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High-pressure synthesis and crystal structure of $\text{HP-Al}_2\text{B}_3\text{O}_7(\text{OH})$

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Abstract: Orthorhombic $\text{HP-Al}_2\text{B}_3\text{O}_7(\text{OH})$ was synthesized in a Walker-type multianvil apparatus under high-pressure/high-temperature conditions of 12.4 GPa and 1200 °C, respectively. Its structure is isotypic to that of $\text{Ga}_2\text{B}_3\text{O}_7(\text{OH})$ and has been determined *via* single-crystal X-ray diffraction at room temperature. $\text{HP-Al}_2\text{B}_3\text{O}_7(\text{OH})$ crystallizes in the space group *Cmce* ($Z = 8$) with the lattice parameters $a = 10.3124(4)$, $b = 7.3313(3)$, $c = 10.4801(5)$ Å, and $V = 792.33(6)$ Å³. The compound has also been characterized by IR and Raman spectroscopy.

Keywords: aluminum borate; crystal structure; high-pressure synthesis; vibrational spectroscopy.

Dedicated to: Professor Robert Glaum on the occasion of his 60th birthday.

1 Introduction

Regarding the system Al-B-O-H , the literature research yields five compounds so far. Besides the well-known mineral Jeremejevite ($\text{Al}_6(\text{BO}_3)_5(\text{F},\text{OH})_3$) [1], our working group recently prepared the compound $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ which represents a new member of the high-pressure structure type $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Al}, \text{Ga}, \text{In}, \text{Ga/In}$) [2, 3]. Jianhua Lin et al. who are working on hydrothermally synthesized zeolite-like borate structures, published the remaining three compounds in the system Al-B-O-H . In detail, this research working group found three

microporous aluminum borates, which they named PKU-1 [4], PKU-2 [5], and PKU-6 [6] (PKU stands for Peking University). PKU-1 with the sum formula $\text{HAl}_3\text{B}_6\text{O}_{12}(\text{OH})_4$ was published in 2003. In this compound all Al atoms are octahedrally coordinated building up a porous structure with 10- and 18-membered ring windows. PKU-2 ($\text{Al}_2\text{B}_5\text{O}_9(\text{OH})_3 \cdot n\text{H}_2\text{O}$) is even more porous featuring 24-membered rings around channels of edge-sharing AlO_6 octahedra. PKU-6 ($\text{Al}_2\text{B}_3\text{O}_7(\text{OH})$ – designated as $\text{HAl}_2\text{B}_3\text{O}_8$ in reference [6]) was published in 2007 and shares the sum formula and point group with our title compound but shows a completely different structure. Infinite chains of square-pyramidally coordinated Al atoms are interlinked by three corner-sharing trigonal planar BO_3 groups. Thus, in the hydrothermally synthesized PKU-6, the Al atoms are pentacoordinated and the B atoms show a three-fold coordination. In our title compound $\text{HP-Al}_2\text{B}_3\text{O}_7(\text{OH})$, the coordination numbers of the aluminum and boron atoms are increased by one as one would expect for a high-pressure phase due to the pressure-coordination rule in solid state chemistry. However, the condensed structure of $\text{HP-Al}_2\text{B}_3\text{O}_7(\text{OH})$ is not unprecedented as it has already been described in 2015 for the gallium containing isotype $\text{Ga}_2\text{B}_3\text{O}_7(\text{OH})$ [7].

The present report contains a detailed description of the synthesis and crystal structure of our title compound as well as vibrational spectroscopic data of $\text{HP-Al}_2\text{B}_3\text{O}_7(\text{OH})$ single crystals.

