Birgit Fuchs and Hubert Huppertz*

High-pressure synthesis and characterization of the non-centrosymmetric scandium borate ScB₆O₉(OH)₃

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Abstract: The non-centrosymmetric scandium borate ScB₆O₉(OH)₃ was obtained through a high-pressure/high-temperature experiment at 6 GPa and 1473 K. Single-crystal X-ray diffraction revealed that the structure is isotypic to InB₆O₉(OH)₃ containing borate triple layers separated by scandium layers. The compound crystallizes in the space group Fdd₂ with the lattice parameters a = 38.935(4), b = 4.4136(4), and c = 7.6342(6) Å. Powder X-ray diffraction and vibrational spectroscopy were used to further characterize the compound and verify the proposed structure solution.

Keywords: crystal structure; high-pressure chemistry; scandium borate; vibrational spectroscopy.

1 Introduction

Borates are a widely investigated substance class, due to their physical and chemical properties, which makes them interesting not only in the academical scope, but also for industrial applications. These properties mainly arise from the large number of crystal structures borates can adopt, based on their ability to form trigonal planar BO₃ groups as well as BO₄ tetrahedra. According to Bubnova and Filatov, more than 2400 borate crystal structures were listed in the ICSD database in 2013 [1], and this number has since been growing steadily.

During the past years, our group reinvestigated the broad field of transition metal borates with astounding results. Through the use of high-pressure conditions for the syntheses, compounds with interesting structural properties could be realized, like HP–MB₂O₄ (M = Fe, Co, Ni) [2–4], the first borates, where every BO₄ tetrahedron shares one common edge with a second one, Cd(NH₃)₂[B₂O₅(NH₃)] [5], the first ammine borate, or Mo₂B₄O₉ [6], which incorporates transition metal clusters into a borate framework. Despite these findings, there are many M–B–O (M = transition metal) systems, where only very few compounds are known. For example, for the ternary system Sc–B–O, only three phases are known: ScBO₃ [7], Sc₃B₅O₁₂ [8], and Sc₁.₆₇B₃O₇ [9]. While ScBO₃ is an ambient pressure compound, built up of layers of trigonal planar BO₃ groups, alternating with scandium layers, the latter two borates are high-pressure phases containing exclusively BO₄ tetrahedra. Interestingly, these two are also closely related to two natural occurring minerals. Sc₃B₅O₁₂ is isomorphous to the beryllium-silicate semenovite [10, 11], and Sc₁.₆₇B₃O₇ represents the first ternary member of the melilitetype structure family [12].

In the present report, we present another high-pressure borate in the system Sc–B–O: ScB₆O₉(OH)₃. It is isotypic to the indium borate InB₆O₉(OH)₃ [13] and also represents the first non-centrosymmetric and the first hydroxylated scandium borate.

2 Results and discussion

2.1 Crystal structure

ScB₆O₉(OH)₃ crystallizes with eight formula units (Z = 8) in the non-centrosymmetric orthorhombic space group Fdd₂ (no. 43) with the lattice parameters a = 38.935(4), b = 4.4136(4), and c = 7.6342(6) Å and a volume of V = 1311.9(2) Å³. All relevant crystallographic and refinement data can be found in Table 1.

Like the already known isotypic compound InB₆O₉(OH)₃ [13], the crystal structure is built up of triple layers of corner-sharing BO₄ tetrahedra, separated by scandium layers (Figure 1, middle). The BO₄ tetrahedra in the first and the third layer of these triples, with the

*Corresponding author: Hubert Huppertz, Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 80–82, 6020 Innsbruck, Austria, E-mail: Hubert.Huppertz@uibk.ac.at

Birgit Fuchs: Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 80–82, 6020 Innsbruck, Austria
Table 1: Crystal data and structure refinement of ScB$_6$O$_9$(OH)$_3$.

