| | | |
|---|---|---|
| | **Experiment title:**<br>High-pressure synthesis of nitride perovskites via azide-mediated oxidation | **Experiment number**:<br>CH-6298 |
| **Beamline**:<br>ID27 | **Date of experiment**:<br>from: 03.06.2022 to: 05.06.2022 | **Date of report**:<br>20.09.2022 |
| **Shifts:**<br>6 | **Local contact(s)**:<br>Gaston Garbarino | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

Maxim Bykov* (University of Cologne, Cologne, Germany)

Georg Krach* (Ludwig-Maximilian University of Munich, Munich, Germany)

Yuqing Yin* (University of Bayreuth, Bayreuth, Germany)

Timofey Fedotenko* (DESY, Hamburg, Germany)

**Report:**

In the experiment CH-6298 we studied high-pressure high-temperature reactions between metal azides $Ca(N_3)_2$, $Ba(N_3)_2$, $Sr(N_3)_2$, $NaN_3$ and transition metals W and Re. Thin foils of transition metals were placed in sample chambers of BX90-type diamond anvil cells (250 μm and 500 μm culet diameter) and the chambers were further filled by azides, which served as reagents and as pressure-tranmitting media. Samples were compressed to a starting pressure of 5 GPa and laser-heated using a focused Nd:YAG laser ($\lambda$ = 1064 nm). Although starting materials were highly textured powders, chemical reaction induced by laser heating leads to the formation of multiple well-crystallized product grains (Figure 1). Therefore, the analysis of reaction mixtures was performed using the methods of multigrain single-crystal X-ray diffraction. Due to the excellent resolution of the new Eiger 9M detector of ID27 we were able to separate reflections belonging to a single grain of target product and perform data integration and further structure solution and refinement without prior knowledge of chemical composition and crystal structure. It should be noted that the high dynamic range of Eiger 9M allowed to collect excellent datasets from compounds containing both heavy and light elements (e.g. Ba, Re together with nitrogen), leading to a combination of very weak and very strong diffraction peaks.

As a result of the experiment we got several novel phases of ternary nitrogen-rich nitrides (including $Sr_3ReN_4$, $Ba_3ReN_5$, $Ca_3W_8N_{13}$ and others).

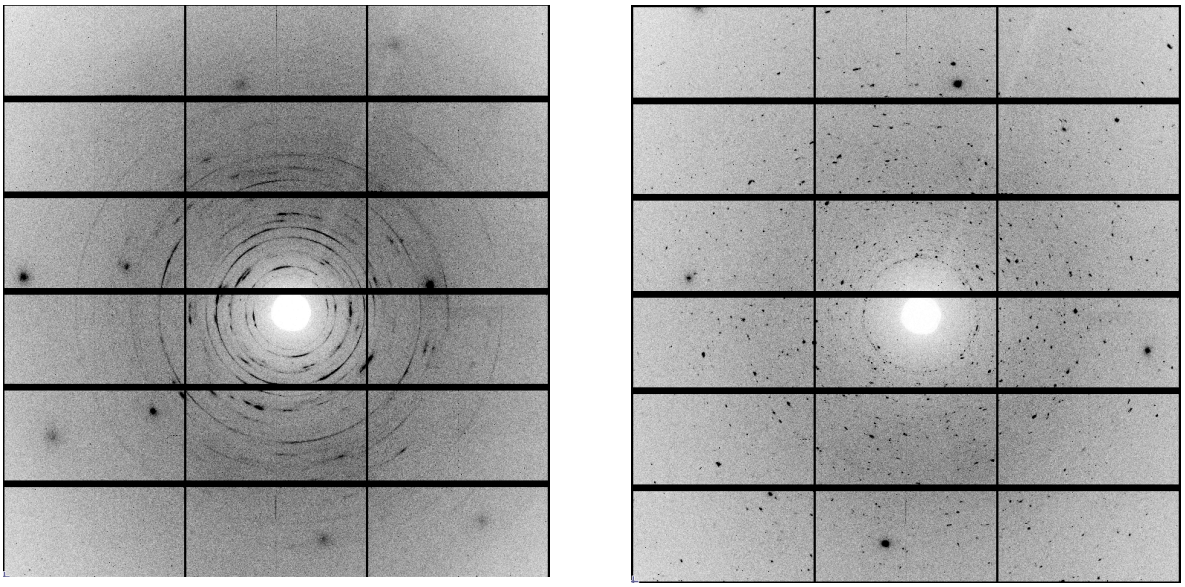

**Figure 1.** Diffracion patterns of metal + azide samples before(left) and after (right) laser heating

The analysis of the products, their properties is still ongoing. In this report we present the structure of a novel layered compound $NaW_2N_3$, synhtesized from a mixture of $NaN_3$ and W. $NaW_2N_3$ has a hexagonal crystal structure with the space group $P6_3/mmc$ and consists of layers of $h$-$W_2N_3$ and sodium intercalated between them. Compared to Na-free $W_2N_3$, which finds applications in catalysis and has exciting topological features in the electronic structure, $NaW_2N_3$ with with intercalated Na atoms may lead to unique electrochemical applications as intercalation allows to tuning the electronic and optical properties of layered materials.

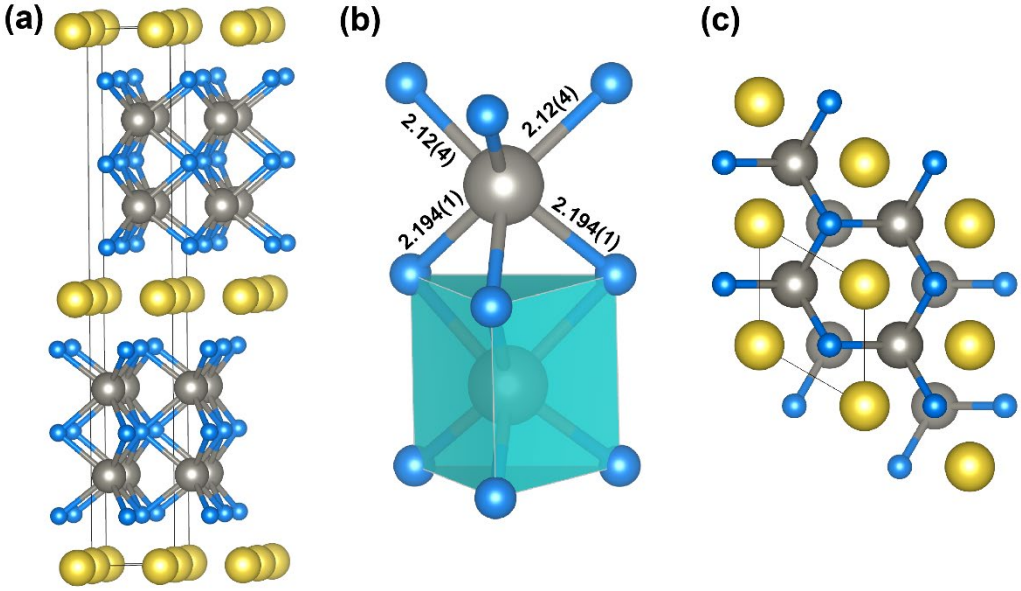


**Figure 2.** Crystal structure of $NaW_2N_3$ in diffferent projections. Yellow, grey and blue balls show the position of sodium, rhenium and nitrogen atoms respectively. Distances are given in Å.