2 Experimental section

2.1 Synthesis

The starting materials $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98\%$, Sigma-Aldrich) and H_3BO_3 (99.5% Carl Roth) were mixed in a stoichiometric ratio of 2:3, ground in an agate mortar and encapsulated in platinum foil (0.027 mm, 99.9%, Chem-PUR). The platinum capsule was then placed into a crucible with a lid, both made of α -BN (Henze Boron Nitride Products AG) and centered in a “14/8” assembly which includes, amongst others, a graphite furnace for resistance heating. Inside a uniaxially compressed Walker-type

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module, six steel wedges and eight tungsten carbide cubes surround the octahedral assembly to generate a quasi-hydrostatic pressure on the sample. A detailed description of the experimental setup is given in the literature [8–10]. HP-Al₂B₃O₇(OH) was formed under the extreme reaction conditions of 12.4 GPa and 1200 °C. The required pressure and temperature were adjusted within 6 h and 10 min, respectively. The heating power was maintained for 10 min and then gradually lowered to $T = 800$ °C within 30 min. Finally, the sample was quenched to room temperature and slowly decompressed to ambient conditions. After freeing the platinum capsule from its surroundings and cutting it open with a scalpel, a clean-white reaction product with colorless single crystals appeared. Compared to our starting mixture, the product quantity was obviously diminished, which we explain with the great amount of volatile parts in aluminum nitrate nonahydrate. HP-Al₂B₃O₇(OH) did also form as a byproduct in syntheses performed with Al₂O₃ (99.9%, Alfa Aesar) instead of Al(NO₃)₃·9H₂O, slightly varying ratios of Al to B, higher temperatures up to 1400 °C, or a lower pressure of 12.0 GPa.

Figure 1: Experimental powder pattern (MoK α_1) of the optimized synthesis leading to HP-Al₂B₃O₇(OH) (top) compared to a simulation of the powder pattern of HP-Al₂B₃O₇(OH) based on single-crystal data (bottom). The asterisk-marked reflections in the experimental powder pattern refer to an unidentified byproduct.

2.2 Crystal structure determination by X-ray diffraction

The reaction product was analyzed with a STOE Stadi P powder diffractometer equipped with a Mythen 1 K detector (Dectris, Switzerland). The measurement was carried out with Ge(111)-monochromatized MoK α_1 radiation ($\lambda = 0.7093$ Å) in transmission geometry across a 2θ range of 2.0–50.0°. Figure 1 shows a comparison of the experimental powder pattern with a simulation derived from single-crystal structure data. HP-Al₂B₃O₇(OH) clearly constitutes the main phase, but nevertheless the experimental powder pattern shows additional reflections of at least one byproduct.

The colorless single crystals of HP-Al₂B₃O₇(OH) were measured with a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS detector. For structure solution and parameter refinement, the software tools SHELXS-2013/1 [11, 12] and SHELXL-2013/4 [13] implemented in the program WINGX-2018.1 [14] were used. According to the systematic reflection conditions, HP-Al₂B₃O₇(OH) was solved and refined in the space group *Cmce* (no. 64) and afterwards standardized with the routine STRUCTURE TIDY [15] implemented in PLATON [16] (version 170613). Except for the proton, all atoms could be refined anisotropically. Details of the data acquisition can be found in the synoptical Table 1. Table 2 contains the positional parameters and Wyckoff positions and Table 3 the displacement parameters of all atoms in HP-Al₂B₃O₇(OH).

Table 1: Single-crystal data and structure refinement of HP-Al₂B₃O₇(OH).

Empirical formula	Al ₂ B ₃ O ₇ (OH)
Molar mass, g mol ⁻¹	215.40
Crystal system	orthorhombic
Space group	<i>Cmce</i> (no. 64)
Single-crystal diffractometer	Bruker D8 Quest Kappa
Radiation/wavelength λ , pm	MoK α /71.07
a , Å	10.3124(4)
b , Å	7.3313(3)
c , Å	10.4801(5)
V , Å ³	792.33(6)
Formula units per cell Z	8
Calculated density, g cm ⁻³	3.61
Crystal size, mm ³	0.030 × 0.050 × 0.090
Temperature, K	183(2)
Absorption coefficient, mm ⁻¹	0.7
$F(000)$, e	848
θ range, deg	3.89–39.44
Range in hkl	$\pm 18; \pm 13; \pm 18$
Refl. total/independent	8079/1236
$R_{\text{int}}/R_{\sigma}$	0.0324/0.0226
Refl. with $I > 2 \sigma(I)$	1095
Data/ref. parameters	1236/69
Absorption correction	multiscan
Final $R1/wR2$ ($I > 2 \sigma(I)$)	0.0198/0.0469
Final $R1/wR2$ (all data)	0.0250/0.0497
Goodness-of-fit on F^2	0.921
Largest diff. peak/hole, $e \text{ Å}^{-3}$	0.38/–0.34

