Daniela Vitzthum, Daniel S. Wimmer, Ingo Widmann and Hubert Huppertz*

$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ – two additional triel borates with the structure type $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$)

<https://doi.org/10.1515/znb-2020-0075>

Received May 12, 2020; accepted May 18, 2020; published online July 6, 2020

Abstract: The isotypic triel borates $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ were synthesized in a Walker-type multianvil apparatus under high-pressure/high-temperature conditions of 12.0 GPa/1400 °C and 12.3 GPa/1200 °C, respectively. The crystal structures of both compounds, determined by single-crystal X-ray diffraction, constitute new representatives of the structure type $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) crystallizing in the space group $I4_1/acd$. The presence of the hydroxyl groups was confirmed via single-crystal IR spectroscopy.

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

1 Introduction

In the last decade, our research group focused on high-pressure gallium and indium borates represented by 11 different compounds in this field since 2015. Recently, we reported on the successful synthesis of $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) [1, 2], a structure type incorporating either gallium or indium as metal cations. This was an intriguing finding, given that until then only the well-known calcite-type ortho-borates $M\text{BO}_3$ ($M = \text{Al}, \text{Ga}, \text{In}, \text{Tl}$) [3, 4] were known to form isotypic compounds in this system. Based on this success, we tried if the even smaller Al^{3+} ion could also function as metal cation in the structure type $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) and succeeded in synthesizing the isotypic compound $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$. Obviously, the structure of $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) is quite flexible concerning the incorporation of different metal cations. In

subsequent experiments, we were able to additionally synthesize a mixed-cation variation with the formula $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ which represents the second known borate hosting indium and gallium on different crystallographic positions besides the recently published $\text{Ga}_4\text{InB}_{15}\text{O}_{33}(\text{OH})_3$ [5]. Actually, the structural motif we found in $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) had previously been observed in different variations in other compounds like e. g. $\text{Ti}_5\text{B}_{12}\text{O}_{26}$ [6] and $\text{CaMg}_2\text{P}_6\text{O}_3\text{N}_{10}$ [7]. In contrast to $\text{Ti}_5\text{B}_{12}\text{O}_{26}$, where the charge of the missing hydrogen atom is simply compensated by titanium being partially oxidized to 4+, $\text{CaMg}_2\text{P}_6\text{O}_3\text{N}_{10}$ bears no resemblance regarding the formula at first glance. However, the oxonitridophosphate shows obvious structural similarities which have already been discussed in our original publication of $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) [1, 2].

In the following, the syntheses, crystal structures and IR spectrometric data of the new isotypic compounds $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ are described in detail.

2 Experimental section

2.1 Synthesis

For the synthesis of $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, the mixture of starting material consisted of Al_2O_3 (99.9%, Alfa Aesar) and H_3BO_3 (99.5%, Carl Roth) in a stoichiometric ratio of 5:24, for the synthesis of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$, the nitrates $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ (99.99%, Strem Chemicals) and $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.99% chempUR) were weighed in with H_3BO_3 in a stoichiometric ratio of 4:1:12. Both mixtures were thoroughly ground and encapsulated in platinum foil. The capsules were placed in a crucible made of α -BN (Henze Boron Nitride Products AG) and put into a “14/8 assembly” surrounded by eight tungsten carbide cubes (Hawedia) and placed into a nest formed by six steel wedges. The high-pressure/high-temperature conditions were generated with a Walker-

*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

Daniela Vitzthum, Daniel S. Wimmer and Ingo Widmann: Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 80–82, 6020 Innsbruck, Austria

1 The initial weight was calculated based on the pentahydrate, however the actual water content can deviate as the compound is quite hygroscopic.

type multianvil press (Voggenreiter) and a graphite furnace for resistance heating. A detailed description of the experimental setup can be found in the literature [8–10]. During the synthesis of $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ the maximum pressure of 12.0 GPa was built up in 317 min, and the maximum temperature of 1400 °C was reached in 8 min, held for 7 min and then lowered to 800 °C within an hour. Afterwards, the heating was turned off and the decompression process of ~16 h was started. The platinum capsule was freed from its surroundings and cracked open. The reaction product appeared clean-white revealing colorless single-crystals. The synthesis of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ was carried out with a maximum pressure of 12.3 GPa which was built up within 334 min. The maximum temperature of 1200 °C was achieved within 10 min and held for another 10 min. After a stepwise down regulation to 800 °C in 30 min, the assembly was quenched to room temperature. The decompression to ambient conditions took ~16.5 h. The reaction product appeared gray-white clearly containing byproducts besides the target compound $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$.

