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High-pressure synthesis and crystal structure of the mixed-cation borate $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$

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Abstract: The mixed cation triel borate $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ was synthesized in a Walker-type multianvil apparatus at high-pressure/high-temperature conditions of 12.5 GPa and 1300°C. Although the product could not be reproduced in further experiments, its crystal structure could be reliably determined *via* single-crystal X-ray diffraction data. $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ crystallizes in the tetragonal space group $I4_1/a$ (origin choice 2) with the lattice parameters $a = 11.382(2)$, $c = 15.244(2)$ Å, and $V = 1974.9(4)$ Å³. The structure of the quaternary triel borate consists of a complex network of BO_4 tetrahedra, edge-sharing InO_6 octahedra in dinuclear units, and very dense edge-sharing GaO_6 octahedra in tetranuclear units.

Keywords: crystal structure; gallium borate; high pressure; indium borate.

1 Introduction

In the last decade, extensive research has been carried out in the field of group 13 element borates which yielded numerous new structures featuring interesting properties. For instance, triel borates have been reported to show luminescence when being doped with a suitable activator ion [1–4], and acentric compounds have been described as possible NLO materials [5–7]. Especially gallium and indium borates shifted into the research focus due to their photocatalytic properties. During the last 5 years, the results of seven photocatalytic studies of indium or gallium borates have been published [1, 8–13]. Up to date, 14 borates are known in the systems Ga-B-O(-H) and In-B-O(-H), from which 12 have been published since 2010. This emerging research field has benefited from the

advancement of high-pressure techniques. More than half of all existing indium or gallium borates in these (partially hydroxylated) ternary systems were synthesized with a multianvil apparatus and formed under conditions of at least 10 GPa.

Likewise, the new compound $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ has now been synthesized at high-pressure conditions *via* a multianvil press. As usual in such dense structures, this mixed cation triel borate solely consists of boron atoms that are coordinated by four oxygen atoms. Ga^{3+} and In^{3+} form diverse edge-sharing octahedral entities. Unlike the solid solution $\text{In}_{1-x}\text{Ga}_x\text{BO}_3$ ($0 \leq x \leq 0.5$) [14], in which the indium position is optionally replaced by gallium, our title compound is the first triel borate containing indium and gallium in crystallographically different positions.

In the following, the synthesis and crystal structure of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ are described in detail.

2 Experimental section

2.1 Synthesis

In_2O_3 (99.9%, ChemPUR, Karlsruhe, Germany), Ga_2O_3 (99.998%, Strem Chemicals, Kehl, Germany), and H_3BO_3 (99.5%, Carl Roth, Karlsruhe, Germany) were weighed in a molar ratio of 1:3:8 and ground in an agate mortar. Then, the mixture was encapsulated in gold foil (99.99%, 0.025 mm, Sigma-Aldrich, USA) and transferred into a boron nitride crucible (α -BN, Henze Boron Nitride Products AG, Kempten, Germany). The high-pressure/high-temperature experiment was performed with a multianvil device based on a Walker-type module (Voggenreiter, Mainleus, Germany) that consisted of a 14/8 assembly surrounded by eight tungsten carbide cubes (ha-7% Co, Hawedia, Marklkofen, Germany). The detailed procedure is described in the literature [15–17]. $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ formed under conditions of 12.5 GPa and 1300°C. The maximum pressure was built up within 342 min and held for 42 min during the heating period. Within 7 min, the maximum temperature of 1300°C was reached, kept for 5 min and afterwards the temperature was decreased to 900°C within 30 min. The following careful pressure reduction to ambient conditions took 1013 min.