Table 2: Wyckoff positions, atomic coordinates, isotropic U_{iso} or equivalent isotropic displacement parameters U_{eq} (Å²) for HP-Al₂B₃O₇(OH). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses).

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (U_{iso} for H4)
Al1	8 <i>f</i>	1/2	0.78853(3)	0.88079(2)	0.00190(6)
Al2	8 <i>d</i>	0.85164(2)	0	0	0.00208(6)
B1	16 <i>g</i>	0.62480(6)	1.14999(9)	0.87176(6)	0.00290(9)
B2	8 <i>e</i>	3/4	0.8957(2)	3/4	0.0030(2)
O1	16 <i>g</i>	0.62447(4)	1.24742(6)	0.98924(4)	0.00291(7)
O2	16 <i>g</i>	0.63173(4)	0.78036(6)	0.73973(4)	0.00280(7)
O3	16 <i>g</i>	0.73359(4)	1.01421(6)	0.86459(4)	0.00263(7)
O4	8 <i>f</i>	1/2	0.53723(8)	0.88783(6)	0.00289(9)
O5	8 <i>f</i>	1/2	1.04199(8)	0.86111(6)	0.00277(9)
H4	8 <i>f</i>	1/2	0.468(3)	0.812(3)	0.065(8)

Table 3: Anisotropic displacement parameters U_{ij} (Å²) of HP-Al₂B₃O₇(OH) (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al1	0.0023(2)	0.0016(2)	0.0019(2)	0	0	0.00032(7)
Al2	0.0023(2)	0.0019(2)	0.0020(2)	0	0	−0.00002(7)
B1	0.0029(2)	0.0030(2)	0.0029(2)	−0.0003(2)	−0.0002(2)	0.0001(2)
B2	0.0032(3)	0.0026(3)	0.0031(3)	0	0.0000(2)	0
O1	0.0035(2)	0.0029(2)	0.0024(2)	−0.0003(2)	0.0002(2)	−0.0007(2)
O2	0.0027(2)	0.0029(2)	0.0028(2)	−0.0007(2)	0.0003(2)	−0.0008(2)
O3	0.0027(2)	0.0028(2)	0.0024(2)	0.0008(2)	−0.0002(2)	−0.0006(2)
O4	0.0035(2)	0.0028(2)	0.0024(2)	0	0	−0.0003(2)
O5	0.0020(2)	0.0023(2)	0.0040(2)	0	0	−0.0001(2)

CSD-2027675 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.3 Vibrational spectroscopy

The transmission FT-IR spectrum of an HP-Al₂B₃O₇(OH) single crystal was measured in the spectral range of 600–4000 cm^{−1} with a Vertex 70 FT-IR spectrometer (spectral resolution 4 cm^{−1}) equipped with a KBr beam splitter, a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector and a Hyperion 3000 microscope (Bruker). 320 scans of the sample were acquired using a Globar (silicon carbide) rod as mid-IR source and a 15× IR objective as focus. During the measurement, the sample was positioned on a BaF₂ window. Atmospheric influences were corrected with the software OPUS 6.5 [17].

