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High-Pressure Borates

Formation of Edge-Sharing BO_4 Tetrahedra in the High-Pressure Borate HP-NiB_2O_4**

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Dedicated to Professor Hanns-Peter Boehm on the occasion of his 80th birthday

In the course of our structural investigations of borates synthesized under high-pressure, high-temperature conditions, we discovered several new high-pressure modifications[1–5] with interesting structural features and physical properties, for example, a new non-centrosymmetric modification of bismuth triborate (δ-BiB_3O_6).[6] Along with the investigation of these phase transitions, we aim to synthesize borates with new compositions, whose existence is presumably based on high-pressure conditions during synthesis. Examples are the borates $RE_3B_5O_{12}$ ($RE = $Tm–Lu),[7] $RE_4B_6O_{15}$ ($RE = $Dy, Ho),[8–10] α-$RE_2B_4O_9$ ($RE = $Sm–Ho),[11–13] β-$RE_2B_4O_9$ ($RE = $Gd, Dy),[14,15] and $Pr_4B_{10}O_{21}$,[16] which have no corresponding ambient-pressure modifications. To our surprise, the borates $RE_4B_6O_{15}$ ($RE = $Dy, Ho)[8–10] revealed edge-sharing as well as corner-sharing BO_4 tetrahedra; such edge-sharing tetrahedra had been previously unknown in the varied structural chemistry of borates. Later on, we discovered a second type of structure, α-$RE_2B_4O_9$ ($RE = $Sm–Ho),[11–13] that also display this new structural feature. Herein, we report the synthesis and characterization of a new nickel borate HP-NiB_2O_4, in which each BO_4 tetrahedron shares a common edge with a second BO_4 tetrahedron.

In the system NiO–B_2O_3, there is only one nickel borate, of the composition $Ni_3(BO_3)_2$.[17–20] This compound displays trigonally coordinated boron atoms and Ni^{2+} ions with octahedral coordination. Recently, Pompetzki and Albert found a new synthetic route to pure $Ni_3(BO_3)_2$; they employed the thermal decomposition of a mixture of $NiCO_3{\cdot}2\,Ni(OH)_2{\cdot}4\,H_2O$ and H_3BO_3.[21] In our own investigations of the Ni-B-O ternary system, we synthesized a second borate of the composition β-NiB_4O_7[22] under high-pressure conditions of 7.5 GPa and at a temperature of 1000 °C; this compound has a structure analogous to the high-pressure modification β-ZnB_4O_7.[5] With HP-NiB_2O_4, we have now found a third composition in the Ni-B-O ternary system, which accentuates the performance of high-pressure synthesis in solid-state chemistry.

HP-NiB_2O_4 was synthesized in a high-pressure, high-temperature reaction at 7.5 GPa and 680 °C in a modified Walker module (multianvil assembly) starting from the oxides NiO and B_2O_3 [Eq. (1)].[23]

$$NiO + B_2O_3 \rightarrow \text{HP-}NiB_2O_4 \quad (1)$$

The compound was obtained as an air- and water-stable, light-green crystalline solid. The crystal structure of HP-NiB_2O_4 was solved and refined on the basis of single-crystal data.[24] Figure 1 shows the structure, which consists of layers of BO_4 tetrahedra connected by strings of edge-sharing NiO_6 octahedra. The layers spread out in the *bc*-plane, while the strings of NiO_6 octahedra run along the *c*-direction.

Figure 2 shows a single layer of edge-sharing BO_4 tetrahedra. Boron is coordinated by oxygen in a distorted

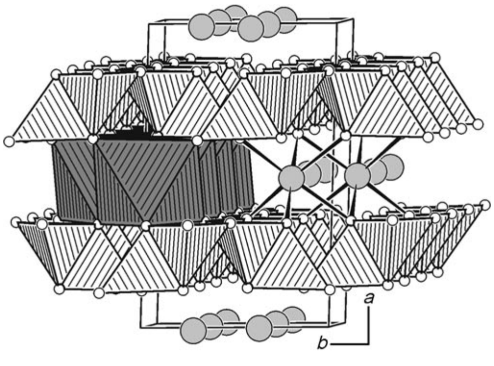

Figure 1. Crystal structure of HP-NiB_2O_4 viewed along [00$\bar{1}$]. Gray spheres: Ni^{2+}, light spheres: O^{2-}, light polyhedra: BO_4 tetrahedra, grey polyhedra: NiO_6 octahedra.

