

Synthesis and Crystal Structure of the High-pressure Iron Borate β -FeB₂O₄

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Z. Naturforsch. **2009**, *64b*, 883–890; received June 4, 2009

The iron borate β -FeB₂O₄ was synthesized under high-pressure/high-temperature conditions of 8 GPa and 1030 °C. The structure of β -FeB₂O₄ is isotypic to HP-NiB₂O₄, representing the second example of a borate in which every BO₄ tetrahedron shares a common edge with a second one. β -FeB₂O₄ crystallizes in the space group *C2/c* (*Z* = 4) with the parameters *a* = 950.0(2), *b* = 562.9(2), *c* = 443.7(1) pm, β = 108.50(3)°, *V* = 0.22495(8) nm³, *R*1 = 0.0293, and *wR*2 = 0.0647 (all data). The structure consists of layers of BO₄ tetrahedra, connected *via* strings of edge-sharing FeO₆ octahedra. A ligand field splitting of $\Delta_o \approx 8860$ cm⁻¹ is estimated from polarized single-crystal electronic absorption spectra of β -FeB₂O₄. The tetragonal distortion of the ligand field in the [Fe^{II}O₆] chromophore amounts to $-(8/3)d\sigma \approx 2900$ cm⁻¹. In the range of 16000 cm⁻¹ $\leq \tilde{\nu} \leq 24000$ cm⁻¹, rather strong spin-forbidden transitions within the [Fe^{II}O₆] chromophore are observed.

Key words: Borate, High Pressure, Crystal Structure

Introduction

Recent investigations in high-pressure/high-temperature syntheses of borates revealed several new compounds like the polymorphs β -MB₄O₇ (*M* = Mn [1], Fe [2], Co [2], Ni [1], Cu [1], Zn [3], Ca [4], Hg [5]), the rare-earth borates RE₃B₅O₁₂ (*RE* = Tm–Lu [6]), and a new centrosymmetric modification of the popular nonlinear optical material bismuth triborate (δ -BiB₃O₆) [7]. Two new rare-earth borates, α -RE₂B₄O₉ (*RE* = Sm–Ho) [8–11] and RE₄B₆O₁₅ (*RE* = Dy, Ho) [8, 12, 13], exhibit edge-sharing BO₄ tetrahedra, a new structural motif in the chemistry of oxoborates. This motif could also be found in HP-NiB₂O₄ [14], which is the first borate to show exclusively BO₄ tetrahedra sharing one common edge with a second one. Latest investigations in the system Fe–B–O led to an isotype of the exceptional HP-NiB₂O₄, the β -FeB₂O₄ presented here.

Under ambient-pressure conditions, there are six compositions in the ternary system Fe–B–O: Fe^{II}₂Fe^{III}(BO₃)O₂ (*Pbam*: *vonsenite* [15, 16]; *P2/m*: *hulsite* [17]), Fe^{II}Fe^{III}₂(BO₄)O₂ (*norbergite* structure) [18, 19], Fe^{II}Fe^{III}(BO₃)O (*Pmcn*: *warwickite* structure [20, 21], *P2₁/c*: distorted *warwickite* structure

[20, 22]), FeB₄O₇ [23, 24], FeBO₃ [25], and Fe₂B₂O₅ [26, 27]. The polymorphic phases Fe^{II}₂Fe^{III}(BO₃)O₂ and Fe^{II}Fe^{III}(BO₃)O, as well as the compounds FeBO₃ and Fe₂B₂O₅, are built up from trigonal-planar BO₃ groups. In contrast, Fe^{II}Fe^{III}₂(BO₄)O₂ exhibits only isolated BO₄ tetrahedra. The compound FeB₄O₇ shows both of these units, BO₃ groups and BO₄ tetrahedra.

Investigations in the high-pressure/high-temperature chemistry of iron borates in our research group led to the new compound α -FeB₂O₄ [28] and the already mentioned polymorph β -FeB₄O₇ [2]. Both structures consist of corner-sharing BO₄ tetrahedra, the former being isotypic to CaGa₂O₄ [29], CaAl₂O₄-II [30, 31], and β -SrGa₂O₄ [32]. We now report the synthesis of a second polymorph of FeB₂O₄, β -FeB₂O₄, its crystal structure, and properties. Furthermore, similarities and differences to the isotypic compound HP-NiB₂O₄ [14] and other structures are discussed.