A single-crystal Raman spectroscopic analysis was performed using a HORIBA JOBIN-YVON LabRam-HR800 spectrometer with a focal length of 800 mm. The spectrum was recorded unpolarized at ambient conditions. The analyzed area was excited using a (green) Nd-YAG laser with an excitation wavelength of 532 nm. Scattered light was dispersed by an optical grating with 1800 grooves per mm resulting in a spectral resolution of 1.92 cm^{−1}, and collected with a cooled Andor™ CCD collector. An Olympus 50× objective, a confocal pinhole of 1000 μm and a slit of 100 μm was used for the measurement to maximize the intensity at a lateral resolution of ~5 μm². Before the analyses, the spectral position of the Raman mode of a Si standard wafer was measured against the position of the Rayleigh line, resulting in the expected Raman shift of 520.7 cm^{−1}. The spectrum was obtained in multi-window acquisition mode provided by the LABSPEC (version 5.93.20) [18] software package in the frequency range of 200–1500 cm^{−1} and represents the average of two single measurements with an acquisition time of 250 s.

each. Background subtraction and the determination of band position were performed with the same software. The background was subtracted using an 8th order line-function. Band positions were obtained by fitting a Gaussian–Lorentzian function to the individual bands.

3 Results and discussion

3.1 Crystal structure

HP-Al₂B₃O₇(OH) crystallizes in the orthorhombic space group *Cmce* (no. 64) with eight formula units (*Z* = 8) and the lattice parameters *a* = 10.3124(4), *b* = 7.3313(3), *c* = 10.4801(5) Å, and *V* = 792.33(6) Å³. Details of the single-crystal data and structure refinement can be found in Table 1. Similar to the isotypic compound Ga₂B₃O₇(OH), HP-Al₂B₃O₇(OH) consists of two fundamental building blocks (BB1 and BB2). BB1 represents a cluster of four edge-sharing AlO₆ octahedra (Figure 2a), and BB2 is composed of 12 corner-sharing BO₄ tetrahedra forming a flexed unit of two sechser rings [19] that are interlinked by two vierer rings (Figure 2b). As depicted in Figure 3, each BB1 is encircled by two BB2s. The flexed BB2 units are interconnected forming endless zig-zag chains along the crystallographic *b* axis. Between these zig-zag chains, the BB1 clusters fill the space in alternating orientations in relation to *c* (visualized in Figure 4). All oxygen atoms belong to both building blocks except O4, which connects to three Al atoms and the proton in HP-Al₂B₃O₇(OH). While the proton position was geometrically constructed in Ga₂B₃O₇(OH), it was possible to freely refine it in the aluminum compound. The proton is located in the middle of a BO₄ sechser ring at a distance of 0.94(3) Å to O4 and forms hydrogen bonds to two O2 atoms and to O5. Figure 5 shows the hydrogen bonding situation in HP-Al₂B₃O₇(OH). As the proton needs space, it provokes the connecting O4 atom to a position

farther away resulting in diminished O–Al–O angles of 76.53(3)° for O4–Al2–O4 and 78.13(2)° for O1–Al2–O4 instead of 90° required for a regular octahedron. All Al–O distances in the range between 1.8439(6) and 2.0086(5) Å and the average values of 1.90 and 1.92 Å are in accordance with data from the literature [20–22]. Likewise, the B–O distances (*Ø* = 1.49 Å) and tetrahedral angles (*Ø* = 109.5°) are as expected [23]. All interatomic distances and angles are given in Tables 4–6. To support the crystal structure solution, the Madelung part of lattice energy (MAPLE value) [24, 25] of HP-Al₂B₃O₇(OH) was calculated and compared to the stoichiometric sum of the compounds α-Al₂O₃, HP-B₂O₃, and H₃BO₃. The results showed only a minimal deviation of 0.15% (see Table 7). The bond valence sums (BVS) for HP-Al₂B₃O₇(OH) were calculated with the bond-length/bond-strength concept [26] and the charge distribution was derived by using the charge distribution in solids (CHARDI) concept [27]. The results are listed in Table 8. Both calculations led to reasonable values with only one noticeable BVS deviation for O4 being the donor of the hydrogen bond.