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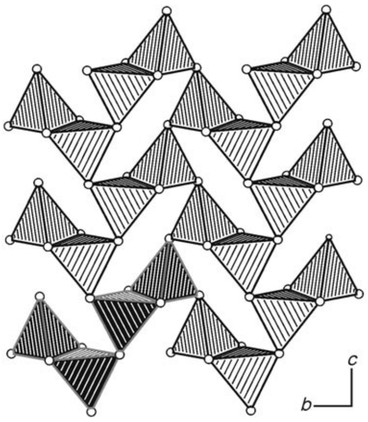

Figure 2. A layer of edge-sharing BO_4 tetrahedra in HP-NiB_2O_4 viewed along [100]. The dark polyhedra represent the fundamental building block of HP-NiB_2O_4.

tetrahedral fashion. Two tetrahedra form a B_2O_6 dimer through edge-sharing. These dimeric units are linked to each other through common vertices, resulting in a layer with the composition $^{2}_{\infty}[B_2O_2O^{2-}_{4/2}]$. Inside the layer, "sechser" rings[25] are formed from four B_2O_6 dimers, and each dimer is part of four "sechser" rings. Similar layers of edge-sharing tetrahedra were observed in the compounds β-$Ca_3[Al_2N_4]$,[26] $Ca_3[Al_2As_4]$,[27] $Sr_3[Al_2P_4]$,[28] $Ba_3[In_2P_4]$,[29] and α-$Ca_3[Ga_2N_4]$.[30] However, the layers in all of these compounds are corrugated, and the metal content between the layers is three times as high as in HP-NiB_2O_4, thus leading to a different crystal structure.

Figure 3 illustrates the linkage of the distorted NiO_6 octahedra, in which the Ni^{2+} ions are coordinated by six oxygen atoms with bond lengths of 203–218 pm. These distances correspond well to the known Ni–O bonds in $Ni_3(BO_3)_2$ (202–213 pm[20]) and $Na_2Ni_2B_{12}O_{21}$ (197–233 pm[21]). On the right-hand side of Figure 3, the bond lengths and angles inside the B_2O_6 dimers of HP-NiB_2O_4 are shown. Obviously, the B–O bond lengths inside the B_2O_2 ring (B1–O1: 151.6(2) and 153.1(2) pm) are larger than those outside the "zweier" rings[25] (B1–O2: 144.5(2) and 144.3(2) pm). The average B–O bond length of 148.4 pm is slightly higher than the average of 147.6 pm in tetrahedral BO_4 groups of borates.[31,32] The B···B separation inside the edge-sharing tetrahedra of HP-NiB_2O_4 is 208.8(2) pm, which corresponds to the values found in the other two structure types that exhibit edge-sharing BO_4 tetrahedra, for example, $RE_4B_6O_{15}$ (RE = Dy: 207.2(8) pm; Ho: 207(1) pm)[8–10] and α-$RE_2B_4O_9$ (RE = Sm: 207.1(9) pm; Gd: 204(2) pm; Eu: 205.3(9) pm; Tb: 205.5(9) pm; Ho: 204(3) pm).[11–13]

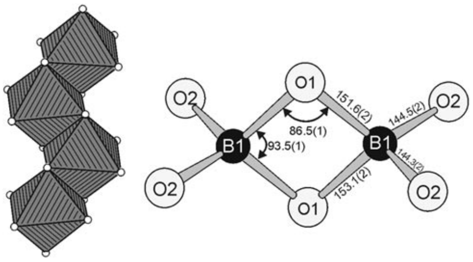

Figure 3. Left: String of NiO_6 octahedra linked through common edges along [001]. Right: Distances [pm] and angels [°] in the edge-sharing BO_4 tetrahedra of HP-NiB_2O_4.

Bond-valence sums were calculated for all atoms using the bond-length/bond-strength (ΣV)[33,34] and CHARDI concepts (charge distribution in solids, ΣQ).[35] A comparison of the charge distribution, calculated with both concepts, confirms the formal charges of Ni^{2+} ($\Sigma V = +1.90$; $\Sigma Q = +2.04$), B^{3+} ($\Sigma V = +2.97$; $\Sigma Q = +2.98$), and O^{2-} (O1: $\Sigma V = -1.91$, $\Sigma Q = -1.87$; O2: $\Sigma V = -2.00$, $\Sigma Q = -2.13$).

