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High-pressure synthesis and crystal structure of the mixed valent iron borate $Fe_8B_{15}O_{28}(OH)_8$

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ABSTRACT

The new mixed valent iron borate $Fe_8B_{15}O_{28}(OH)_8$ was synthesized under high-pressure/high-temperature conditions of 12 GPa and 850 °C in a multianvil device (Walker-type module). It crystallizes with four formula units in the tetragonal space group $I4_1/a$ with the structural parameters a = 1142.3(2) and c = 1537.4(2) pm (V = 2.006(1) nm^3, R_1 = 0.0586, wR_2 = 0.0721 (all data)). $Fe_8B_{15}O_{28}(OH)_8$ is composed exclusively from corner-sharing BO_4 tetrahedra and can be described as two identical interpenetrating three-dimensional networks that are built up from $B_{11}O_{28}$ building blocks and interconnecting $BO_2O(OH)$ units. The Fe^{II} and Fe^{III} ions in $Fe^{II}_5Fe^{III}_3B_{15}O_{28}(OH)_8$ are located in the interspaces between the two networks. ^{57}Fe Mössbauer, Raman, and infrared spectroscopic data are reported.

1. Introduction

In the last decades, investigations concerning compounds with stable network structures received rapidly growing attention. Due to the potentially useful properties of *e.g.* catalytic or electronic nature, a magnitude of new compounds was synthesized and characterized. Some of these framework structures form remarkable interpenetrating networks [1,2]. However, interpenetrating network structures are not only subject to normal pressure chemistry under mild conditions. A good example therefore is the crystal structure of the high-pressure compound $Ti_5B_{12}O_{26}$ [3] that can be described as two interpenetrating diamond structures similar to those in NaTl. In the course of our high-pressure/high-temperature investigations into the iron borates, a new compound $Fe_8B_{15}O_{28}(OH)_8$ with interpenetrating networks could be obtained.

For the ternary iron borates, six different compositions are known under ambient pressure conditions: FeB_4O_7 [4,5], $Fe_2B_2O_5$ [6,7], and $FeBO_3$ [8] as well as the mixed valent borates $Fe^{II}_2Fe^{III}O_2(BO_3)$ (*vonsenite* (*Pbam*) [9,10], *hulsite* (*P2/m*) [11]), $Fe_3(BO)_4O_2$ [12,13], and $Fe^{II}Fe^{III}O(BO_3)$ (*warwickite* structure (*Pmcn*), distorted *warwickite* structure ($P2_1/c$)) [14,15]. The compound FeB_4O_7 is built up from BO_3 groups and BO_4 tetrahedra, while $Fe^{II}Fe^{III}_2(BO_4)O_2$ exclusively exhibits isolated BO_4 tetrahedra. By contrast, the polymorphic phases $Fe^{II}_2Fe^{III}O_2(BO_3)$ and $Fe^{II}Fe^{III}O(BO_3)$ as well as the compounds $FeBO_3$ and $Fe_2B_2O_5$ are solely built up from trigonal planar BO_3-groups. The high content of BO_3 groups compared to BO_4 tetrahedra is typical for ambient pressure compounds. High-pressure borates [16] often exhibit a higher content of four-fold coordinated boron, which is in good agreement with the pressure coordination rule [17]. This was proven true by our group with the synthesis of three ternary high-pressure borates, namely α-FeB_2O_4 [18], β-FeB_2O_4 [19], and β-FeB_4O_7 [20], all exclusively exhibiting BO_4 tetrahedra. Alongside, systematic high-pressure investigations into hydrous iron borates led to the two hydrated compounds $Fe_6B_{22}O_{39}\cdot H_2O$ [21] and $Fe_3B_7O_{13}(OH)\cdot 1.5\ H_2O$ [22].

The mixed valent iron borate $Fe_8B_{15}O_{28}(OH)_8$, presented in the following, was synthesized during these systematic investigations. Next to synthesis and crystal structure, first results concerning the properties of this compound are given.