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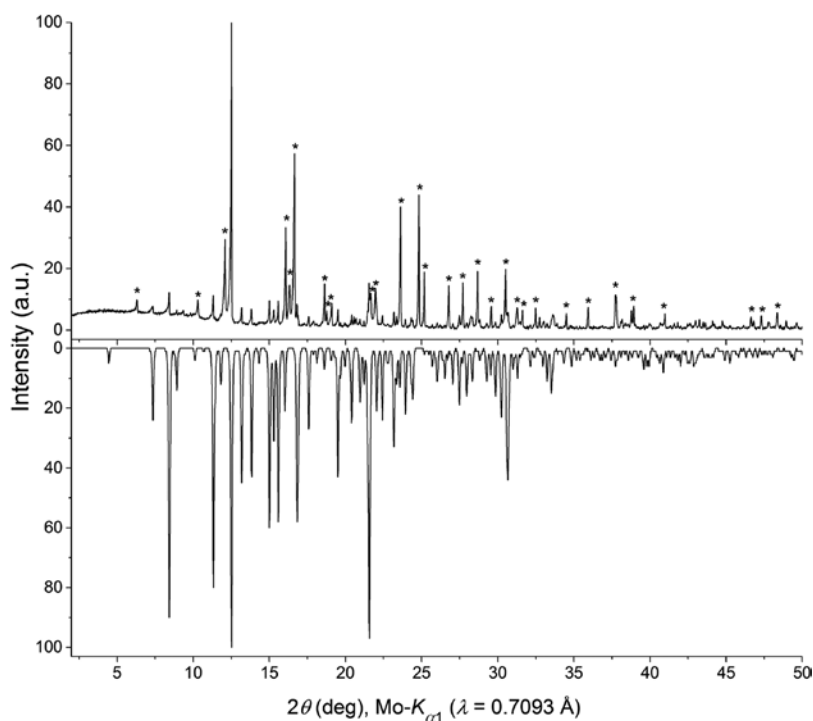


Fig. 1: Experimental powder pattern of the reaction product (top) compared to a simulation of the theoretical powder pattern of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ based on single-crystal data (bottom). Reflections marked with an asterisk do not result from the title compound.

The reaction product appeared grey-white and its powder pattern did not match that of any known phase. A suitable single-crystal was isolated from the sample. The solution of the structure of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ explains some of the reflections in the powder pattern of the reaction product (see Fig. 1). However, the majority of the reflections is still unknown up to now. All subsequent attempts to purposefully and stoichiometrically synthesize $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ failed up to now.

2.2 X-ray structure determination

At first, 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 $\text{MoK}\alpha_1$ radiation ($\lambda = 0.7093 \text{ \AA}$) in transmission geometry across a 2θ range of $2.0\text{--}60.5^\circ$. Figure 1 shows the experimental powder pattern. Most of the reflections could not be associated with any known phases. All reflections that do not match with the simulation of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ derived from single-crystal data are marked with asterisks.

A colorless, prismatic single-crystal of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ was isolated from the reaction product and measured on a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS detector. The data was

Table 1: Crystal data and structure refinement of tetragonal $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$.

Empirical formula	$\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$
Molar mass, g mol^{-1}	1479.33
Crystal system	tetragonal
Space group	$I4_1/a$ (no. 88, origin choice 2)
Single-crystal diffractometer	Bruker D8 Quest Kappa
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
a , \AA	11.382(2)
c , \AA	15.244(2)
V , \AA^3	1974.9(4)
Formula units per cell Z	4
Calculated density, g cm^{-3}	4.98
Crystal size, mm^3	$0.05 \times 0.04 \times 0.02$
Temperature, K	297(2)
Detector distance, mm	50
Exposure time, $^\circ \text{s}^{-1}$	130
Absorption coefficient, mm^{-1}	10.2
$F(000)$, e	2744
θ range, deg	$2.2\text{--}36.0$
Range in hkl	$\pm 18; \pm 18; \pm 25$
Reflections total/independent	28476/2348
R_{int}	0.0450
Reflections with $I \geq 2\sigma(I)$	2260
R_σ	0.0202
Data/ref. parameters/restraints	2348/139/1
Absorption correction	multi-scan
Final $R1/wR2$ [$I \geq 2\sigma(I)$]	0.0175/0.0417
Final $R1/wR2$ (all data)	0.0192/0.0422
Goodness-of-fit on F_o^2	1.078
Largest diff. peak/hole, $e \text{ \AA}^{-3}$	0.53/−1.78