Experimental Section

Synthesis

β -FeB₂O₄ was synthesized under high-pressure/high-temperature conditions of 8 GPa and 1030 °C in a modi-

Table 1. Crystal data and structure refinement of β -FeB₂O₄ (standard deviations in parentheses).

Empirical formula	β -FeB ₂ O ₄
Molar mass, g mol ⁻¹	141.47
Crystal system	monoclinic
Space group	<i>C2/c</i>
Powder diffractometer	Stoe Stadi P
Radiation; λ , pm	MoK α ; 71.073
Powder data	
<i>a</i> , pm	950.5(3)
<i>b</i> , pm	562.8(2)
<i>c</i> , pm	444.2(2)
β , deg	108.48(3)
<i>V</i> , nm ³	0.22535(8)
Single-crystal diffractometer	Stoe IPDS-I
Radiation; λ , pm	MoK α ; 71.073 (graphite monochromator)
Single-crystal data	
<i>a</i> , pm	950.0(2)
<i>b</i> , pm	562.9(2)
<i>c</i> , pm	443.7(1)
β , deg	108.50(3)
<i>V</i> , nm ³	0.22495(8)
Formula units per cell	<i>Z</i> = 4
Calculated density, g cm ⁻³	4.18
Crystal size, mm ³	0.16 × 0.11 × 0.04
Temperature, K	293(2)
Detector distance, mm	50.0
Exposure time, min	8.0
Absorption coefficient, mm ⁻¹	6.5
Absorption correction	numerical [42, 43]
<i>F</i> (000), e	272
θ range, deg	4.3–30.5
Range in <i>hkl</i>	±13, –8/ +7, ±5
Reflections total / independent / <i>R</i> _{int}	1150 / 314 / 0.0265
Reflections with <i>I</i> ≥ 2 σ (<i>I</i>)/ <i>R</i> _{σ}	296 / 0.0179
Data / ref. parameters	314 / 34
Final <i>R</i> 1/ <i>wR</i> 2 [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0276 / 0.0635
Final <i>R</i> 1/ <i>wR</i> 2 (all data)	0.0293 / 0.0647
Goodness-of-fit on <i>F</i> ²	1.172
Largest diff. peak and hole, e Å ⁻³	0.64 / –0.70

fied Walker-type multianvil apparatus. A stoichiometric mixture of “FeO” (Sigma-Aldrich Chemie GmbH, Munich, Germany, 99.9 %) and B₂O₃ (Strem Chemicals, Newburyport, USA, 99.9 %) in the ratio 1:1 was ground together and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint[®] S10, Kempten, Germany). This crucible was positioned in the center of a 14/8-assembly and compressed by eight tungsten carbide cubes (TSM-10, Ceratizit, Reutte, Austria). The pressure was applied *via* a Walker-type multianvil device and a 1000 t press (both devices from the company Voggenreiter, Mainleus, Germany). A detailed description of the assembly and its preparation can be found in refs. [33–37]. For the synthesis, the sample was compressed to 8 GPa within 1.5 h and kept at this pressure for the heating period. The temperature was increased within 10 min to 1030 °C, kept there for 5 min, and decreased to

Table 2. Atomic coordinates and isotropic equivalent displacement parameters *U*_{eq} (Å²) for β -FeB₂O₄ (space group: *C2/c*) (standard deviations in parentheses). *U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Atom	W.-position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Fe	4 <i>e</i>	1/2	0.8423(2)	1/4	0.0096(3)
B	8 <i>f</i>	0.3126(3)	0.6079(6)	0.6230(8)	0.0092(6)
O1	8 <i>f</i>	0.6464(2)	0.8480(4)	0.9774(5)	0.0083(4)
O2	8 <i>f</i>	0.3600(2)	0.5857(4)	0.9647(5)	0.0085(4)

625 °C within 15 min. The sample was cooled down to r. t. by switching off the heating, followed by a decompression period of 4.5 h. The recovered pressure medium was broken apart and the surrounding boron nitride crucible removed from the sample. The compound β -FeB₂O₄ was obtained as an oxidation-sensitive, orange-brown, crystalline solid. The sample also contained the normal-pressure phase *vonsenite* (Fe^{II}₂Fe^{III}(BO₃)O₂) and the already known high-pressure borate α -FeB₂O₄.