2. Experimental section

2.1. Synthesis

The compound $Fe_8B_{15}O_{28}(OH)_8$ was synthesized under high-pressure/high-temperature conditions of 12 GPa and 850 °C in a

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multianvil device with a modified Walker-type module. For the synthesis of $Fe_8B_{15}O_{28}(OH)_8$, a stoichiometric mixture of Fe_2O_3 (Merck, Germany, 99%) and H_3BO_3 (Merck, Germany, 99.5%) was finely ground and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint® S100, Kempten, Germany). The crucible was inserted into a 14/8-assembly, surrounded by eight tungsten carbide cubes (TSM-10, Ceratizit, Reutte, Austria) and placed in the modified Walker-type module (Voggenreiter, Mainleus, Germany). To apply the pressure, a hydraulic 1000 t multianvil press (Voggenreiter, Mainleus, Germany) was used. Further details concerning the assembly and its preparation are given in Refs. [23–27].

To synthesize the new compound $Fe_8B_{15}O_{28}(OH)_8$, the educts were compressed to 12 GPa within 5.6 h and kept at this pressure. During the heating period, the temperature was increased to 850 °C in 10 min, kept there for 15 min, and lowered to 580 °C in 20 min. After the sample was cooled to room temperature by switching off the heating, the pressure was decreased within 16.3 h. To obtain the sample, the recovered pressure medium was broken apart and the sample separated from the surrounding boron nitride crucible. The compound $Fe_8B_{15}O_{28}(OH)_8$ was gained in form of black air-resistant crystals. During the synthesis, the iron cations were partially reduced to the oxidation state 2+. A reduction of the metal ions is often observed in this multianvil setup and is described *e.g.* in Ref. [7].

2.2. Crystal structure analysis

The powder diffraction data were collected on a Stoe Stadi P powder diffractometer with Ge(111)-monochromatized Mo$K_{\alpha1}$ (λ = 70.93 pm) radiation in transmission geometry. Fig. 1 depicts the measured diffraction pattern (top) in comparison to the theoretical pattern simulated from single-crystal data of $Fe_8B_{15}O_{28}(OH)_8$ (bottom). The experimental powder pattern shows an excellent match with the theoretical pattern, but also a few minor reflections of an unknown by-product (marked with asterisks). By indexing the measured powder pattern, the lattice parameters a = 1142.7(2) and c = 1537.8(3) pm and a cell volume of 2.008(1) nm^3 were derived. This confirmed the structural parameters (a = 1142.3(2), c = 1537.4(2) pm and V = 2.006(1) nm^3) received from the single-crystal X-ray diffraction analysis (Table 1).

For the analysis of the single-crystal structure, small irregularly shaped crystals of $Fe_8B_{15}O_{28}(OH)_8$ were isolated by mechanical fragmentation. The single crystal intensity data of the compound

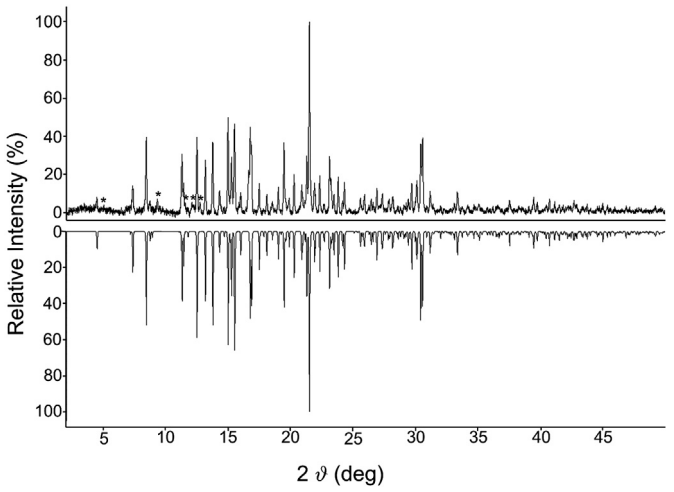

Fig. 1. Powder diffraction pattern of $Fe_8B_{15}O_{28}(OH)_8$ (Mo$K_{\alpha1}$; λ = 71.073 pm), measured from a sample (top) and computed from single crystal data (bottom). Reflections that do not belong to $Fe_8B_{15}O_{28}(OH)_8$ are marked with asterisks.

