



## Experiment Report Form



	<b>Experiment title:</b> High-pressure routes to pentavalent lanthanoids	<b>Experiment number:</b> CH-6475
<b>Beamline:</b> ID27	<b>Date of experiment:</b> from: 17.02.2023 to: 20.02.2023	<b>Date of report:</b>
<b>Shifts:</b> 9	<b>Local contact(s):</b> Mohamed Mezouar, Bjorn Wehinger	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> *Maxim Bykov, University of Cologne, Germany *Niko Flosbach, University of Cologne, Germany *Lukas Brüning, University of Cologne, Germany *Pascal Jurzik, University of Cologne, Germany		

### Preliminary report (submitted 2 weeks after the beatmime):

Praseodymium dioxide was loaded in diamond anvil cells (BX90 type, Boehler-Almax type diamonds) together with oxygen by cryogenic loading. One of the cells was compressed to 27 GPa and laser heated at ID27. After locating the sample position in the DAC, a two-dimensional grid was created by collecting still images of the x-ray diffraction patterns in various positions. Single crystal diffraction data were collected at several selected points of the grid. From multi grain single crystal diffraction data the praseodymium oxide peroxide  $\text{Pr}_2(\text{O}_2)\text{O}_3$  could be identified. Instead of being oxidized to its +V oxidation state, praseodymium retains the oxidation state +IV, while the oxide anions of praseodymium(IV) oxide react with oxygen to form peroxide.  $\text{Pr}_2(\text{O}_2)\text{O}_3$  crystallizes in the orthorhombic space group  $Pbcn$  with only one crystallographically distinguishable praseodymium ion that is coordinated by ten oxygen atoms. Four of the oxygen atoms coordinating the  $\text{Pr}^{4+}$ -ions are part of the peroxide anions, whereas the remaining six are oxide anions. The sublattice of praseodymium

ions consists of a slightly distorted body centered cubic packing (*bcc*) in which the oxide anions fill tetrahedral gaps and the peroxide anion sits in octahedral voids.

In order to investigate the behavior of  $\text{Pr}_2(\text{O}_2)\text{O}_3$  at lower pressures, the DAC was decompressed in steps to lower pressure points at which more x-ray diffraction data was collected. The phase could unambiguously be identified at both 17 and 11 GPa by multi grain single crystal diffraction, allowing for the determination of the relation of structural parameters and pressure. At ambient pressure,  $\text{Pr}_2(\text{O}_2)\text{O}_3$  was no longer present in the cell as a result of its decomposition into other phases. The analysis of the remaining data points including  $\text{PrO}_2 + \text{O}_2$  heated at higher pressures is still ongoing.

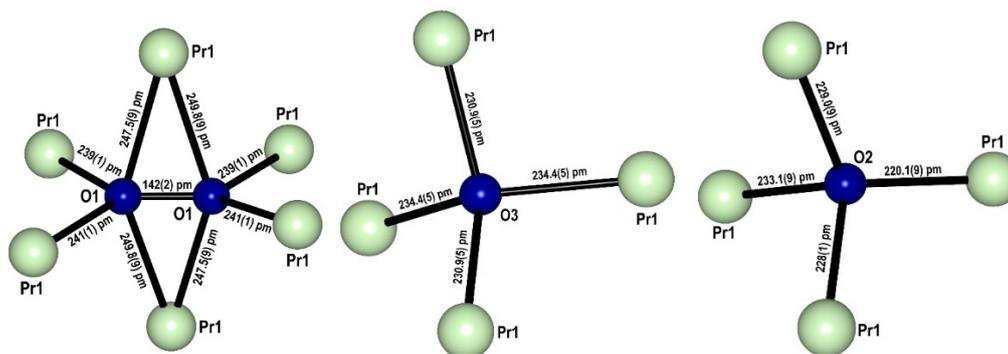


Fig. 1: Coordination geometries of the peroxide anion (left) and the oxide anions (middle and right) in  $\text{Pr}_2(\text{O}_2)\text{O}_3$ .

The experimental goal of the present proposal was to investigate if praseodymium can be oxidized to its +V oxidation state with oxygen under high pressure. Instead of praseodymium, oxide anions of  $\text{PrO}_2$  are oxidized to peroxide. The goal was achieved, in the sense that it was proven impossible to oxidize praseodymium to +V at least at  $\sim 30$  GPa. Moreover, this experiment sheds light on the chemical properties of oxygen under extreme conditions. Instead of its typical behavior as an oxidizing agent, here oxygen demonstrated a comproportionating reaction forming a peroxide in a reaction  $2\text{PrO}_2 + 0.5\text{O}_2 = \text{Pr}_2(\text{O}_2)\text{O}_3$ . This can have some implications for understanding the behavior of geologically relevant iron oxides. The data is currently being prepared for publication. Further analysis of data collected at higher pressures may reveal new exciting findings.