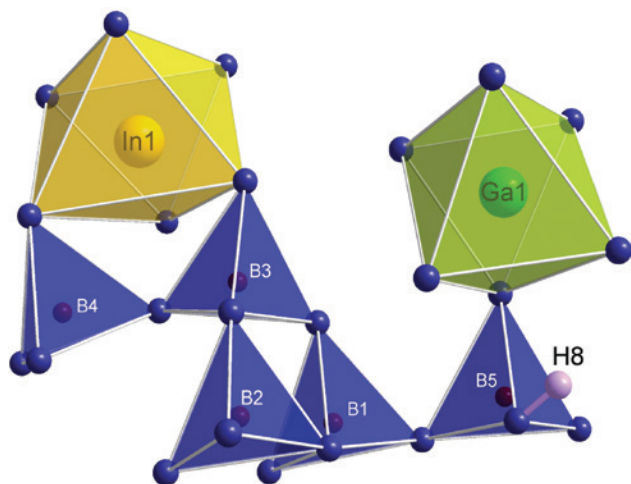


Fig. 2: Asymmetric unit of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ consisting of five different boron atom positions forming corner-sharing BO_4 tetrahedra, an InO_6 octahedron, a GaO_6 octahedron, and a hydroxyl group (atoms O8 and H8).

collected at room temperature and a multiscan absorption correction was performed with SADABS 2014/5 [18]. For the structure solution and parameter refinement, the SHELXS/L-2013 [19, 20] software implemented in the program WINGX-2013.3 [21] was used. The single-crystal was treated as a non-merohedral twin with a domain fraction of 0.165–0.835 and was refined with the twin matrix $[010\ 100\ 00\bar{1}]$. Aside from the proton, all atoms in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ could be refined anisotropically with site

occupancy factors of 1. The proton position was fixed with the DFIX command in a distance of 0.83 Å to O8, since this is the only oxygen atom with otherwise only two coordination partners. Due to charge neutrality reasons, the proton H8 was refined with a site occupancy factor of 0.75. In the end, the refinement of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ led to satisfying results with total R (all data) values of $R_1=0.0192$ and $wR_2=0.0422$ as well as a Goodness-of-fit of 1.078.

CCDC 1895780 ($\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

3.1 Crystal structure

$\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ crystallizes in the tetragonal space group $I4_1/a$ (no. 88, origin choice 2) with four formula units ($Z=4$) and the lattice parameters $a=11.382(2)$, $c=15.244(2)$ Å, and $V=1974.9(4)$ Å³. Details of the crystal structure refinement can be found in Table 1. Figure 2 shows the asymmetric unit of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$. The structure consists of five different boron atom positions (corner-sharing BO_4 tetrahedra) and one octahedrally coordinated indium and gallium atom position. The proton, which

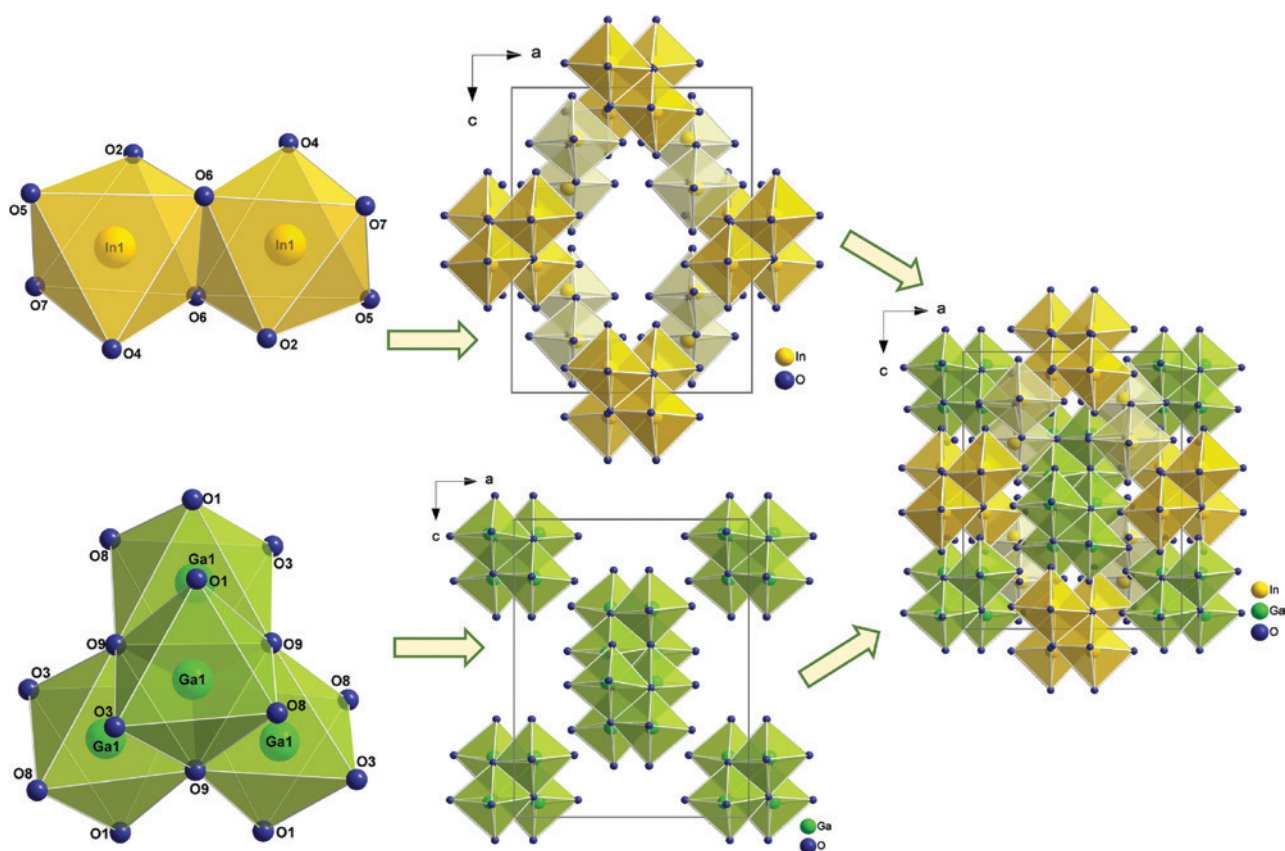
Table 2: Wyckoff positions, occupancy factors, atomic coordinates, isotropic U_{iso} or equivalent isotropic displacement parameters U_{eq} (Å²) of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$.