In the 1990s, Burns, Grice, and Hawthorne introduced a new concept of fundamental building blocks (FBB) to describe complex borate structures.[36,37] In 2003, we extended the descriptors used by Burns et al. by the symbol "⧄⧅" for the new structural motif of edge-sharing BO_4 tetrahedra.[9] The application of this concept to HP-NiB_2O_4 leads to a fundamental building block characterized by the descriptor 4□:⧄⧅⧄⧅. Figure 2 shows this fundamental building block (dark polyhedra) inside the borate layer of HP-NiB_2O_4.

Considering the synthetic conditions (7.5 GPa and 680 °C), we investigated the assumed metastable character of the high-pressure phase HP-NiB_2O_4. Temperature-programmed X-ray powder diffraction patterns of HP-NiB_2O_4 revealed that the compound is remarkably stable up to 750 °C in ambient-pressure conditions.[38] At higher temperatures, HP-NiB_2O_4 decomposes into the normal-pressure nickel borate $Ni_3(BO_3)_2$ and presumably boron oxide. Further heating (up to 1100 °C) and subsequent cooling to room temperature did not succeed in producing any phase other than $Ni_3(BO_3)_2$.

In former work, we tried to determine the Raman-active modes of the new B_2O_6 unit from the Raman spectra of $Dy_4B_6O_{15}$[9] and α-$Gd_2B_4O_9$.[12] These spectra revealed several peaks in the range 1200–1450 cm^{-1} that normally correspond to BO_3 groups. As neither compound contains boron in threefold coordination, these bands are probably Raman-active modes of the B_2O_6 unit of the edge-sharing BO_4 tetrahedra. Figure 4 shows the Raman spectra of $Dy_4B_6O_{15}$,[9] α-$Gd_2B_4O_9$,[12] and HP-NiB_2O_4.[39]

As HP-NiB_2O_4 possesses only BO_4 tetrahedra with a common edge to a second tetrahedron, a comparison of the intensities of all three compounds should lead to an agreement about those peaks that belong exclusively to Raman-active modes of the B_2O_6 group. Figure 4 shows that the peaks, which are marked with an arrow, occur in all three spectra of the compounds with edge-sharing tetrahedra. These peaks do not occur in a spectrum of β-NiB_4O_7,[22] which exhibits only corner-sharing BO_4 tetrahedra. Thus, the bands at 1262 and 1444 cm^{-1} (HP-NiB_2O_4), 1253 and 1431 cm^{-1} (α-$Gd_2B_4O_9$), and 1271 and 1435 cm^{-1} ($Dy_4B_6O_{15}$) can presumably be assigned to Raman-active modes of the edge-sharing BO_4 tetrahedra.

The inverse magnetic susceptibility of HP-NiB_2O_4 showed Curie–Weiss behavior between room temperature and approximately 150 K.[40] From the Curie constant, we determined an effective magnetic moment of 3.50(1) μ_B per nickel

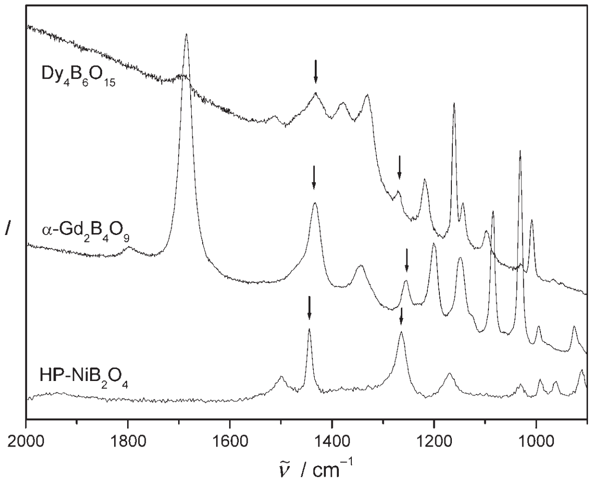

Figure 4. Raman spectra of $Dy_4B_6O_{15}$, α-$Gd_2B_4O_9$, and HP-NiB_2O_4. The arrows mark peaks that presumably belong to Raman-active modes of the B_2O_6 group.

atom. This value is at the upper limit observed for Ni^{2+} (2.80–3.50 μ_B),[41] which may be due to crystal field effects or to an incomplete correction for ferromagnetic impurities (traces of metallic Ni). The paramagnetic Curie temperature (Weiss constant) of −83.3(1) K indicated antiferromagnetic interactions among the moments. A sharp upward bend of $\chi^{-1}(T)$ at $T \approx 32$ K is most likely the onset of antiferromagnetic ordering. This conclusion is supported by linear magnetization isotherms down to 2 K.

