

MS20-O4 High-pressure synthesis of the new nickel borate HP-NiB₄O₇Martin K. Schmitt¹, Hubert Huppertz¹

1. Institute of General, Inorganic and Theoretical Chemistry, Leopold-Franzens-University Innsbruck, A-6020 Innsbruck, Austria

email: martin.schmitt@uibk.ac.at

During the last decade, our research on the field of transition metal borates led to numerous new compounds like β -ZnB₄O₇ [1], M₆B₂₂O₃₉·nH₂O (M = Fe, Co) [2], or HP-NiB₂O₄ [3], which is the first borate that shows exclusively BO₄-tetrahedra sharing one common edge with a second BO₄-tetrahedron. Here we present the new transition metal oxoborate HP-NiB₄O₇, which was synthesized starting from NiO and B₂O₃ 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 -NiB₄O₇ [4], which was synthesized at 7.5 GPa and 1150 °C. HP-NiB₄O₇ crystallizes in the acentric, chiral space group P6₂22 (No. 179) with Z = 6, a = 4.258(6) Å, and c = 34.882(7) Å. The structure consists of chains of BO₄-tetrahedra, which are interconnected by B₂O₇ 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.

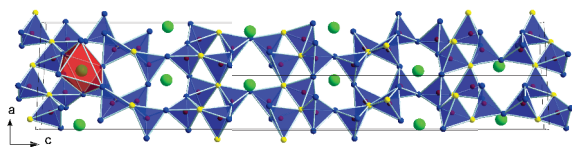


Figure 1. Crystal structure of NiB₄O₇

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

Jorge Sotelo^{1,2,3}, Christopher Woodall¹, Paul A. Wright³, John Mowat³, Stephen A. Moggach^{1,2}

1. Centre for Science in Extreme Conditions, The University of Edinburgh, UK.
2. EaStChem School of Chemistry, The University of Edinburgh, UK.
3. EaStChem School of Chemistry, The University of St. Andrews, UK.

email: j.sotelo@ed.ac.uk

The development of new methods of storing, trapping or separating light gases, such as CO₂ or CH₄ 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, Sc₂BDC₃ (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, CH₄ 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 Sc₂BDC₃, 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 CH₄. 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)