Atom	Wyckoff position	Occupancy	x	y	z	U_{eq} (U_{iso} for H8)
In1	16f	1	0.23415(2)	0.65795(2)	0.32996(2)	0.00510(3)
Ga1	16f	1	0.41303(2)	0.64704(2)	0.70048(2)	0.00335(4)
B1	16f	1	0.1577(2)	0.9068(2)	0.6132(2)	0.0037(3)
B2	8e	1	0	3/4	0.6196(2)	0.0041(5)
B3	16f	1	0.1624(2)	0.7336(2)	0.5071(2)	0.0042(3)
B4	4b	1	0	3/4	3/8	0.0069(7)
B5	16f	1	0.3358(2)	0.5774(2)	0.5190(2)	0.0041(3)
O1	16f	1	0.0752(2)	0.8315(2)	0.67198(9)	0.0048(2)
O2	16f	1	0.0798(2)	0.6775(2)	0.56575(9)	0.0052(2)
O3	16f	1	0.2279(2)	0.8245(2)	0.5570(2)	0.0049(2)
O4	16f	1	0.1010(2)	0.7899(2)	0.43024(9)	0.0052(2)
O5	16f	1	0.2484(2)	0.6495(2)	0.47177(9)	0.0043(2)
O6	16f	1	0.0894(2)	0.9828(2)	0.55999(9)	0.0049(2)
O7	16f	1	0.2430(2)	0.9697(2)	0.66984(9)	0.0044(2)
O8	16f	1	0.4032(2)	0.5060(2)	0.45766(9)	0.0059(2)
O9	16f	1	0.4178(2)	0.6616(2)	0.56737(9)	0.0048(2)
H8	16f	0.75	0.446(6)	0.553(6)	0.432(4)	0.09(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses).