The UV/Vis/NIR spectrum of light-green HP-NiB_2O_4 shows three absorption bands, as expected for Ni^{2+} ions in octahedral coordination ($E[^3A_{2g}\rightarrow{}^3T_{2g}(F)] = 8620\ cm^{-1}$, $E[^3A_{2g}\rightarrow{}^3T_{1g}(F)] = 13\,940\ cm^{-1}$, $E[^3A_{2g}\rightarrow{}^3T_{1g}(P)] = 24\,600\ cm^{-1}$).[42] As a consequence of low-symmetry components in the ligand field ($\{Ni^{II}O_6\}$ chromophores with C_2 symmetry), the second and third absorption bands are split. The observed transition energies $\Delta_o = 8620\ cm^{-1}$ and $B = 845\ cm^{-1}$ ($\beta = B/B_0 = 0.81$) were estimated according to a procedure described by Lever.[43] It is quite remarkable that the ligand-field splitting observed for yellow $Ni_2P_4O_{12}$ ($\Delta_o = 7300\ cm^{-1}$) is significantly smaller, despite its very similar geometric structure of the $\{Ni^{II}O_6\}$ chromophore.[44] We attribute this difference to stronger π-donating oxygen ligands in the phosphate than in the borate. The essentially negligible π bonding of the oxygen ligands in HP-NiB_2O_4, a typical second-sphere ligand-field effect,[45] is a consequence of the higher coordination number of the oxygen atoms in the borate ($CN(O^{2-}) = 4\,(2\,B^{3+} + 2\,Ni^{2+})$) than in the phosphate ($CN(O^{2-}) = 2\ (2\times)$ and $3\ (4\times)$). With the transition energy of $\Delta_o = 8620\ cm^{-1}$, the nephelauxetic ratio of $\beta = 0.81$, and the spin–orbit coupling parameter for the free ion ($\zeta_0(Ni^{2+}) = 630\ cm^{-1}$), a magnetic moment of 3.16 μ_B per nickel atom can be calculated.[46]

Systematic investigations in the field of high-pressure borates led to the synthesis of HP-NiB_2O_4, the first borate in which every BO_4 tetrahedron shares a common edge with a second one. This high-pressure borate represents an excellent candidate for in situ investigations inside a laser-heated diamond anvil cell. The goal of such investigations under extremely high pressure is to increase the coordination number of the boron atoms from four to five or maybe even six.

Experimental Section

The starting materials for the synthesis of HP-NiB_2O_4 [see Eq. (1)] were stoichiometric mixtures of nickel oxide (Avocado Research Chemicals Ltd, 99.5%) and B_2O_3 (Strem Chemicals, Newburyport, USA, 99.9%). The mixture was compressed and heated in a multianvil assembly. A precast MgO octahedron (Ceramic Substrates & Components, Isle of Wight, UK) with an edge length of 18 mm was used as the pressure medium. Eight tungsten carbide cubes (TSM 10, Ceratizit, Austria) with a truncation of 11 mm, separated by pyrophyllite gaskets, compressed the octahedron (18/11 assembly). The reaction mixture (ca. 60 mg) was filled into a cylindrical boron nitride crucible that was sealed by a boron nitride plate. Further details of the construction of the assembly can be found in reference [23].

For the synthesis of HP-NiB_2O_4, the assembly was compressed within 180 min to 7.5 GPa and heated to 680 °C in the following 10 min. After holding this temperature for 5 min, the sample was rapidly cooled to room temperature within 1 min. After decompression (9 h), the recovered experimental octahedron was broken apart, and the sample was carefully separated from the surrounding hexagonal boron nitride. The air- and humidity-stable compound HP-NiB_2O_4 was obtained as a crystalline, light-green solid.