The powder diffraction pattern clearly identified β -FeB₂O₄ as the main product of the high-pressure/high-temperature reaction. The elemental analysis of β -FeB₂O₄ by energy dispersive X-ray spectroscopy (Jeol JFM-6500F, Jeol. Ltd, Tokyo, Japan) led to values of 12(1) % Fe (14 %), 25(3) % B (29 %), and 63(3) % O (57 %) (theoretical values in parentheses).

Electronic absorption spectra

The single-crystal polarized electronic absorption spectra of β -FeB₂O₄ were recorded at 293 K in the NIR/Vis/UV region (5800–28000 cm⁻¹, step width $\Delta\lambda$ (UV/Vis) = 1 nm, $\Delta\lambda$ (NIR) = 2 nm) using a strongly modified CARY 17 microcrystal spectrophotometer (Spectra Services, ANU Canberra, Australia). The details of the single-beam spectrometer have already been described in the literature [38, 39]. A dichroic crystal (yellow/orange) with dimensions 0.1 × 0.1 × 0.05 mm³ was selected for examination. The rather noisy spectra (see Fig. 6) result from the small size and modest optical quality of the crystals available. The reference intensity was measured using a pinhole instead of the crystal mounted on an aperture.

Crystal structure analysis

The powder-diffraction pattern was obtained in transmission geometry, using a Stoe Stadi P powder diffractometer with monochromatized MoK α (λ = 71.073 pm) radiation. The diffraction pattern was indexed with the program ITO [40] on the basis of a monoclinic unit cell. The lattice parameters (Table 1) were calculated from least-squares fits of the powder data. The correct indexing of the pattern of β -FeB₂O₄ was confirmed by intensity calculations, taking the atomic positions from the structure refinement [41].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0094(3)	0.0106(4)	0.0094(4)	0	0.0040(2)	0
B	0.008(2)	0.011(2)	0.008(2)	0.000(2)	0.003(2)	−0.000(2)
O1	0.0082(9)	0.0090(9)	0.008(2)	−0.0007(6)	0.0033(7)	−0.0007(7)
O2	0.0091(9)	0.0093(9)	0.007(2)	−0.0006(7)	0.0022(7)	−0.0009(7)

Table 4. Interatomic distances (pm) for β -FeB₂O₄ (space group: $C2/c$), based on single-crystal data (standard deviations in parentheses).

Fe–O2 (2×)	209.5(2)	B–O2a	144.3(4)	O1–Ba	151.2(4)
Fe–O1b (2×)	211.3(2)	B–O2b	144.3(4)	O1–Bb	152.5(4)
Fe–O1a (2×)	225.8(2)	B–O1a	151.2(4)		av. = 151.9
	av. = 215.3	B–O1b	152.5(4)		
			av. = 148.1		

Table 5. Interatomic angles (deg) for β -FeB₂O₄ (space group: $C2/c$), based on single-crystal data (standard deviations in parentheses).

O2a–Fe–O2b	92.8(2)	B–O1–B	86.6(2)
O2a–Fe–O1a	94.10(8)	B–O2–B	122.3(2)
O2b–Fe–O1a	87.09(8)		av. = 104.5
O2a–Fe–O1b	87.09(8)		
O2b–Fe–O1b	94.10(8)	O2a–B–O2b	113.8(2)
O2b–Fe–O1c	94.56(8)	O2a–B–O1b	112.4(3)
O1a–Fe–O1c	79.65(8)	O2b–B–O1a	111.3(2)
O1b–Fe–O1c	99.00(7)	O2a–B–O1a	111.0(2)
O2a–Fe–O1d	94.56(8)	O2b–B–O1b	113.3(3)
O1a–Fe–O1d	99.00(7)	O1a–B–O1b	93.4(2)
O1b–Fe–O1d	79.65(8)		av. = 109.2
O1c–Fe–O1d	78.96(2)		
	av. = 90.0		