3.2 Vibrational spectroscopy

For the isotypic compound Ga₂B₃O₇(OH) [7], the IR and Raman bands were assigned based on DFT calculations and therefore provide a good basis for the interpretation of the spectra of HP-Al₂B₃O₇(OH). The FT-IR spectrum of an HP-Al₂B₃O₇(OH) single crystal is shown in Figure 6. In the fingerprint region up to ~1200 cm^{−1}, at the lower wavenumbers presumably O–Al–O bending as well as Al–O stretching vibrations contribute to the spectral pattern, followed mainly by O–B–O bending and B–O stretching vibrations. As in Ga₂B₃O₇(OH), the O–H stretching vibrations give a distinct signal at about 3500 cm^{−1}. Unlike the Ga containing analog, the single

Figure 2: Building blocks in HP-Al₂B₃O₇(OH). a) BB1: a cluster of four edge-sharing AlO₆ octahedra; b) BB2: an interlinked ring-formation of 12 corner-sharing BO₄ tetrahedra.

Figure 3: Two BB2 building blocks consisting of BO₄ tetrahedra fully enclose one BB1 Al₄O₁₆ cluster.

Figure 4: Structural buildup of HP-Al₂B₃O₇(OH): Alternatingly oriented Al₄O₁₆ clusters (BB1) are connected through endless chains of BO₄ tetrahedra along c. For reasons of clarity, the protons and the interlinking BO₄ tetrahedra forming the vierer rings in BB2 are omitted.

Figure 5: Hydrogen bonding situation in HP-Al₂B₃O₇(OH).

Table 4: Interatomic distances (Å) in HP-Al₂B₃O₇(OH) (standard deviations in parentheses).

Al1–	O4	1.8439(6)	B1–	O1	1.4234(7)
	O5	1.8696(6)		O3	1.5017(8)
	O1	1.8900(5) 2×		O2	1.5112(7)
	O2	2.0086(5) 2×		O5	1.5152(7)
∅ Al1–O		1.92	∅ B1–O		1.49
Al2–	O3	1.8726(5) 2×	B2–	O2	1.4880(7) 2×
	O1	1.8715(5) 2×		O3	1.4919(7) 2×
	O4	1.9486(4) 2×	∅ B2–O		1.49
∅ Al2–O		1.90			

Table 5: Interatomic angles (deg) in HP-Al₂B₃O₇(OH) (standard deviations in parentheses).

O4–Al1–O1	80.32(2) 2×	O4–Al2–O4	76.53(3)
O2–Al1–O2	85.11(3)	O1–Al2–O4	78.13(2) 2×
O1–Al1–O1	85.55(3)	O1–Al2–O4	89.93(2) 2×
O5–Al1–O2	87.04(2) 2×	O3–Al2–O4	92.61(2) 2×
O4–Al1–O2	89.98(2) 2×	O3–Al2–O1	94.37(2) 2×
O1–Al1–O2	93.8(2) 2×	O3–Al2–O1	95.45(2) 2×
O5–Al1–O1	102.6(2) 2×	O3–Al2–O3	98.9(3)
∅ O–Al1–O ₉₀	89.9	∅ O–Al2–O ₉₀	89.7
O1–Al1–O2	170.25(2) 2×	O1–Al2–O1	164.87(3)
O4–Al1–O5	175.96(3)	O3–Al2–O4	167.26(2) 2×
∅ O–Al1–O ₁₈₀	172.2	∅ O–Al2–O ₁₈₀	166.5
O3–B1–O5	106.53(4)	O3–B2–O2	107.23(2) 2×
O2–B1–O5	108.28(4)	O3–B2–O3	108.76(6)
O1–B1–O5	108.9(4)	O2–B2–O2	110.74(6)
O3–B1–O2	110.2(4)	O3–B2–O2	111.45(2) 2×
O1–B1–O2	110.58(4)	∅ O–B3–O	109.5
O1–B1–O3	112.19(4)		
∅ O–B1–O	109.5		