2.2 X-ray structure determination

The reaction products were 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 2.0–60.5°. Figure 1 shows a comparison of the experimental powder patterns with calculated patterns derived from single-crystal structure data. All reflections that belong to side phases and therefore do not match the theoretical pattern are marked with asterisks. In the synthesis attempt for $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, the desired phase could be obtained nearly phase pure, however the reaction product of the synthesis aiming at $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ showed prominent reflections of at least one byproduct. Further experiments varying the reaction conditions or the molar ratio of the starting materials did not improve the result which can probably be explained by difficulties in obtaining the exact mass ratio of the hygroscopic gallium and indium nitrates.

Table 1: Single-crystal data and structure refinement of $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$.

Empirical formula	$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$	$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$
Molar mass, g mol ⁻¹	681.63	940.43
Crystal system	tetragonal	
Space group	$I4_1/acd$ (no. 142)	
Single-crystal diffractometer	Bruker D8 Quest Kappa	
Radiation/wavelength λ , pm	$\text{MoK}\alpha/71.07$	
a , Å	10.872(2)	11.1767(6)
c , Å	21.460(4)	21.888(2)
V , Å ³	2536.5(9)	2734.2(3)
Formula units per cell Z	8	8
Calculated density, g cm ⁻³	3.57	4.57
Crystal size, mm ³	$0.050 \times 0.045 \times 0.035$	$0.030 \times 0.030 \times 0.030$
Temperature, K	293(2)	213(2)
Absorption coefficient, mm ⁻¹	0.7	9.6
$F(000)$, e	2672	3536
θ range, deg	3.26–39.16	3.18–39.38
Range in hkl	$\pm 15; \pm 15; \pm 31$	$-19/+18; \pm 19; \pm 39$
Refl. total/independent	24,148/1014	45,785/2046
$R_{\text{int}}/R_{\sigma}$	0.0572/0.0266	0.0454/0.0166
Refl. with $I > 2 \sigma(I)$	868	1873
Data/ref. parameters	1014/103	2046/104
Absorption correction	multiscan	multiscan
Final $R1/wR2$ ($I > 2 \sigma(I)$)	0.0381/0.1021	0.0214/0.0509
Final $R1/wR2$ (all data)	0.0458/0.1069	0.0256/0.0526
Goodness-of-fit on F^2	1.087	1.089
Largest diff. peak/hole, e Å ⁻³	1.59/−0.60	3.55/−0.89

Figure 1: Experimental powder patterns of the products of the best syntheses leading to $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ (black) and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ (blue) compared to their theoretical patterns calculated from single-crystal data (gray and light blue, respectively). Asterisks mark the reflections of byproducts.

Table 2: Comparison of the lattice parameters (Å), volumes (Å³), and metal ion radii (3+, six-fold coordination) (Å) [30, 31] of Al₅B₁₂O₂₅(OH), Ga₅B₁₂O₂₅(OH) [1, 2], Ga₄InB₁₂O₂₅(OH), Ti₅B₁₂O₂₆ [6], and In₅B₁₂O₂₅(OH) [1, 2].

Compound	<i>a</i>	<i>c</i>	<i>V</i>	<i>r</i>
Al ₅ B ₁₂ O ₂₅ (OH)	10.872(2)	21.460(4)	2536.5(9)	0.675
Ga ₅ B ₁₂ O ₂₅ (OH)	11.150(5)	21.76(2)	2705(3)	0.760
Ga ₄ InB ₁₂ O ₂₅ (OH)	11.1767(6)	21.888(2)	2734.2(3)	
Ti ₅ B ₁₂ O ₂₆	11.211(2)	22.115(4)	2779.5(8)	0.810
In ₅ B ₁₂ O ₂₅ (OH)	11.639(2)	22.282(5)	3018(2)	0.940

The colorless single crystals of Al₅B₁₂O₂₅(OH) and Ga₄InB₁₂O₂₅(OH) were measured with a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS detector. The intensity data was corrected by a multi-scan absorption correction with SADABS 2014/5 [11]. For the structure solution and parameter refinement, the software tools SHELXS-2013/1 [12, 13] and SHELXL-2013/4 [14] implemented in the program WINGX-2018.1 [15] were used. According to

the systematic reflection conditions, both compounds were solved and refined in the space group *I*4₁/*acd* (no. 142, origin choice 2). To allow an easy comparison of the isotopic compounds, the data sets were standardized with the routine STRUCTURE TIDY [16] as implemented in PLATON [17] (version 170613). In both compounds, the H atom position H5 was fixed with the DFIX command at a distance of 0.83 Å to O5. Due to charge neutrality reasons, H5 can only be occupied by 1/4th. Except the hydrogen atoms, all atoms in the presented structures could be refined anisotropically. Details of the data collection can be found in the synoptical Table 1. In Table 3 and Table 4, the positional and displacement parameters, the Wyckoff positions, and the site occupancy factors are given.

