MS20-O4 High-pressure synthesis of the new nickel borate HP-NiB_4O_7

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During the last decade, our research on the field of transition metal borates led to numerous new compounds like β-ZnB_4O_7 [1], $M_6B_{22}O_{39}$□H_2O (M = Fe, Co) [2], or HP-NiB_2O_4 [3], which is the first borate that shows exclusively BO_4-tetrahedra sharing one common edge with a second BO_4-tetrahedron. Here we present the new transition metal oxoborate HP-NiB_4O_7, which was synthesized starting from NiO and B_2O_3 under high-pressure/high-temperature conditions of 5 GPa and 900 °C in a Walker-type multianvil apparatus. Thus, this compound constitutes the low-pressure/low-temperature modification of the compound β-NiB_4O_7 [4], which was synthesized at 7.5 GPa and 1150 °C. HP-NiB_4O_7 crystallizes in the acentric, chiral space group $P6_522$ (No. 179) with Z = 6, a = 4.258(6) Å, and c = 34.882(7) Å. The structure consists of chains of BO_4-tetrahedra, which are interconnected by B_2O_7 groups, thus forming a three-dimensional framework which contains the helically arranged nickel atoms (Fig. 1). This structure type is yet unknown in the field of borate chemistry underlining the importance of the parameter pressure in synthetic solid state chemistry. The characterization of the compound is complemented by magnetic and spectroscopic investigations.

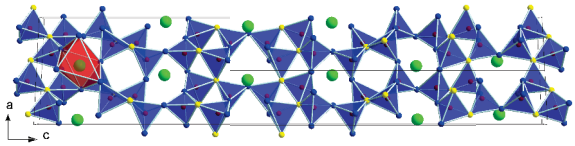

Figure 1. Crystal structure of NiB4O7

Keywords: Borates, High-pressure, Synthesis

MS20-O5 Extreme-pressure loading of fuel related gases into nanoporous materials: unusual uptake behaviour in a Sc-based metal-organic framework

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The development of new methods of storing, trapping or separating light gases, such as CO_2 or CH_4 has become of outmost importance from an environmental and energetic point of view. Porous materials such as zeolites and porous organic polymers have long been considered good candidates for this purpose. More recently, the ample spectrum of existing metal organic frameworks (MOFs) together with their functional and mechanical properties have attracted even further interest.[1] The channels found in these materials are ideal for the uptake of guests of different shapes and sizes, and with careful design they can show high selectivity. Adsorption properties of MOFs have been thoroughly studied,[2] however obtaining in depth structural insight into the adsorption/desorption mechanism of these materials is challenging, usually because the adsorbed species is hard to locate using crystallographic methods within the large porous cavities of a MOF, resulting in only partially occupied guests even at tens of bars of gas pressure and low temperatures.

Here we present high-pressure structural data on the microporous scandium framework, Sc_2BDC_3 (BDC = benzene-1,4-dicarboxylate) with included methane molecules from 2 to 25 kbar.[3] Using a modified Merrill Bassett Diamond Anvil Cell (DAC) setup, CH_4 was cryoloaded into the DAC to 2 kbar. On initially loading the cell, it was possible to locate fully ordered adsorption sites for methane, in which previously only partially ordered sites were observed using an environmental gas-cell set-up (on the small molecule beamline I19, at the DIAMOND light source, UK), with methane loaded at much lower pressures (5 bar). Furthermore, increasing the pressure beyond 10 kbar resulted in a transition to a previously unobserved phase of Sc_2BDC_3, where the b-axis of the ortho-*F* cell tripled. Although, the framework remains largely unaltered, the superfilling of the pores at high-pressures with methane translates into a re-ordering of the adsorption sites which permit a greater uptake of CH_4. High-pressure cryoloading of gaseous molecules under ambient conditions may therefore provide a fruitful way in which to study much more easily the adsorption sites in porous MOFs via diffraction techniques, obtaining atomistic models which were previously unobtainable.

[1] T. D. Bennet, *et al.*, *CrystEngComm*, 17(2), 286 (2015)

[2] Special Issue on Metal-Organic Frameworks, *Chem Rev.*, 112, 673 (2012)

[3] S. R. Miller, *et al.*, *Chem. Commun.*, 30, 3850 (2005)

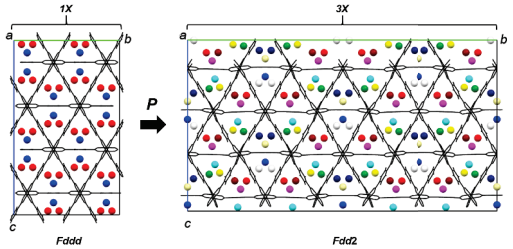

Figure 1. Upon application of pressure a transition to a previously unobserved phase of Sc_2BDC_3 is observed. The new phase has the b-axis of the ortho-*F* cell tripled and a rearrangement of the CH_4 adsorption sites.

Keywords: High-pressure crystallography, gas storage, nanoporous materials.

MS21. Advances in high-pressure methods

Chairs: Leonid Dubrovinsky, Ronald Miletich

MS21-O1 Extreme conditions beamline at Petra III, DESY: status and perspectives

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Fast evolution of applied and fundamental sciences requires probing of material properties in the space of pressure, temperature and time. Application of X-ray diffraction to the matter subjected to extreme conditions can lead to new fascinating discoveries and improve our understanding of physical phenomena on macro- and micro-scale. Diamond Anvil Cell (DAC) high pressure technique has de facto become a standard, and its development has made it possible to perform direct experimental tests of old and new scientific concepts previously considered as extremely challenging or even impossible. The constantly growing strong demand from different scientific communities stimulates large scale facilities to provide more and more stations either dedicated or stations capable to conduct high pressure studies a part of their operation time.

Extreme Conditions Beamline (ECB - P02.2) of Petra III, DESY, Hamburg, Germany, is dedicated to micro X-ray diffraction studies of matter (powder or single crystal) at simultaneous high-pressure and high/low-temperatures.

We review current capabilities of the beamline and provide a description of sample environments available to users for high-pressure studies conducted in the DAC (e.g. laser heating, cryostat, resistive heating and etc.). As an overview of our capabilities we present case studies and demonstrate results obtained at the beamline (geoscience, material science, etc.). Then, we discuss future plans to upgrade the beamline. Here, we highlight developments of single crystal diffraction at simultaneous high-pressure and high/low temperatures employing laser/resistive heated DAC as well as cryogenically cooled DACs. Finally, we discuss the possibility to conduct time resolved single crystal diffraction studies using partial or 'pink' Laue diffraction - a technique under commission at the ECB at the moment.

Keywords: X-ray diffraction, static compression, Petra III large scale facility,