser-heated to temperatures above 2000 K at our home laboratory in Bayreuth. After laser-hating the pressure increased to 52 GPa.

The X-ray diffraction mapping of the heated sample revealed the formation of a novel phase since diffraction lines not belonging to any known phases (*i.e.* gadolinium, cubic GdN, or nitrogen) were detected. Single-crystal X-ray diffraction was collected on the positions with the highest-quality diffraction spots. The structure of the novel gadolinium-nitrogen compound was fully determined onsite. The solid has the Gd_5N_{14} stoichiometry and comprises nitrogen dimers (Fig.1 inset). The Gd_5N_{14} compound is isostructural to Y_5N_{14}, synthesized by our group under similar conditions (49 GPa and 2000 K). To determine the equation of state and existence pressure of Gd_5N_{14}, its decompression in several steps (Fig. 1) down to 1 bar was done. The single-crystal diffraction spots of Gd_5N_{14} were traced down to 9 GPa, and at 1 bar its diffraction lines could no longer be observed indicating the decomposition of Gd_5N_{14}. Fitting of the Gd_5N_{14} experimental pressure-volume datapoints with the 2nd order Birch-Murnaghan equation of state gives the bulk modulus K_0=129(12) GPa.

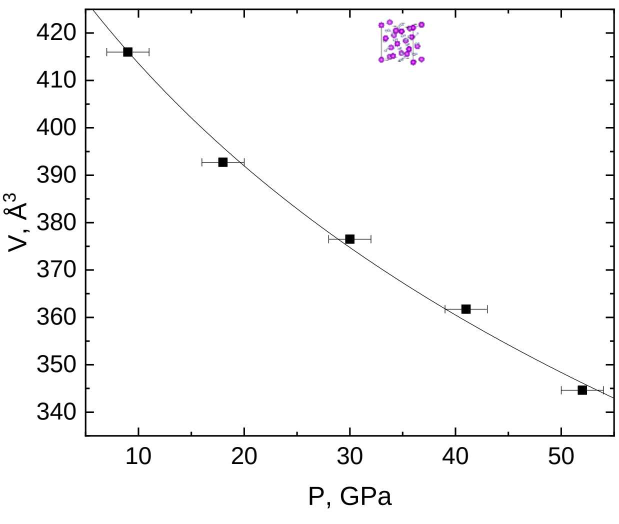

Figure. 1. Pressure-volume data points of the novel Gd_5N_{14} compound and its crystal structure as inset.

The formation of Gd_5N_{14} compound isostructural to Y_5N_{14} under similar conditions was expected since both metals possess only +3 oxidation state and the ionic radius of gadolinium ion r(Gd^{3+}) = 1.078 Å is close to yttrium ionic radius r(Y^{3+}) = 1.04 Å. These results demonstrate that M_5N_{14} structure type is common for high-pressure rare-earth nitrides and the crystallization in this structure type can be expected for nitrides of M = Tb, Dy, Ho, Er (with r(M^{3+}) = 1.03-1.06 Å ionic radii) and perhaps for an even greater number of lanthanides.

The obtained data should result in one scientific publication. This result provides prerequisites for further studying of the Gd-N system at the megabar regime, since the formation of unique polynitrides isostructural to recently discovered Y_2N_{11} and YN_6 with polynitrogen double-helix and N_{18} macrocycles, can be expected.