CSD-2002397 (Al₅B₁₂O₂₅(OH)) and CSD-2002398 (Ga₄InB₁₂O₂₅(OH)) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 3: Wyckoff positions, atomic coordinates, isotropic *U*_{iso} or equivalent isotropic displacement parameters *U*_{eq} (Å²) and site occupancy factors (s.o.f.) for Al₅B₁₂O₂₅(OH) and Ga₄InB₁₂O₂₅(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>	<i>U</i> _{eq} (<i>U</i> _{iso} for H5)	s.o.f.
Al ₅ B ₁₂ O ₂₅ (OH)						
Al1	32 <i>g</i>	0.34388(4)	0.07391(4)	0.04473(2)	0.0040(2)	1
Al2	8 <i>b</i>	0	1/4	1/8	0.0076(2)	1
B1	32 <i>g</i>	0.0761(2)	0.3362(2)	0.25099(8)	0.0028(3)	1
B2	32 <i>g</i>	0.2527(2)	0.3213(2)	0.08254(7)	0.0030(3)	1
B3	32 <i>g</i>	0.2598(2)	0.1573(2)	0.16829(7)	0.0045(3)	1
O1	32 <i>g</i>	0.0004(2)	0.08635(9)	0.29233(4)	0.0026(3)	1
O2	32 <i>g</i>	0.0119(2)	0.0654(2)	0.12463(4)	0.0027(3)	1
O3	32 <i>g</i>	0.1625(2)	0.3930(2)	0.04453(6)	0.0032(3)	1
O4	32 <i>g</i>	0.1625(2)	0.2655(2)	0.29132(5)	0.0026(3)	1
O5	32 <i>g</i>	0.1701(2)	0.0666(2)	0.04187(6)	0.0035(3)	1
O6	32 <i>g</i>	0.3430(2)	0.0782(2)	0.13080(6)	0.0027(3)	1
O7	16 <i>d</i>	0	1/4	0.03496(8)	0.0022(3)	1
H5	32 <i>g</i>	0.17(2)	0.133(8)	0.062(6)	0.08(6)	0.25
Ga ₄ InB ₁₂ O ₂₅ (OH)						
In1	8 <i>b</i>	0	1/4	1/8	0.00561(4)	1
Ga1	32 <i>g</i>	0.34740(2)	0.06874(2)	0.04495(2)	0.00422(4)	1
B1	32 <i>g</i>	0.0727(2)	0.3382(2)	0.25223(6)	0.0033(2)	1
B2	32 <i>g</i>	0.2546(2)	0.3155(2)	0.08221(6)	0.0029(2)	1
B3	32 <i>g</i>	0.2657(2)	0.1538(2)	0.16823(6)	0.0043(2)	1
O1	32 <i>g</i>	0.00110(8)	0.08635(8)	0.29240(4)	0.0030(2)	1
O2	32 <i>g</i>	0.01711(8)	0.05319(8)	0.12414(4)	0.0033(2)	1
O3	32 <i>g</i>	0.16067(8)	0.38208(8)	0.04600(4)	0.0033(2)	1
O4	32 <i>g</i>	0.16100(8)	0.27201(8)	0.29080(4)	0.0032(2)	1
O5	32 <i>g</i>	0.17028(9)	0.06217(8)	0.04311(5)	0.0038(2)	1
O6	32 <i>g</i>	0.34650(8)	0.07511(8)	0.13262(4)	0.0031(2)	1
O7	16 <i>d</i>	0	1/4	0.02915(6)	0.0031(2)	1
H5	32 <i>g</i>	0.16(2)	0.135(3)	0.050(6)	0.03(3)	0.25

2.3 IR spectroscopy

The transmission FT-IR spectra of single crystals of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ and $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ were 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, liquid nitrogen cooled (Mercury Cadmium Telluride (MCT) detector and a Hyperion 3000 microscope (Bruker). 180 scans of the samples were acquired using a Globar (silicon carbide) rod as mid-IR source and a 15× IR objective as focus. During the measurements, the samples were positioned on a BaF_2 window. Atmospheric influences were corrected with the software OPUS 6.5.