Table 3: Anisotropic displacement parameters U_{ij} (\AA^2) of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In1	0.00709(6)	0.00417(6)	0.00403(5)	-0.00103(4)	-0.00059(4)	0.00039(4)
Ga1	0.00390(9)	0.00340(9)	0.00274(8)	-0.00011(7)	0.00015(6)	0.00007(6)
B1	0.0030(8)	0.0048(8)	0.0032(7)	-0.0006(6)	0.0002(6)	0.0004(6)
B2	0.003(2)	0.005(2)	0.004(2)	-0.0005(9)	0	0
B3	0.0049(8)	0.0040(8)	0.0037(8)	0.0001(6)	0.0003(6)	0.0004(6)
B4	0.008(2)	0.008(2)	0.005(2)	0	0	0
B5	0.0047(8)	0.0043(8)	0.0034(7)	0.0005(6)	0.0003(6)	0.0001(6)
O1	0.0053(6)	0.0058(6)	0.0035(5)	-0.0023(5)	0.0009(4)	-0.0002(4)
O2	0.0057(6)	0.0038(6)	0.0061(5)	-0.0006(4)	0.0025(4)	0.0003(4)
O3	0.0035(6)	0.0055(6)	0.0058(5)	-0.0007(4)	0.0009(4)	-0.0024(4)
O4	0.0051(6)	0.0048(6)	0.0057(5)	-0.0012(5)	-0.0009(4)	0.0006(4)
O5	0.0048(6)	0.0046(6)	0.0035(5)	0.0014(5)	0.0001(4)	-0.0002(4)
O6	0.0039(6)	0.0059(6)	0.0049(5)	0.0002(5)	-0.0001(4)	0.0007(4)
O7	0.0038(6)	0.0040(6)	0.0053(5)	-0.0004(5)	-0.0019(4)	-0.0012(4)
O8	0.0058(6)	0.0055(6)	0.0064(5)	0.0000(5)	0.0022(4)	-0.0012(4)
O9	0.0045(6)	0.0047(6)	0.0050(5)	-0.0003(5)	-0.0004(4)	-0.0003(4)

**Fig. 3:** Isolated edge-sharing InO_6 octahedra (top left, yellow) and GaO_6 octahedra (bottom left, green) and their arrangement in the unit cell of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ (middle and right).

forms a hydroxyl group with the donor atom O8, is the only atom site that shows a diminished occupancy factor of 0.75 for charge neutrality reasons. A complete list of

occupancy factors, Wyckoff positions, fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters can be found in Table 2. All anisotropic

Table 4: Interatomic distances (Å) in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ (standard deviations in parentheses).

In1–O6	2.121(2)	Ga1–O8	1.928(2)
In1–O6	2.134(2)	Ga1–O3	1.933(2)
In1–O7	2.145(2)	Ga1–O1	1.964(2)
In1–O5	2.170(2)	Ga1–O9	2.029(2)
In1–O2	2.216(2)	Ga1–O9	2.037(2)
In1–O4	2.219(2)	Ga1–O9	2.126(2)
ØIn1–O	2.17	ØGa1–O	2.00
B1–O6	1.418(3)	B4–O4	1.496(2) 4 ×
B1–O7	1.484(3)	ØB4–O	1.50
B1–O3	1.500(3)		
B1–O1	1.556(3)	B5–O8	1.458(3)
ØB1–O	1.49	B5–O5	1.477(3)
B2–O2	1.477(2) 2 ×	B5–O7	1.480(3)
B2–O1	1.493(2) 2 ×	B5–O9	1.527(3)
ØB2–O	1.49	ØB5–O	1.49
B3–O2	1.446(3)		
B3–O5	1.471(3)		
B3–O3	1.485(3)		
B3–O4	1.507(3)		
ØB3–O	1.48		

displacement parameters are listed in Table 3. The structure of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ will now be explained in detail starting with the In–O and Ga–O networks.

Both metal atoms are coordinated octahedrally by oxygen atoms. Due to the symmetry of the space group, indium forms edge-sharing octahedra in dinuclear units caused by an inversion axis, and gallium assembles dense units of four edge-sharing octahedra induced by the $\bar{4}$ axis. The whole unit cell contains four isolated tetranuclear Ga–O units and eight isolated dinuclear In–O units. Figure 3 shows both octahedral units and their arrangement in the unit cell of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$. All metal–oxygen distances are in good accordance with values reported in the literature (Ga–O = 1.928(2)–2.126(2) Å, Ø = 2.00 Å; In–O = 2.121(2)–2.219(2) Å, Ø = 2.17 Å) [1, 7, 9, 22], while the axial angles with average values of 168.6° for O–Ga–O and 170.3° for O–In–O are a bit smaller than the expected one of 180°. A complete list of distances and angles is given in Tables 4 and 5.

The complex network of exclusively corner-sharing BO_4 tetrahedra interconnects the various isolated metal–oxygen units. In doing so, the different BO_4 tetrahedra form *dreier* and *vierer* rings [23]. B5O_4 is the only tetrahedron that does not contribute to a ring system but connects to the proton H8 *via* O8 instead (see Fig. 4). The complete structure is shown in Fig. 5. The hydrogen bonding situation is illustrated in Fig. 6, angles and distances of the hydrogen bonds are given in Table 6. All B–O bond lengths

Table 5: Interatomic angles (deg) in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ (standard deviations in parentheses).