| Empirical formula | ScB$_6$O$_9$(OH)$_3$ |
|------------------|----------------------|
| Molar mass, g mol$^{-1}$ | 304.84 |
| Crystal system | orthorhombic |
| Space group | Fdd (no. 43) |
| Single-crystal data | |
| $T$, K | 183(2) |
| Radiation/wavelength $\lambda$, pm | MoKα/71.07 |
| $a$, Å | 38.935(4) |
| $b$, Å | 4.4136(4) |
| $c$, Å | 7.6342(6) |
| $V$, Å$^3$ | 1311.9(2) |
| $Z$ | 8 |
| Calculated density, g cm$^{-3}$ | 3.09 |
| Absorption coeff., mm$^{-1}$ | 1.2 |
| $F(000)$, e | 1200 |
| Crystal size, mm$^3$ | 0.110 $\times$ 0.070 $\times$ 0.020 |
| $\theta$ range, deg | 2.1–35.1 |
| Index ranges | $-62 \leq h \leq 59$ $-7 \leq k \leq 7$ $-12 \leq l \leq 12$ |
| Reflections collected | 8536 |
| Independent reflections | 1439 |
| $R_{int}$/Ko | 0.0293/0.0232 |
| Completeness to $\theta = 25.2^\circ$, % | 100 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 1349/1/105 |
| Final $R_1$/wR2 indices [1 > 2 $\sigma$(I)] | 0.0246/0.0702 |
| Final $R_1$/wR2 indices (all data) | 0.0298/0.0859 |
| Goodness-of-fit on $F^2$ | 1.240 |
| Flack parameter | 0.02(2) |
| Largest diff. peak/hole, e Å$^{-3}$ | 0.91–0.93 |

Powder diffraction data

| Radiation/wavelength $\lambda$, pm | MoKα/70.93 |
| $a$, Å | 38.928(5) |
| $b$, Å | 4.4187(3) |
| $c$, Å | 7.6418(5) |
| $V$, Å$^3$ | 1314.4(2) |
| $2\theta$ range, deg | 2.0–42.0 |
| $2\theta$ step width, deg | 0.015 |
| $R_{exp}$, % | 2.17 |
| $R_{wp}$, % | 11.21 |
| $R_p$, % | 7.79 |

alternating central boron atoms B1 and B2, both form six-membered rings, where all the tetrahedra point towards the same direction (Figure 1, bottom left and right). In the first layer, this direction is $+a$, whereas in the third layer the orientation is changed to $-a$. The third layer is shifted by 1/4 in the direction of $b$ and 1/4 in the direction of $c$, in relation to the first layer. Very similar six-membered rings can be found in other high-pressure borates, for example in Cd$_2$B$_4$O$_8$ [14] and α-FeB$_2$O$_4$ [15]. In contrast to ScB$_6$O$_9$(OH)$_3$ presented here, where all BO$_4$ tetrahedra show the same orientation in one layer – downwards (D) for the first and upwards (U) for the third layer – the sequences UDUDUD (for one-fourth of the six-membered rings) and UUUDDD are developed for the cadmium-compound, and UUDUDD for the iron-compound. In ScB$_6$O$_9$(OH)$_3$, the layers of six-membered rings are connected via an intermediate layer, consisting of corrugated bands of BO$_4$ tetrahedra. In this middle layer, there are two half-occupied boron and the accompanying oxygen positions, designated as B3/B3a and O6/O6a, respectively, where only one is occupied at a time (Figure 1, bottom middle), leading to layers consisting exclusively either of B3O$_4$ tetrahedra (light blue) or of B3aO$_4$ tetrahedra (orange). The bands run in direction of [011] or [011] for the tetrahedra with the central cation B3 and in direction of [011] or [011] for the tetrahedra with the central cation B3a (Figure 1, top). In contrast, the isotopic indium compound InB$_2$O$_5$(OH)$_3$ [13] features only one fully occupied boron position in this layer, which is identical to the boron position B3 here. It is also within this middle layer, where we presume two hydrogen atoms to be bound to O6 and O6a. Due to the only half occupied positions, they could not be assigned in the refinement process, but this assumption coincides with the result for the isotopic InB$_2$O$_5$(OH)$_3$ [13], where this position could be refined. This leads to two hydrogen atoms in the overall formula MB$_2$O$_5$(OH)$_3$ ($M =$ Sc, In), where the third one is postulated based on charge neutrality reasons.

Looking at the B–O bond lengths in this structure, a distinction can be made for the boron atoms B1 and B2, where the B–O distances lie within a much narrower range than for the only half-occupied atoms B3 and B3a. For the first two boron atoms, the average B–O distance is 1.471 Å, which is in good agreement with the literature (1.476(35) Å) [16]. In contrast, the overall average value of 1.466 Å is markedly shorter. A similar situation is found for the O–B–O angles. While the angles for the B1O$_4$ and B2O$_4$ tetrahedra vary only slightly, the angles for the tetrahedra with the half occupied central boron positions lie within a wider range of 104.8(7) to 113.6(8)°. Nevertheless, the average values of 109.4 and 109.5° match well with the expected tetrahedral angle. All the bond lengths and angles are listed in Tables 2 and 3, the atomic coordinates and isotropic displacement parameters are found in Table 4.

