ESRF	**Experiment title:** Characterization of novel lanthanum nitrides	**Experiment number**: CH-6091
Beamline: ID12	**Date of experiment**: from: 01.12.2021 to: 06.12.2021	**Date of report**: 21.02.2022
Shifts: 15	**Local contact(s)**: Fabrice Wilhelm	*Received at ESRF:*

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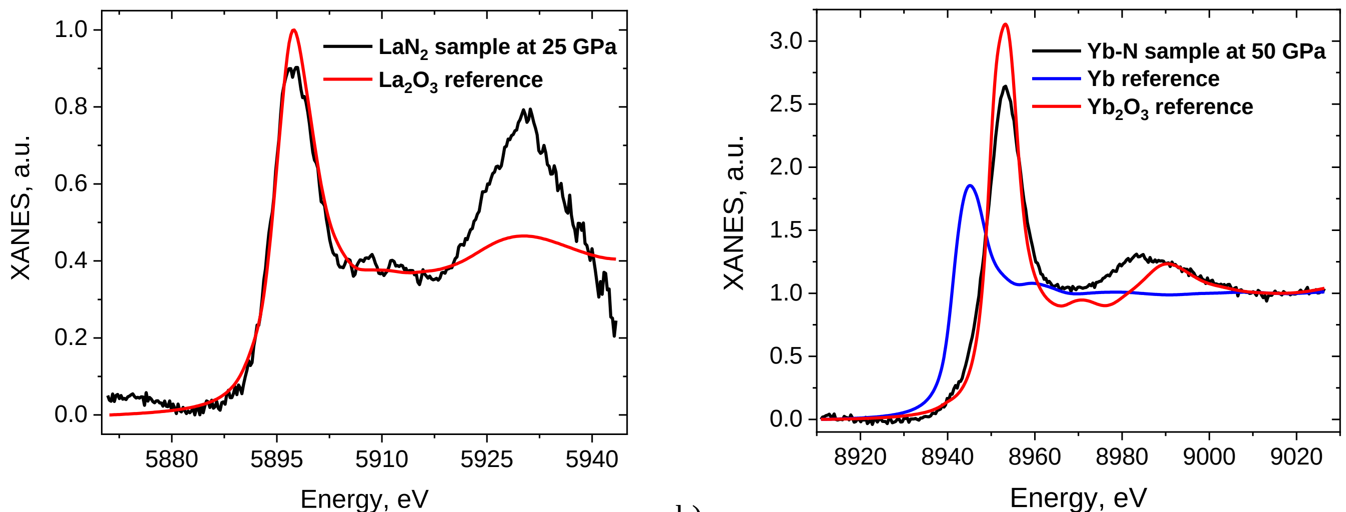
Report:

The aim of the spectroscopy part of this proposal was to determine the oxidation state of lanthanum in the novel LaN_2 phase by XANES to check the preliminary conclusion of unusual La^{2+} oxidation state made from crystal-chemistry analysis of LaN_2 structure.

All sample preparation was done at our home laboratory in Bayreuth. The planned preparation of diamond anvil cell (DAC) with special purchased mini-diamonds for XANES measurements (thickness of 0.5 mm) was not successful (diamonds broke during the nitrogen gas-loading). Hence, DAC equipped with standard diamonds (thickness of 1.5 mm) composed of LaN_2 sample at 25 GPa, which was studied before at X-ray diffraction beamline was used to investigate LaN_2 sample. Usually, such thick diamonds do not allow to measure La L_{III}-edge due to the low transmission of the diamond at such energies. Therefore, backup DAC#2 was prepared containing laser-heated Yb piece embedded in molecular nitrogen at 50 GPa. The DAC#2 was previously studied at X-ray diffraction beamline, where a mixture of two new Yb-N phases with unique N_8 nitrogen units and N_6 rings respectively were found. Ytterbium could possess two typical Yb^{2+} and Yb^{3+} oxidation states, that's why this sample is also an interesting case for XANES spectroscopy. A grand total of two diamond anvil cells and three reference samples (La_2O_3, Yb_2O_3 powders and Yb metal piece) were brought to ID12 beamline.



a) b)

Figure. 1. a) La L_{II} edge XANES spectra of LaN_2 sample at 25 GPa and La_2O_3 reference sample at ambient conditions. b) Yb L_{III} edge XANES spectra of "Yb-N" sample at 50 GPa and Yb and Yb_2O_3 reference samples at ambient conditions.

After setting up the ID12 beamline and many attempts to optimize it for lanthanum XANES high-pressure measurements we managed to get—though weak—the La L_{II}-edge XANES signal from LaN_2 sample in the DAC. The comparison of the collected spectrum with La_2O_3 reference sample spectrum revealed the oxidation state of +3 for lanthanum in LaN_2 (Fig. 1a). This result refutes the hypothesis about the unusual La^{2+} oxidation state and shows that instead the nitrogen species should have unusual charge states in the LaN_2 structure. We had enough time to study backup DAC#2 cell with Yb-N sample. As long as Yb $L_{II,III}$ absorption edge energies are higher than La $L_{II,III}$ edge energies the diamond transmission is higher which results in the much better quality of high-pressure XANES signal. The analysis of Yb L_{III} edge XANES spectra of Yb-N sample at 50 GPa, Yb (Yb^{2+} spectroscopy standard) and Yb_2O_3 (Yb^{3+} spectroscopy standard) reference samples clearly demonstrated that both Yb-N phases contain only Yb^{3+}. This result will help to shed the light on the charge state of exotic N_8 and N_6 nitrogen units.

The results of this beamtime together with previously obtained X-ray diffraction data should result in two scientific publications.