To get a single-crystal structure analysis, small irregularly shaped single-crystals of the sample were isolated by mechanical fragmentation and examined through a Buerger precession camera, equipped with an image plate system (Fujifilm BAS-1800), in order to establish both, symmetry and suitability for the intensity data collection. Measurements of the single-crystal intensity data were performed at r.t. by a Stoe IPDS-I diffractometer with graphite-monochromatized $\text{MoK}\alpha$ ($\lambda = 71.073$ pm) radiation. All relevant details of the data collection and evaluation are listed in Table 1. In accordance with the systematic extinctions hkl with $h + k \neq 2n$ and $h0l$ with $h, l \neq 2n$, the space groups $C2/c$ (no. 15) and Cc (no. 9) were derived. For the intensity data of β -FeB₂O₄, a numerical absorption correction was applied with the program X-SHAPE [42, 43]. Due to the isotopy of β -FeB₂O₄ to HP-NiB₂O₄, the structural refinement could be successfully performed in the centrosymmetric space group $C2/c$, employing the positional parameters of HP-NiB₂O₄ as starting values [SHELXL-97 [44] (full-matrix least-squares on F^2)]. All atoms were refined with anisotropic displacement parameters. The final difference Fourier syntheses did not reveal any significant peaks. Tables 2–5 list the positional parameters, anisotropic displacement parameters, interatomic distances, and angles.

Table 3. Anisotropic displacement parameters U_{ij} (\AA^2) for β -FeB₂O₄ (space group: $C2/c$) (standard deviations in parentheses).

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420403.

Results and Discussion

Fig. 1 gives a view of the crystal structure of β -FeB₂O₄ along $[00\bar{1}]$. This centrosymmetric oxoborate

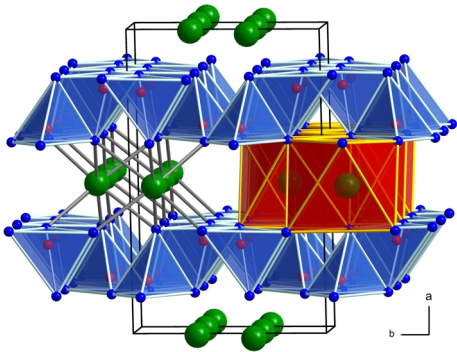


Fig. 1. (Color online). Crystal structure of β -FeB₂O₄, viewed along $[00\bar{1}]$. Blue polyhedra (top and bottom layer): BO₄ tetrahedra; red polyhedra (center layer): FeO₆ octahedra; green spheres (large): Fe²⁺; blue spheres (corners of tetrahedra): O^{2−}; red spheres (center of tetrahedra): B³⁺.

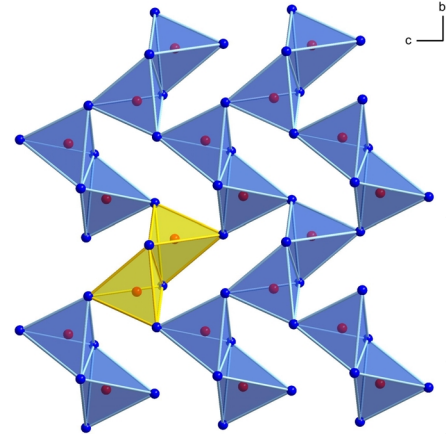


Fig. 2. (Color online). Layer of edge- and corner-sharing BO₄ tetrahedra in β -FeB₂O₄, viewed along $[100]$. One B₂O₆ unit is highlighted.

is composed of distorted BO₄ tetrahedra. Fig. 2 shows that each of these tetrahedra is connected to a second one *via* edge-sharing, forming B₂O₆ building blocks. These groups are interconnected *via* common vertices, resulting in layers in the crystallographic *bc* plane, that are linked by strings of edge-sharing FeO₆ octahedra, running along the *c* direction. Inside the layers, “sechser” rings [45] are formed by four B₂O₆ units, each unit being part of four “sechser” rings.

As already mentioned, the structure of β -FeB₂O₄ is isotypic to HP-NiB₂O₄ [14]. Unfortunately, the designation (prefix) is not identical because this nickel borate was identified as the first compound in this structure type. When the nickel borate was synthesized under high-pressure conditions, we designated this compound with the prefix HP (*High Pressure*), because up to now, there exists no normal-pressure phase of the composition NiB₂O₄. In contrast, when β -FeB₂O₄ was synthesized, there already existed the iron borate α -FeB₂O₄ [28], synthesized under high-pressure conditions, too. So, the here presented compound got the prefix β to distinguish these two polymorphs.