3 Results and discussion

3.1 Crystal structure

The title compounds crystallize in the tetragonal space group $I4_1/acd$ (no. 142, origin choice 2) with eight formula units ($Z = 8$). $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ show exactly the same site symmetry and are clearly isotypic to

each other. In the two other known triel borates with the formula $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) [1, 2], the second metal cation position showed large displacement ellipsoids leading to a preferred refinement of a disordered position slightly shifted from the octahedral center. Both $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ did not show this kind of disorder and the second metal cation could be refined in the octahedral center. Despite this discrepancy $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$, $\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, and $\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ can be regarded as isotypic to each other. Table 2 gives a comparison of the lattice parameters of these four compounds and the related borate $\text{Ti}_5\text{B}_{12}\text{O}_{26}$. As expected, $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ features the smallest unit cell and the lattice parameters of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ lie between those of $\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$. The augmentation of the unit cells with increasing ionic radii of the metal cations is illustrated in Figure 2. The $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($\text{Al}, \text{Ga}, \text{In}, \text{Ga}/\text{In}$) structure type features two crystallographically different metal cation positions in octahedral coordination, three different boron positions forming a complex network of corner-sharing BO_4 tetrahedra, and one disordered proton site. Figure 3 gives an overview of the arrangement of the metal cation octahedra. Both polyhedra shown in green and orange represent the dinuclear $M_2\text{O}_{10}$ units in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$

Table 4: Anisotropic displacement parameters U_{ij} ($\text{\AA}^2$) of $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$						
Al1	0.0047(3)	0.0041(3)	0.0033(3)	−0.0009(2)	−0.0005(2)	−0.0003(2)
Al2	0.0098(3)	0.0098(3)	0.0034(4)	−0.0058(4)	0	0
B1	0.0030(6)	0.0031(6)	0.0022(7)	−0.0013(5)	−0.0005(5)	0.0003(5)
B2	0.0035(7)	0.0029(7)	0.0027(7)	0.0007(5)	0.0000(5)	0.0003(5)
B3	0.0047(7)	0.0054(7)	0.0032(7)	0.0016(5)	−0.0013(5)	−0.0017(5)
O1	0.0026(5)	0.0020(5)	0.0031(5)	−0.0004(3)	0.0006(4)	0.0009(3)
O2	0.0029(5)	0.0018(5)	0.0033(5)	0.0003(4)	0.0013(4)	−0.0002(3)
O3	0.0024(5)	0.0036(5)	0.0035(5)	−0.0003(4)	−0.0019(4)	−0.0007(4)
O4	0.0019(5)	0.0029(5)	0.0029(5)	−0.0001(4)	−0.0013(3)	−0.0005(4)
O5	0.0034(5)	0.0037(5)	0.0033(5)	−0.0012(4)	0.0002(4)	0.0002(4)
O6	0.0019(5)	0.0031(5)	0.0030(5)	0.0004(4)	−0.0005(4)	0.0000(3)
O7	0.0027(6)	0.0025(6)	0.0015(6)	−0.0016(5)	0	0
$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$						
In1	0.00700(5)	0.00700(5)	0.00284(7)	−0.00337(5)	0	0
Ga1	0.00570(6)	0.00377(6)	0.00321(6)	−0.00113(4)	−0.00100(4)	−0.00005(4)
B1	0.0031(4)	0.0033(4)	0.0033(5)	−0.0004(3)	0.0002(4)	−0.0003(4)
B2	0.0025(4)	0.0027(4)	0.0035(5)	−0.0002(3)	0.0000(4)	0.0003(4)
B3	0.0035(5)	0.0049(5)	0.0047(5)	0.0007(4)	−0.0013(4)	−0.0007(4)
O1	0.0025(3)	0.0032(3)	0.0032(3)	−0.0002(2)	−0.0001(2)	0.0010(2)
O2	0.0033(3)	0.0025(3)	0.0042(3)	0.0006(2)	0.0016(3)	0.0004(2)
O3	0.0036(3)	0.0027(3)	0.0036(3)	0.0003(2)	−0.0018(2)	−0.0004(3)
O4	0.0029(3)	0.0033(3)	0.0036(3)	−0.0001(2)	−0.0009(3)	−0.0008(2)
O5	0.0034(3)	0.0038(3)	0.0043(3)	−0.0010(2)	−0.0003(3)	0.0007(3)
O6	0.0032(3)	0.0029(3)	0.0032(3)	0.0012(2)	0.0000(3)	0.0002(2)
O7	0.0031(4)	0.0035(5)	0.0027(5)	−0.0015(3)	0	0