In1		Ga1	
O6–In1–O2	75.45(6)	O9–Ga1–O9	78.00(6)
O6–In1–O6	81.01(6)	O9–Ga1–O9	80.26(6)
O6–In1–O2	84.74(6)	O9–Ga1–O9	82.83(7)
O6–In1–O4	85.62(6)	O8–Ga1–O9	87.90(6)
O7–In1–O5	87.17(5)	O1–Ga1–O9	90.21(6)
O7–In1–O4	90.04(6)	O8–Ga1–O1	90.44(6)
O6–In1–O7	90.92(5)	O3–Ga1–O9	91.17(6)
O7–In1–O2	90.94(6)	O3–Ga1–O9	92.04(6)
O5–In1–O2	91.50(5)	O1–Ga1–O9	92.91(6)
O5–In1–O4	98.17(5)	O8–Ga1–O9	94.59(6)
O6–In1–O5	99.97(5)	O8–Ga1–O3	96.49(7)
O6–In1–O4	102.20(6)	O3–Ga1–O1	100.19(6)
ØO–In1–O ₉₀	89.8	ØO–Ga1–O ₉₀	89.8
O6–In1–O7	164.69(6)	O1–Ga1–O9	166.98(6)
O2–In1–O4	170.32(5)	O3–Ga1–O9	168.64(6)
O6–In1–O5	175.76(6)	O8–Ga1–O9	170.15(6)
ØO–In1–O ₁₈₀	170.3	ØO–Ga1–O ₁₈₀	168.6
B1		B4	
O7–B1–O3	106.5(2)	O4–B4–O4	108.47(6) 3 ×
O3–B1–O1	107.9(2)	O4–B4–O4	108.48(6)
O7–B1–O1	109.0(2)	O4–B4–O4	111.5(2) 2 ×
O6–B1–O1	109.6(2)	ØO–B4–O	109.5
O6–B1–O3	110.3(2)		
O6–B1–O7	113.4(2)	B5	
ØO–B1–O	109.4	O8–B5–O7	105.4(2)
B2		O5–B5–O9	107.4(2)
O2–B2–O1	106.99(8) 2 ×	O8–B5–O9	109.7(2)
O2–B2–O1	107.61(8) 2 ×	O8–B5–O5	110.6(2)
O2–B2–O2	112.4(2)	O7–B5–O9	111.4(2)
O1–B2–O1	115.4(2)	O5–B5–O7	112.4(2)
ØO–B2–O	109.5	ØO–B5–O	109.5
B3			
O5–B3–O4	107.5(2)		
O5–B3–O3	107.9(2)		
O2–B3–O3	108.5(2)		
O3–B3–O4	109.5(2)		
O2–B3–O4	111.5(2)		
O2–B3–O5	111.8(2)		
ØO–B3–O	109.5		

are within the range of 1.418(3)–1.556(3) Å (average 1.49 Å) and fit to reported distances in tetrahedral borate groups [24]. The average O–B–O angles of 109.4° (for B1) and 109.5° (for B2–5) indicate perfectly shaped polyhedra.

To evaluate the charge distribution, we performed bond-length/bond-strength calculations (see Table 7) [25, 26]. Solely O9 shows an unusually high charge which can be attributed to the number of bonding partners. While all other oxygen atoms in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ coordinate

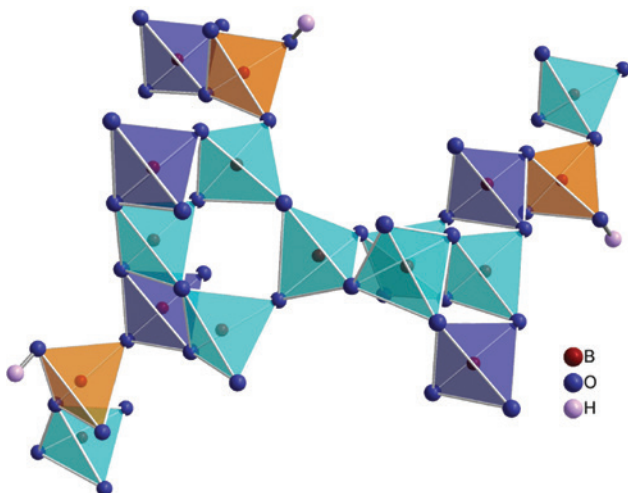


Fig. 4: Visualization of the network of corner-sharing B-O tetrahedra in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$. Tetrahedra centered by the boron atoms B2, B3 and B4 build up *vierer* rings (turquoise) that are further connected to *dreier* rings via B1O_4 tetrahedra (blue). The ring-systems are interlinked by the B5O_4 tetrahedra containing the hydroxyl group (orange).