Besides HP-NiB₂O₄ and β -FeB₂O₄, there are two other borate structure types with the motif of B₂O₆ units: the rare-earth borates α -RE₂B₄O₉ (*RE* = Sm–Ho) [8–11] and RE₄B₆O₁₅ (*RE* = Dy, Ho) [8, 12, 13].

Fig. 3 shows the interatomic angles and distances inside the B₂O₆ unit of β -FeB₂O₄. As we could expect, the B–O distances inside the B₂O₂ ring (B1–O1: 151.2(4), 152.5(4) pm) are longer than those outside of the “zweier” rings [45] [B1–O2: 144.3(4) pm (2 \times)]. The average B–O bond length of 148.1 pm is slightly increased in comparison to the average distance in isolated BO₄ tetrahedra of 147.6 pm [46, 47]. Inside the B₂O₆ unit, the B \cdots B distance comes to 208.3(5) pm, which corresponds to values found in other high-

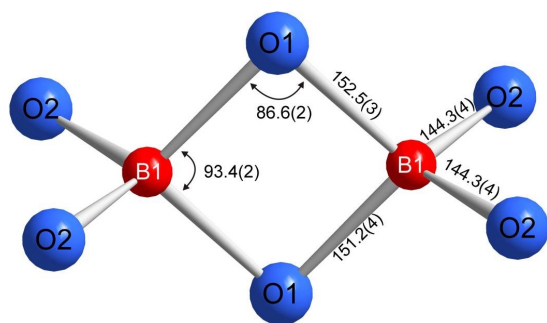


Fig. 3. (Color online). Distances (pm) and angles (deg) in the B₂O₆ unit of β -FeB₂O₄.

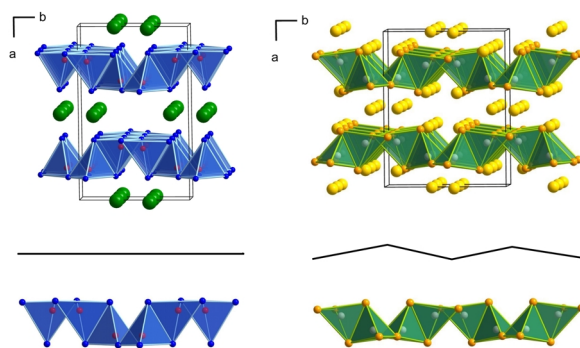


Fig. 4. (Color online). Comparison of the layer structures of β -FeB₂O₄ (left) and β -Ca₃[Al₂N₄] (right), viewed along [00 $\bar{1}$].

pressure borates exhibiting edge-sharing BO₄ tetrahedra, *e. g.* HP-NiB₂O₄ (208.8(2) pm), α -RE₂B₄O₉ (*RE* = Sm: 207.1(9); Eu: 205.3(9); Gd: 204(2); Tb: 205.5(9); Ho: 204(3) pm) [8–11], and RE₄B₆O₁₅ (*RE* = Dy: 207.2(8), Ho: 207(1) pm) [8, 12, 13].

The Fe–O distances inside the distorted FeO₆ octahedra vary between 209.5(2) and 225.8(2) pm and average out to 215.3 pm. As expected, these distances are slightly increased compared to the average iron oxygen distances in six-fold coordinated Fe³⁺ ions in borates, *e. g.* in Fe^{II}Fe^{III}₂(BO₄)O₂ (203.8 pm) [18, 19] or FeBO₃ (202.8 pm) [25]. The average Fe²⁺–O bond length of 218.5 pm for the recently published high-pressure compound α -FeB₂O₄ agrees well with the average value of β -FeB₂O₄ (215.3 pm). For a more detailed description of the HP-NiB₂O₄ structure type see ref. [14].

Similar layers of edge-sharing tetrahedra with different atoms were observed in the compounds β -Ca₃[Al₂N₄] [48], Ca₃[Al₂As₄] [49], α -Ca₃[Ga₂N₄] [50], Sr₃[Al₂P₄] [51], and Ba₃[In₂P₄] [52]. Due to the fact that the layers in these compounds are corrugated, and the metal content between the layers is three times as high as in β -FeB₂O₄, these structures differ substantially. Fig. 4 depicts a comparison of the layers of β -FeB₂O₄ (Fig. 4 left) and β -Ca₃[Al₂N₄] (Fig. 4 right).