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[1] H. Emme, C. Despotopoulou, H. Huppertz, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1717.
[2] H. Emme, C. Despotopoulou, H. Huppertz, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2450.
[3] G. Heymann, T. Soltner, H. Huppertz, *Solid State Sci.* **2006**, *8*, 821.
[4] A. Haberer, G. Heymann, H. Huppertz, *Z. Naturforsch. B* **2007**, *62*, 759.
[5] H. Huppertz, G. Heymann, *Solid State Sci.* **2003**, *5*, 281.
[6] J. S. Knyrim, P. Becker, D. Johrendt, H. Huppertz, *Angew. Chem.* **2006**, *118*, 8419; *Angew. Chem. Int. Ed.* **2006**, *45*, 8239.
[7] H. Emme, M. Valldor, R. Pöttgen, H. Huppertz, *Chem. Mater.* **2005**, *17*, 2707.
[8] H. Huppertz, B. von der Eltz, *J. Am. Chem. Soc.* **2002**, *124*, 9376.
[9] H. Huppertz, *Z. Naturforsch. B* **2003**, *58*, 278.
[10] H. Huppertz, H. Emme, *J. Phys. Condens. Matter* **2004**, *16*, S1283.
[11] H. Emme, H. Huppertz, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2165.
[12] H. Emme, H. Huppertz, *Chem. Eur. J.* **2003**, *9*, 3623.
[13] H. Emme, H. Huppertz, *Acta Crystallogr. Sect. C* **2005**, *61*, i29.
[14] H. Emme, H. Huppertz, *Acta Crystallogr. Sect. C* **2005**, *61*, i23.
[15] H. Huppertz, S. Altmannshofer, G. Heymann, *J. Solid State Chem.* **2003**, *170*, 320.
[16] A. Haberer, G. Heymann, H. Huppertz, *J. Solid State Chem.* **2007**, *180*, 1595.
[17] S. V. Berger, *Acta Chem. Scand.* **1949**, *3*, 660.
[18] W. Götz, *Naturwissenschaften* **1963**, *50*, 567.
[19] C. E. Weir, R. A. Schroeder, *J. Res. Natl. Bur. Stand.* **1964**, *86 A*, 465.

[20] J. Pardo, M. Martinez-Ripoll, S. Garcia-Blanco, *Acta Crystallogr. Sect. B* **1974**, *30*, 37.

[21] M. Pompetzki, B. Albert, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2550.

[22] J. S. Knyrim, J. Friedrichs, S. Neumair, F. Roeßner, Y. Floredo, S. Jakob, D. Johrendt, R. Glaum, H. Huppertz, *Solid State Sci.* **2007**, DOI: 10.1016/j.solidstatesciences.2007.09.004.

[23] H. Huppertz, *Z. Kristallogr.* **2004**, *219*, 330.

[24] Crystal data for HP-NiB_2O_4: $M = 144.3\ \mathrm{g\,mol^{-1}}$, light-green crystal, $0.02 \times 0.04 \times 0.05\ \mathrm{mm^3}$, monoclinic, space group $C2/c$, $a = 924.7(2)$, $b = 552.3(2)$, $c = 442.9(1)$ pm, $\beta = 108.30(3)°$, $V = 0.215(1)\ \mathrm{nm^3}$, $Z = 4$, $\rho_{calcd} = 4.464\ \mathrm{g\,cm^{-3}}$, Enraf-Nonius Kappa CCD, $Mo_{K\alpha}$-radiation ($\lambda = 71.073$ pm), graphite monochromator, $F(000) = 280$, $\mu = 8.78\ \mathrm{mm^{-1}}$, $T = 293(2)$ K, 2648 measured reflections in the range $4.4° < \theta < 46.6°$, 939 independent reflections ($I > 0\sigma(I)$), multiscan absorption correction, $R_{int} = 0.0362$. Structure solution and parameter refinement (full-matrix least-squares against F^2) was performed using the SHELX-97 software suite. G. M. Sheldrick, SHELX-97 and SHELXL-97, Program Suite for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, **1997**. All atoms were refined anisotropically. There were 34 refined parameters, $R1 = 0.0260$ and $wR2 = 0.0520$ for $I > 2\sigma(I)$ and $R1 = 0.0314$ and $wR2 = 0.0542$ for all data, GOF = 1.070. Ni is positioned at the site $4e$ (1/2, 0.84699(4), 1/4), boron and oxygen at the sites $8f$: B (0.3151(2), 0.6077(2), 0.6283(3)); O1 (0.64364(9), 0.8509(2), 0.9805(2)); O2 (0.36336(9), 0.5911(2), 0.9713(2)). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-418385.