The scandium cations separate the triple layers and are positioned between the centres of two six-membered rings (Figure 2). Here, the upper layer is rotated about 180° compared to the lower layer, which is the reason for the very long $a$ axis of 38.935(4) Å. Because of this rotation
of the triple layers against each other, four triple layers
are needed to return to the initial position instead of two
without the rotation. The Sc$^{3+}$ cations between the anionic
triple layers are sixfold coordinated by oxygen atoms in
an octahedral alignment. The Sc–O distances are in a
narrow range of 2.130(2) to 2.139(2) Å, with an average

Table 2: Interatomic B–O and Sc–O distances (Å) for ScB$_6$O$_9$(OH)$_3$ (standard deviations in parentheses).

|    | B1  | B2  | B3  | B3a | Sc1 | d  | d  |
|----|-----|-----|-----|-----|-----|----|----|
| O1 | 1.462(5) | 1.467(3) | 1.45(2) | 1.447(8) | 1.479(9) | 1.46(5) | 1.46(3) |
| O2 | 1.469(3) | 1.469(4) | 1.469(4) | 1.469(4) | 1.469(4) | 1.46(4) | 1.46(4) |
| O3 | 1.475(4) | 1.472(5) | 1.472(5) | 1.472(5) | 1.472(5) | 1.47(4) | 1.47(4) |
| O4 | 1.480(4) | 1.473(4) | 1.473(4) | 1.473(4) | 1.473(4) | 1.47(4) | 1.47(4) |

Figure 1: Top: Different orientations of the disordered middle layer. Middle: Crystal structure of ScB$_6$O$_9$(OH)$_3$ along [010]. Bottom (from left to right): First layer of six-membered rings pointing towards $+a$; second layer of either the light blue or the orange corrugated BO$_4$ chains (half occupied B3/B3a position); third layer of six-membered rings pointing towards $-a$. 
distance of 2.136 Å. This distance is significantly shorter than in the two other known high-pressure scandium borates Sc$_3$B$_5$O$_{12}$ ($\text{O Sc–O: 2.246 Å}$) [8] and Sc$_{1.76}$B$_3$O$_7$ ($\text{O Sc–O: 2.244 Å}$) [9]. In these already known compounds, the scandium is coordinated by eight oxygen atoms in the form of distorted square antiprisms in contrast to the octahedral coordination in ScB$_6$O$_9$(OH)$_3$. This sixfold coordination is related to the octahedral coordination of scandium in the ambient pressure compound ScBO$_3$. Moreover, the Sc–O distance in this compound is 2.1200(4) Å, which is not far from the value derived from the crystal structure of ScB$_6$O$_9$(OH)$_3$.

Corresponding to the increased In$^+$ cation size compared to Sc$^{3+}$, the cell parameters of the indium compound are slightly larger and also the B–O ($\text{O = 1.489 Å}$) and In–O distances ($\text{O = 2.177 Å}$) are longer than in the presented scandium compound [13]. Nevertheless, these values are in good agreement with distances found in other high-pressure indium borates [17, 18].

The calculation of bond valence sums according to the bond length/bond strength ($\Sigma V$) concept [19, 20] reveals a more positive formal charge for O6 ($\Sigma V = -1.55$) and O6a ($\Sigma V = -1.66$), respectively, indicating a missing coordination, which agrees with the assumption that these two atoms are the bonding partners for two hydrogen atoms. The resulting formal ionic charges for the other atoms correspond well with the expected values within the limits of this concept and are shown in Table 5.

### 2.2 X-ray powder diffraction

The comparison between the experimental powder diffraction data and the pattern derived from the single-crystal refinement are depicted in Figure 3. Although ScB$_6$O$_9$(OH)$_3$ is clearly the main reaction product, a certain amount of Sc$_3$B$_5$O$_{12}$ can be seen in the powder pattern, refined to a fraction of 10(1)%.