A comparison of selected structure parameters of the isotypic structures β -FeB₂O₄ and HP-NiB₂O₄ is shown in Table 6. A closer look at the lattice parameters reveals remarkable differences in *a* (β -FeB₂O₄: 950.0(2), HP-NiB₂O₄: 924.7(2) pm). In contrast, the lattice parameters *b* (β -FeB₂O₄: 562.9(2), HP-NiB₂O₄: 552.3(2) pm) and *c* (β -FeB₂O₄: 443.7(1), HP-NiB₂O₄: 442.9(1) pm) show only a minor or nearly

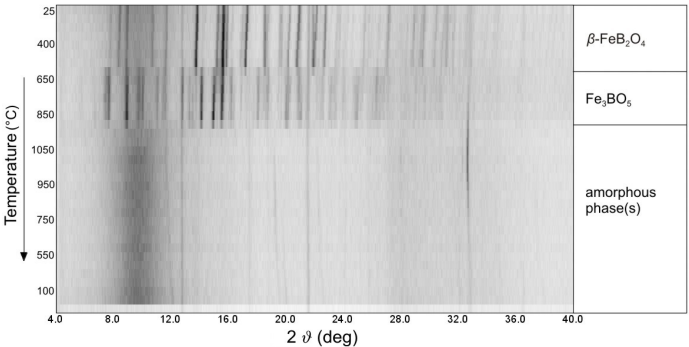


Fig. 5. Temperature-programmed diffraction patterns of β -FeB₂O₄.

Table 6. Comparison of the isotypic structures β -FeB₂O₄ and HP-NiB₂O₄ [14].

Empirical formula	β -FeB ₂ O ₄	HP-NiB ₂ O ₄
Molar mass, g mol ⁻¹	141.5	144.3
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions:		
<i>a</i> , pm	950.0(2)	924.7(2)
<i>b</i> , pm	562.9(2)	552.3(2)
<i>c</i> , pm	443.7(1)	442.9(1)
β , deg	108.50(3)	108.30(3)
<i>V</i> , nm ³	0.225(1)	0.215(1)
B–O bond lengths, pm:		
B–O1	151.2(4), 152.5(4)	151.6(2), 153.1(2)
B–O2	144.3(4), 144.3(4)	144.5(2), 144.3(2)
av. B–O distance, pm	148.1	148.4
B···B distance in B ₂ O ₆ unit, pm	208.3(5)	208.8(2)
av. M–O distance, pm	215.3	208.6

no difference, respectively. The reason that the differences in the BO₄ tetrahedra of both compounds are negligible can be found in the ionic radii of the cations. The increased ionic radius for Fe²⁺ leads to an enlargement of the interlayer distance in β -FeB₂O₄ along *a* and a broadening of the strings of FeO₆ octahedra along *b*. In the *c* direction, no elongation of the strings of octahedra can be observed.

Because of the extreme synthetic conditions of 8 GPa and 1030 °C, we investigated the metastable character of the high-pressure phase β -FeB₂O₄. Temperature-programmed X-ray powder diffraction experiments were performed on a Stoe Stadi P powder diffractometer [monochromatized MoK α radiation (λ = 71.073 pm)] with a computer-controlled Stoe furnace. The sample was enclosed in a silica capillary and heated from r. t. to 500 °C in 100 °C steps, and from 500 °C to 1100 °C in steps of 50 °C. Afterwards, the sample was cooled to 500 °C in

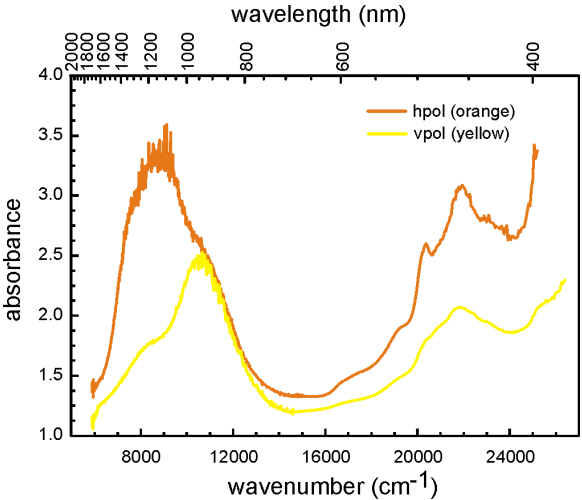


Fig. 6. (Color online). Polarized single-crystal electronic absorption spectra of β -FeB₂O₄. Crystal face not indexed; thickness \sim 0.05 mm; the colors orange and yellow refer to the color of the crystal in the corresponding polarization directions.