Table 6: Hydrogen bonds (Å, deg) in HP-Al₂B₃O₇(OH) (standard deviations in parentheses).

	d(D–H)	d(H···A)	d(D···A)	∠(D–H–A)
O4–H4···O2 2×	0.94(3)	2.01(2)	2.6793(7)	127(2)
O4–H4···O5	0.94(3)	1.90(3)	2.6091(8)	131(2)

Table 7: Comparison of the calculated MAPLE value (Madelung Part of Lattice Energy) of HP-Al₂B₃O₇(OH) and the MAPLE value received from α-Al₂O₃ [28], HP-B₂O₃ [29], and H₃BO₃ [30] according to the reaction equation: 3 Al₂O₃ + 4 B₂O₃ + H₃BO₃ → 3 HP-Al₂B₃O₇(OH).

Calculated MAPLE value for HP-Al ₂ B ₃ O ₇ (OH), kJ mol ^{–1}	161077
Calculated MAPLE value based on α-Al ₂ O ₃ , HP-B ₂ O ₃ , and H ₃ BO ₃ , kJ mol ^{–1}	161316
Difference, %	0.15

Table 8: Charge distribution in HP-Al₂B₃O₇(OH), calculated with the bond-length/bond-strength (V) and CHARDI (Q) concept.

	Al1	Al2	B1	B2	O1	O2	O3	O4	O5	H4
V	2.96	3.10	2.93	2.90	-1.94	-1.84	-1.97	-2.34	-1.97	1.01
Q	2.98	2.94	3.01	3.09	-2.04	-1.99	-2.11	-1.90	-2.04	0.98

Figure 6: IR spectrum of an HP-Al₂B₃O₇(OH) single crystal in the range of 600–4000 cm⁻¹. **Figure 7:** Raman spectrum of an HP-Al₂B₃O₇(OH) single crystal in the range of 200–1500 cm⁻¹. The following band positions can be assigned to the HP-Al₂B₃O₇(OH) structure (cm⁻¹): 251, 266, 277, 303, 316, 321, 339, 350, 364, 412, 429, 438, 492, 501, 539, 582, 607, 616, 650, 674, 683, 702, 720, 749, 772, 788, 817, 833, 871, 899, 969, 1023, 1059, 1104, 1136, 1098.

crystal of HP-Al₂B₃O₇(OH) does not show any contamination with organic compounds.

The Raman spectrum is presented in Figure 7 and shows only the frequency range between 200 and 1500 cm⁻¹ due to strong luminescence at higher Raman shifts that becomes even more pronounced when exciting with a red (633 nm) laser, so that OH-related vibrations (expected between 3000 and 4000 cm⁻¹) are not displayed. The DFT calculations for the isotopic compound Ga₂B₃O₇(OH) also allow assignments for the aluminum analog. The Al³⁺ = Ga³⁺ exchange mainly results in higher vibrational frequencies and consequently increasing Raman shifts of Al-related bands if compared to the respective Ga-related counterparts. Bands in the 250–700 cm⁻¹ frequency range can be mainly assigned to vibrations of the AlO₆ units. The Al–O–H, Al–O–Al bending vibrations are expected to appear in a wide range between 250 and 1150 cm⁻¹, while the stretching vibrations for the BO₄ tetrahedra appear in the 800–1150 cm⁻¹ region.

4 Conclusion

The present report presents a detailed synthesis protocol and the determination and discussion of the crystal structure of the new aluminum borate HP-Al₂B₃O₇(OH), which is isotopic to Ga₂B₃O₇(OH). While the proton position in the gallium compound had to be calculated geometrically, it was possible to locate it in the electron density map and refine it *via* difference Fourier analysis of the aluminum analog. IR data additionally confirm the presence of the hydroxyl group. Attempts to synthesize the isotopic indium compound have not been successful yet.

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