### 2.3 Vibrational spectroscopy

Figure 4 shows the IR spectrum of a ScB$_6$O$_9$(OH)$_3$ powder sample in the range from 400 to 3800 cm$^{-1}$. The peak at

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**Table 3**: Bond angles (deg) for ScB$_6$O$_9$(OH)$_3$ (standard deviations in parentheses).

| O5–B1–O3 | 107.8(3) | O4–B2–O3 | 108.0(2) |
| O5–B1–O4 | 108.5(2) | O5–B2–O4 | 108.7(2) |
| O4–B1–O3 | 108.9(2) | O3–B2–O2 | 109.2(2) |
| O4–B1–O1 | 110.2(2) | O5–B2–O2 | 109.6(2) |
| O3–B1–O1 | 110.4(2) | O5–B2–O3 | 110.0(2) |
| O5–B1–O1 | 111.1(2) | O4–B2–O2 | 111.3(2) |

| Atom  | s.o.f. | x    | y    | z    | $U_{eq}$ |
|-------|-------|------|------|------|----------|
| Sc1   | 1     | 1/2  | 1/2  | 0.25263(9) | 0.0031(2) |
| B1    | 1     | 0.5473(1) | 0.5026(5) | 0.5808(4) | 0.0043(7) |
| B2    | 1     | 0.5470(1) | 0.9946(6) | 0.4164(4) | 0.0030(6) |
| B3    | 0.5   | 0.6057(2) | 0.778(2)  | 0.535(2)  | 0.005(2)  |
| B3a   | 0.5   | 0.6065(3) | 0.718(2)  | 0.476(2)  | 0.008(2)  |
| O1    | 1     | 0.58484(7) | 0.5196(4) | 0.5828(3) | 0.0089(5) |
| O2    | 1     | 0.58472(7) | 0.9854(5) | 0.4270(3) | 0.0085(5) |
| O3    | 1     | 0.53245(5) | 0.8056(4) | 0.5564(2) | 0.0035(3) |
| O4    | 1     | 0.53465(4) | 0.3756(3) | 0.7474(3) | 0.0043(3) |
| O5    | 1     | 0.53508(5) | 0.3082(4) | 0.4357(2) | 0.0038(3) |
| O6    | 0.5   | 0.6372(2)  | 0.809(2)  | 0.8615(7) | 0.021(2)  |
| O6a   | 0.5   | 0.6376(2)  | 0.696(2)  | 0.4489(7) | 0.023(2)  |

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**Figure 2**: Octahedrally coordinated scandium position between the borate layers and in the middle of two six-membered rings. Sc–O distances in Å.
around 3200 cm\(^{-1}\) can be attributed to stretching vibrations associated with the hydroxyl groups [21], thus confirming their existence in the structure. Even though the sample used for this measurement also contained a small amount of Sc\(_3\)B\(_5\)O\(_{12}\), any contribution to the peak at the upper range of the spectrum can be ruled out, because this by-product does not contain any hydrogen atoms. The tetrahedral BO\(_4\) groups typically lead to the absorption bands in the range of 800–1150 cm\(^{-1}\) [22–24]. The broad absorption between ~1300 and 1500 cm\(^{-1}\) and the peaks below 800 cm\(^{-1}\) most likely originate from complex O–B–O, B–O–B, B–O, and Sc–B–O vibrations, which was confirmed by quantum mechanical calculations on \(\beta\)-ZnB\(_4\)O\(_7\) and \(\beta\)-CaB\(_4\)O\(_7\), two high pressure compounds with complex borate frameworks consisting of crystallographically independent BO\(_4\) tetrahedra and O\(_3\)B groups [25].

3 Conclusion

ScB\(_6\)O\(_9\)(OH)\(_3\), representing the first non-centrosymmetric and the first hydroxylated scandium borate, was obtained at a pressure of 6 GPa and a temperature of 1473 K from scandium nitrate and boron oxide. Crystals of the compound are isotypic to the indium borate InB\(_6\)O\(_9\)(OH)\(_3\) and built up of anionic borate triple layers, the top and bottom ones forming six-membered rings and the middle one forming corrugated chains. They are separated by scandium layers in the bc plane, where the scandium atoms are octahedrally coordinated by oxygen atoms. The triple

|         | Sc1 | B1  | B2  | B3  | B3a | O1  | O2  | O3  | O4  | O5  | O6  | O6a |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \(\Sigma V\) | +2.77 | +3.05 | +3.06 | +3.11 | +3.15 | −2.38 | −2.21 | −1.99 | −1.97 | −1.98 | −1.55 | −1.66 |

Table 5: Bond valence sums according to the bond length/bond strength (\(\Sigma V\)) concept.