50 °C steps, and below 500 °C in 100 °C steps. At each temperature, a diffraction pattern was recorded. Fig. 5 shows that the high-pressure phase β -FeB₂O₄ remains stable up to a temperature of 500 °C. A further increase of temperature leads to the decomposition of the high-pressure phase into *vonsenite* (Fe^{II}₂Fe^{III}(BO₃)O₂). Above 900 °C and during cooling, no crystalline phases could be detected. The reflections visible above 900 °C are caused by the oven. The temperature-programmed X-ray powder investigations of the isotypic high-pressure phase HP-NiB₂O₄ revealed a higher temperature stability up to 750 °C. At higher temperatures, HP-NiB₂O₄ decomposed into the normal-pressure borate Ni₃(BO₃)₂ and presumably B₂O₃.

Table 7. Ligand field splittings and interatomic distances of the $[M^{II}O_6]$ chromophores in β -FeB₂O₄, Fe₂P₄O₁₂, HP-NiB₂O₄, and Ni₂P₄O₁₂.

Compound	Δ_o (cm ⁻¹)	$-(8/3)d\sigma$ (cm ⁻¹)	$d(M-O)$ (Å)	References
β -FeB ₂ O ₄	8860	2900	2.10, 2.11, 2.26 (2×)	this work
Fe ₂ P ₄ O ₁₂ ^a	~ 8700	~ 4500	2.05, 2.14, 2.20 (2×) ^b 2.05, 2.12, 2.20 (2×)	[54, 70]
HP-NiB ₂ O ₄	8620	≤ 1500	2.05, 2.05, 2.18 (2×)	[14]
Ni ₂ P ₄ O ₁₂	7300	≤ 1500	1.99, 2.06, 2.07 (2×) ^b 1.99, 2.09, 2.12 (2×)	[55, 71]

^a The powder reflectance spectrum of Fe₂P₄O₁₂ shows a broad band around 9200 cm⁻¹ with pronounced shoulders at 7000 and 11500 cm⁻¹ [54]; ^b the structure of the metaphosphates consists of two independent metal sites.

Crystals of β -FeB₂O₄ show dichroism (orange/yellow). From their polarized single-crystal electronic absorption spectra, a ligand field splitting $\Delta_o \approx 8860$ cm⁻¹ is estimated. Note that Δ_o for tetragonally distorted chromophores containing d^1 , d^4 , d^6 , or d^9 ions is not identical, but slightly smaller than the average of the two absorption bands, in the case of β -FeB₂O₄ observed at $\nu = 7840$ and $\nu = 10725$ cm⁻¹. The energy difference between these two bands (Fig. 6) reflects the tetragonal distortion of the ligand field (and the splitting of the excited state 5E_g , for O_h symmetry) in the $[Fe^{II}O_6]$ chromophore and amounts for β -FeB₂O₄ to $-(8/3)d\sigma \approx 2900$ cm⁻¹. Assuming (in accordance with literature [53]) that the splitting of the ground state ($^5T_{2g}$ for O_h symmetry) is about one quarter of the excited state, leads to our estimate of Δ_o . This estimated value tallies well with $\Delta_o(Fe_2P_4O_{12}) = 8700$ cm⁻¹ [54], $\Delta_o(Ni_2P_4O_{12}) = 7300$ cm⁻¹ [55], and $\Delta_o(HP-NiB_2O_4) = 8620$ cm⁻¹ [14]. Apparently, there is a slightly higher ligand-field splitting in the borates. We attribute this higher splitting to the higher coordination number of the ligating oxygen atoms in the borates, c. n. (O²⁻) = 4 in contrast to c. n. (O²⁻) = 2 and 3 in the metaphosphates. As a result, slightly lower π -bonding should be exerted by the oxygen ligands in the borates. The distortion of the $[Ni^{II}O_6]$ and $[Fe^{II}O_6]$ octahedra in the borates and the metaphosphates is quite similar (Table 7). Therefore, we have to note that the tetragonal splitting of the ligand field, as it is observed from the electronic absorption spectra, is much higher for the $[Fe^{II}O_6]$ chromophores. We believe that this effect follows from a strong vibronic coupling in the iron(II) compounds, as already discussed in the literature [53]. Our attempts to model the observed $d-d$ transition energies for β -FeB₂O₄ and Fe₂P₄O₁₂ within the angular overlap model [56–58] led for both compounds to much smaller splittings than those observed.