[25] The term "sechser" ring was coined by F. Liebau (*Structural Chemistry of Silicates*, Springer, Berlin, **1985**) and is derived from the German word sechs, which means six. However, a sechser ring is not a six-membered ring, but rather a ring with six tetrahedral centers (B) and six electronegative atoms (O). Similar terms exist for rings made up of two and three tetrahedral centers (and the corresponding number of electronegative atoms), namely "zweier" and "dreier" rings.

[26] M. Ludwig, J. Jäger, R. Niewa, R. Kniep, *Inorg. Chem.* **2000**, *39*, 5909.

[27] G. Cordier, E. Czech, M. Jacowski, H. Schäfer, *Rev. Chim. Mineral.* **1981**, *18*, 9.

[28] M. Somer, W. Carrillo-Cabrera, K. Peters, H. G. von Schnering, *Z. Kristallogr. New Cryst. Struct.* **1998**, *213*, 230.

[29] M. Somer, W. Carrillo-Cabrera, K. Peters, H. G. von Schnering, *Z. Kristallogr. New Cryst. Struct.* **1998**, *213*, 4.

[30] S. J. Clarke, F. J. DiSalvo, *Inorg. Chem.* **1997**, *36*, 1143.

[31] E. Zobetz, *Z. Kristallogr.* **1990**, *191*, 45.

[32] "The Crystal Chemistry of Boron": F. C. Hawthorne, P. C. Burns, J. D. Grice in *Boron: Mineralogy, Petrology and Geochemistry, Vol. 33*, 2nd ed. (Eds.: E. S. Grew, L. M. Anovitz), Mineralogical Society of America, Washington, **1996**, pp. 41.

[33] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244.

[34] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192.

[35] R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H. P. Müller, K. J. Bernet, *J. Less-Common Met.* **1989**, *156*, 105.

[36] P. C. Burns, J. D. Grice, F. C. Hawthorne, *Can. Mineral.* **1995**, *33*, 1131.

[37] J. D. Grice, P. C. Burns, F. C. Hawthorne, *Can. Mineral.* **1999**, *37*, 731.

[38] These investigations were performed on a STOE Stadi P powder diffractometer ($Mo_{K\alpha}$) with a computer-controlled STOE furnace. The sample was enclosed in a silica-glass capillary and heated from room temperature to 500 °C in steps of 100 °C and from 500 °C to 1100 °C in steps of 50 °C. Afterwards, the sample was cooled down to 500 °C in steps of 50 °C and further on to room temperature in steps of 100 °C. At each temperature, a powder diffraction pattern was recorded over the range $9.0° < 2\theta < 21.5°$.

[39] The Raman spectrum of HP-NiB_2O_4 was measured on a single crystal with a Raman microscope Horiba Jobin yvon HR800 (x50LWD) using a Melles Griot ion laser with a wavelength of 514 nm.

[40] Magnetic moments of HP-NiB_2O_4 were measured using a SQUID magnetometer (Quantum-Design MPMS-XL5) between 1.8 and 300 K with magnetic flux densities as large as 5 T. Samples of about 15 mg were loaded in gelatin capsules and fixed in a straw as the sample holder. The data were corrected for the sample holder, the core diamagnetism, and for traces of ferromagnetic impurities (Ni metal). Magnetic parameters were determined using the Curie–Weiss law $\chi = C/(T-\theta)$.

[41] H. Lueken, *Magnetochemie*, Teubner, Stuttgart, Leipzig, **1999**.

[42] A single-crystal electronic spectrum of an arbitrary face of a crystal of HP-NiB_2O_4 (cross section: $0.1 \times 0.2\ \mathrm{mm^2}$, $d = 0.05$ mm; $T = 298$ K) was measured using a strongly modified CARY 17 microcrystal spectralphotometer. (Spectra Services, ANU Canberra, Australia. For details on the spectrometer, see: E. Krausz, *Aust. J. Chem.* **1993**, *46*, 1041.)

[43] A. B. P. Lever, *J. Chem. Educ.* **1968**, *45*, 711.

[44] K. Maaß, *Neues von quaternären Phosphaten der zweiwertigen 3d-Übergangsmetalle*, Ph.D. thesis (in German), University of Gießen, **2002**. URL: http://bibd.uni-giessen.de/ghtm/2002/uni/d020119.htm.

[45] D. Reinen, M. Atanasov, S.-L. Lee, *Coord. Chem. Rev.* **1998**, *175*, 91.

[46] B. N. Figgis, M. A. Hitchman, *Ligand Field Theory and its Applications*, Wiley-VCH, **2000**.