Figure 3: Rietveld refinement of a ScB\(_6\)O\(_9\)(OH)\(_3\) sample, containing the side phase Sc\(_3\)B\(_5\)O\(_{12}\).

Figure 4: IR spectrum of a ScB\(_6\)O\(_9\)(OH)\(_3\) powder sample, also containing a certain amount of Sc\(_3\)B\(_5\)O\(_{12}\).
layers are arranged in four slightly shifted orientations, resulting in a long unit cell with \( a = 38.935(4) \) Å. Even though the hydrogen atoms could not be identified unambiguously in the crystal structure refinement, they were verified via vibrational spectroscopy.

4 Experimental section

4.1 Synthesis

The title compound ScB\(_6\)O\(_9\)(OH)\(_3\) was first obtained through a high-pressure/high-temperature experiment at 6 GPa and 1473 K. The synthesis was performed in an 18/11 assembly in a hydraulic 1000 t press with a modified Walker-type module (both Max Vogenreiter GmbH, Germany). Sc(NO\(_3\))\(_3\)-5H\(_2\)O (99.9%) and B\(_2\)O\(_3\) (both Strem Chemicals, Inc., Newburyport, Massachusetts, USA, >99.9%) were ground together in a stoichiometric ratio under ambient conditions and filled into a Pt capsule, which was placed in a crucible made of α-BN and closed with a lid of the same material (both Henze Boron Nitride‐Products AG, Germany). For a more detailed description of the experimental setup, the reader is referred to the literature [26–28].

The 18/11 assembly was compressed to 6 GPa within 150 min and heated to \( T = 1473 \) K in the following 10 min at a constant pressure. After keeping this temperature for the next 30 min, the sample was cooled to \( T = 773 \) K within another 180 min. Then, the sample was quenched to room temperature by switching off the heating and a 450 min decompression process was started. The recovered pressure medium was broken apart and the product carefully separated from the surrounding crucible and Pt capsule. A mixture of ScB\(_6\)O\(_9\)(OH)\(_3\) and Sc\(_3\)B\(_5\)O\(_{12}\) appeared as colourless platelets.

4.2 Powder X-ray diffraction

A flat sample of the reaction product, containing ScB\(_6\)O\(_9\)(OH)\(_3\) and Sc\(_3\)B\(_5\)O\(_{12}\), was characterized by powder diffraction analysis in transmission geometry on an STOE Stadi P powder diffractometer (STOE & Cie GmbH, Darmstadt, Germany) equipped with a Mythen 1K microstrip detector (Dectris). The measurement was carried out with Ge(111)-monochromatized MoK\(_\alpha\) radiation (\( \lambda = 70.93 \) pm) in the 2θ range of 2–52° with a step size of 0.015°. For a comparison with the values derived from the single-crystal structure analysis, a Rietveld refinement was performed employing the Topas 4.2 software [29].

4.3 Single-crystal X-ray analysis

The single-crystal structure determination was performed on a Bruker D8 Quest Kappa diffractometer with monochromatized MoK\(_\alpha\) radiation (\( \lambda = 71.07 \) pm), equipped with an Incoatec microfocus X-ray tube and a Photon 100 CMOS detector. The structure solution and parameter refinement were performed with Direct Methods using SHELXS [30, 31] and the refinement against \( F^2 \) was carried out with SHELXL, both implemented in the WinGX software [32]. Despite measuring the crystal at \( T = 183(2) \) K, it was not possible to unambiguously identify the position of the hydrogen atoms, also attributed to the half-occupied layer in which these atoms are expected to be found. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Further details of the crystal structure investigation of ScB\(_6\)O\(_9\)(OH)\(_3\) may be obtained from The Cambridge Crystallographic Data Centre CCDC/FIZ Karlsruhe deposition service via www.ccdc.cam.ac.uk/structures on quoting the deposition number CCDC 2000250.

4.4 Vibrational spectroscopy

For further characterization and to prove the existence of the postulated hydroxy groups in this compound, an FTIR-ATR (Attenuated Total Reflection) spectrum of a powder sample of ScB\(_6\)O\(_9\)(OH)\(_3\) was recorded. A Bruker ALPHA Platinum-ATR spectrometer (Bruker, Billerica, USA) with a 2 × 2 mm diamond ATR-crystal and a DTGS detector were used to collect the spectrum in the spectral range of 400–3800 cm\(^{-1}\). A total of 320 scans of the powder sample were obtained and corrected for atmospheric influences afterwards, employing the Opus 7.2 software [33].

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