$Fe_8B_{15}O_{28}(OH)_8$ were collected at *r.t.* using a Nonius Kappa-CCD diffractometer with graphite monochromatized MoK_α radiation (λ = 71.073 pm). A semiempirical absorption correction based on equivalent and redundant intensities (Scalepack [28]) was applied to the intensity data. Table 1 lists all relevant details concerning the data collection and evaluation of the refinement.

Based on the systematic extinctions, the tetragonal centrosymmetric space group $I4_1/a$ was derived. Structure solution and parameter refinement (full-matrix least-squares on F^2) were successfully performed with anisotropic displacement parameters for all atoms except hydrogen using the Shelxl-97 software suite [29]. The final difference Fourier syntheses did not reveal any significant peaks in the refinement. The positional parameters, anisotropic displacement parameters, interatomic distances, and angles are listed in Tables 2–5.

Additional information concerning the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-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-426256.

2.3. Vibrational spectra

The confocal unpolarized Raman spectrum of a single crystal of $Fe_8B_{15}O_{28}(OH)_8$ was recorded with a Horiba Jobin Yvon LabRam-HR 800 Raman micro-spectrometer in the range of 100–4000 cm^{-1}. For the excitation of the sample, the 532 nm emission line of a 100 mW Nd:YAG-laser and the 633 nm line of a 17 mW helium-neon laser were used. The size and power of the laser spot on the surface were approximately 1 μm and 2–5 mW. The spectral resolution was about 2 cm^{-1} and the accuracy of the Raman line shifts was in the order of 0.5 cm^{-1}. The dispersed light was collected using

Table 1
Crystal data and structure refinement of $Fe_8B_{15}O_{28}(OH)_8$ (standard deviations in parentheses).

Empirical formula	$Fe_8B_{15}O_{28}(OH)_8$
Molar mass, g mol^{-1}	1193.0
Crystal system	Tetragonal
Space group	$I4_1/a$
Powder diffractometer	STOE Stadi P
Radiation	Mo$K_{\alpha1}$ (λ = 70.93 pm)
a, pm	1142.7(2)
c, pm	1537.8(3)
V, nm^3	2.008(1)
Single crystal diffractometer	Enraf-Nonius Kappa CCD
Radiation	MoK_α (λ = 71.073 pm) (graphite monochromator))
Single-crystal data	
a, pm	1142.3(2)
c, pm	1537.4(2)
V, nm^3	2.006(1)
Formula units per cell Z	4
Calculated density, g cm^{-3}	3.95
Crystal size, mm^3	0.06 × 0.05 × 0.04
Temperature, K	293(2)
Absorption coefficient, mm^{-1}	5.8
F(000), e	2316
θ range, °	2.2–37.9
Range in hkl	$-19 < h < 18$, $-19 < k < 19$, $-26 < l < 24$
Total no. of reflections	17,672
Independent reflections/R_{int}/R_σ	2691/0.0758/0.0424
Reflections with $I \geq 2\sigma(I)$	2134
Data/ref. parameters	2691/142
Absorption correction	Multi-scan [28]
Goodness-of-fit on F	1.098
Final $R1$/$wR2$ [$I \geq 2\sigma(I)$]	0.0382/0.0676
$R1$/$wR2$ (all data)	0.0586/0.0721
Largest diff. peak/hole, e Å^{-3}	0.63/−0.90