We understand this mismatch as additional evidence for the strong influence of the vibrational coupling on the electronic absorption spectra of the iron(II) compounds.

In the range of $16000 \leq \tilde{\nu} \leq 24000$ cm⁻¹, rather strong spin-forbidden transitions within the $[Fe^{II}O_6]$ chromophore are observed. The polarization of these bands is actually responsible for the observed dichroism. A detailed assignment of these spin-forbidden transitions is impossible on the basis of our data. The whole appearance of the observed spectra is, however, very similar to other spectra reported in the literature for the chromophore $[Fe^{II}O_6]$ (in *e. g.*: MgO:Fe²⁺ [59], *vivianite* Fe₃(PO₄)₂ · 8 H₂O [60], *olivine* Fe₂SiO₄, *orthopyroxene* and *clinopyroxene* FeSiO₃, *cordierite* (Mg,Fe)₂Al₄Si₅O₁₈ · *n* X^{Channel}, *alamandine* Ca₃Fe₂Si₃O₁₂ [61] and references there).

Additionally, bond valence sums were calculated for all atoms of β -FeB₂O₄, using the bond length/bond strength concept (ΣV) [62,63] and the CHARDI concept (*charge distribution in solids*, ΣQ) [64]. The results of both concepts confirm the supposed formal ionic charges derived from the crystal structure analysis [ΣV : +1.96 (Fe), +2.99 (B), -1.94 (O1), -2.02 (O2), and ΣQ : +2.03 (Fe), +2.98 (B), -1.88 (O1), -2.12 (O2)].

The MAPLE values (*madelung part of lattice energy*) [65–67] were calculated in order to compare them with those of the binary components, *viz.* FeO and the high-pressure modification B₂O₃-II. Due to the additive potential of the MAPLE values, it is possible to calculate hypothetical values for β -FeB₂O₄, starting from the binary oxides. A value of 26277 kJ mol⁻¹ was obtained in comparison to 26427 kJ mol⁻¹ (deviation = 0.57 %), starting from the binary oxides (1 × FeO (4489 kJ mol⁻¹) [68] + 1 × B₂O₃-II (21938 kJ mol⁻¹) [69]).

Conclusions

In this paper, we report the synthesis, crystal structure, and properties of the high-pressure phase β -FeB₂O₄ in comparison to the data of the isotopic phase HP-NiB₂O₄. The structure shows the rare feature of edge-sharing BO₄ tetrahedra, found before in the compounds α -RE₂B₄O₉ (RE = Sm–Ho), RE₄B₆O₁₅ (RE = Dy, Ho), and HP-NiB₂O₄. While in the rare-earth compounds only 1/10th [α -RE₂B₄O₉ (RE = Sm–Ho)] or 1/3rd [RE₄B₆O₁₅ (RE = Dy, Ho)] of the BO₄ tetrahedra are linked *via* a common edge, β -FeB₂O₄ and its isotype HP-NiB₂O₄ have BO₄ tetrahedra sharing a common edge with an adjacent BO₄-unit.

Acknowledgements

Special thanks go to Prof. Dr. W. Schnick, Department Chemie of the University of Munich (LMU) for the continuous support of this work. We thank T. Miller for collecting the single-crystal data and the temperature-programmed powder diffraction data. We also thank Mr. V. Dittrich, University of Bonn, for his dedicated measurement of the single-crystal absorption spectra. This work was financially supported by the Deutsche Forschungsgemeinschaft (HU 966/ 2-3) and the Fonds der Chemischen Industrie.

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