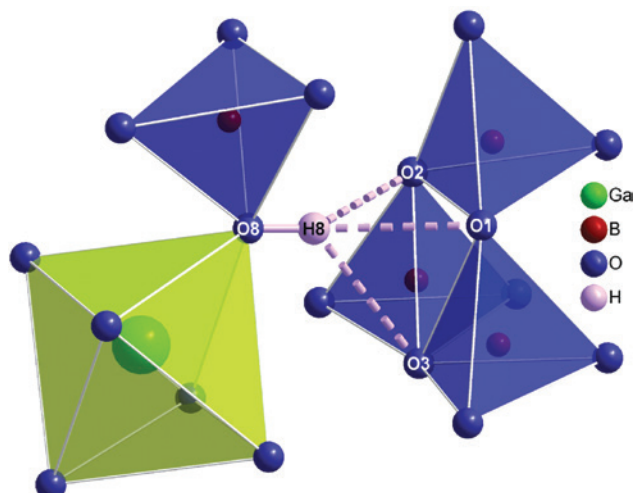


Fig. 6: Hydrogen bonds in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$.

Table 6: Hydrogen bonds (\AA , deg) in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ (standard deviations in parentheses).

	D–H	H...A	d(D...A)	D–H–A
O8–H8...O1	0.83(2)	2.08(4)	2.847(2)	154(7)
O8–H8...O2	0.83(2)	2.22(6)	2.872(2)	136(7)
O8–H8...O3	0.83(2)	2.42(7)	3.018(2)	130(7)

Table 7: Charge distribution in $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$, calculated with the bond-length/bond-strength (Σ) concept.

	In1	Ga1	B1	B2	B3	B4	B5	O1
Σ	2.94	2.92	2.93	2.94	3.01	2.85	2.94	–1.86
	O2	O3	O4	O5	O6	O7	O8	O9
Σ	–2.00	–2.02	–1.83	–2.00	–1.97	–2.00	–2.16	–2.61

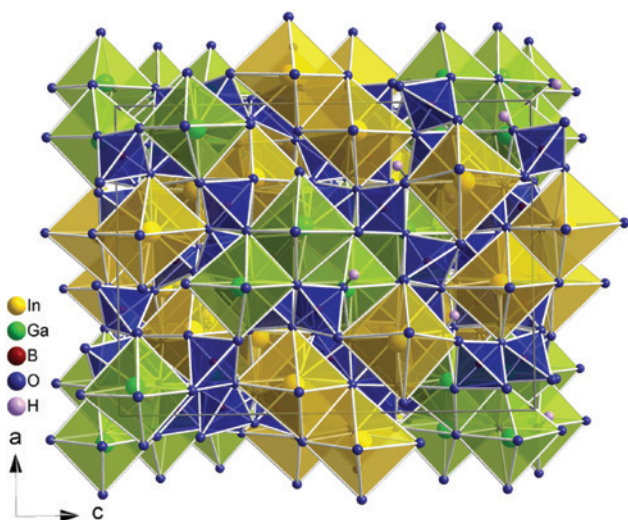


Fig. 5: Complete unit cell of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$.

three other atoms, O9 forms quite long but nonetheless definite bonds to three Ga atoms and one B atom.

4 Conclusions

A high-pressure/high-temperature experiment in a multianvil press led to the formation of the first mixed cation triel borate in which indium and gallium occupy

crystallographically different positions. Although the bulk reaction product was not phase pure, the structure of $\text{Ga}_4\text{In}_4\text{B}_{15}\text{O}_{33}(\text{OH})_3$ could be determined reliably *via* a single-crystal structure determination. This new hydroxylated high-pressure borate is built up of a complex, dense BO_4 tetrahedra network. Indium and gallium form di- or tetranuclear units of edge-sharing octahedra, respectively. This finding complements a series of current publications in the aspiring research field of triel borates.

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