Figure 2: Illustration of the coherence of the ionic radii and the lattice parameters of $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{Ti}_5\text{B}_{12}\text{O}_{26}$ [6], and $\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$.

centered by Ga or Al. Along the crystallographic c axis, every second unit is dislocated along b or rotated by 90° pertaining to the corresponding unit. The In or Al₂ atoms form 12 isolated MO_6 octahedra per unit cell, which fill the holes in the structure along the $\bar{4}$ inversion axis (depicted in yellow). The Al₁–O and Ga–O distances of the edge-sharing double-octahedra are with average values of 1.89 and 1.99 Å in good accordance with those reported in the literature [18–23]. However, presumably because of the shared edge, the octahedra are slightly tilted with average angles of 175.2° and 174.0° instead of 180° . The isolated InO_6 octahedra show interatomic distances ($\bar{\theta} = 2.17$ Å) and angles ($\bar{\theta} = 90.0^\circ$ and 179.3°) as expected [4, 24, 25]. However, the Al₂–O bond lengths ranging from 1.932(2) to 2.011(2) Å with an average value of 1.98 Å are extraordinarily long. This peculiarity that the metal cations on the Wyckoff position $8b$ exhibit

exceptionally long distances to the surrounding oxygen atoms has also been observed in $\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, and $\text{Ti}_5\text{B}_{12}\text{O}_{26}$. A detailed list of bond lengths and angles is given in Table 5 and Table 6. The two different metal centered octahedra are linked via hydrogen bonds. Figure 4 shows that each isolated InO_6 or Al_2O_6 octahedron is surrounded by four Ga_2O_{10} or Al_2O_{10} entities and connected through a hydrogen bond between $\text{O5-H5}\cdots\text{O2}$. Although the illustration shows four possible hydrogen bonds, only one is present at the same time since the hydrogen atom H5 is occupied by 1/4. It is likely that O5 also forms significantly weaker hydrogen bonds to *e. g.* O1 and O7, however the refinement yielded plausible distances and angles only for $\text{O5-H5}\cdots\text{O2}$ (see Table 7) which is hardly surprising considering the 1/4 charge at this position. The complex B–O network consisting of 96 corner-sharing BO_4 tetrahedra is built up by $\text{B}_{12}\text{O}_{30}$ clusters. Four B_3O_9 units (= BO_4 dreier rings [26]) are assembled in a $\text{B}_{12}\text{O}_{30}$ cluster as shown in Figure 5. This figure displays the cluster arrangement throughout the unit cell which is – even with the used color code – confusingly complex. However, the linkage pattern becomes clear, if the $\text{B}_{12}\text{O}_{30}$ units are depicted as B_{12} clusters in a stick model (see Figure 6). Each cluster is tetrahedrally connected to four more clusters to yield the complete B–O network in $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{In, Ga, Al, Ga/In}$). Figure 6 exemplarily shows the linking mode of the clusters and their arrangement in relation to the isolated octahedra which fill the holes shaped by this cluster network. The B–O bond lengths in the BO_4 tetrahedra vary between 1.459 and 1.513 Å in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and 1.450–1.511 Å in $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ with mean values of 1.48 Å for both. In the literature, a potential variation of the mean B–O distances in BO_4 tetrahedra between 1.444 and 1.534 Å is described [27]. Even the individual distances of our title

Figure 3: Visualization of the arrangement of the metal-centered octahedra in $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{In, Ga, Al, Ga/In}$). For clarity, the crystallographically identical $M_2\text{O}_{10}$ entities are depicted in green and orange. The yellow polyhedra correspond to the isolated MO_6 octahedra.

Table 5: Interatomic distances (Å) in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ (standard deviations in parentheses).

$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$				$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$			
$M1-$	O6	1.848(2)	1.920(2)	$B1-$	O7	1.469(2)	1.450(2)
	O5	1.866(2)	1.939(2)		O3	1.474(2)	1.487(2)
	O4	1.873(2)	1.967(2)		O1	1.479(2)	1.471(2)
	O5	1.893(2)	1.981(2)		O4	1.492(2)	1.495(2)
	O1	1.913(2)	2.0182(9)	$\emptyset B1-O$		1.48	1.48
	O3	1.968(2)	2.0883(9)				
$\emptyset M1-O$		1.89	1.99	$B2-$	O6	1.470(2)	1.477(2)
					O1	1.476(2)	1.466(2)
$M2-$	O7	1.932(2) 2×	2.098(2) 2×		O2	1.487(2)	1.477(2)
	O2	2.011(2) 4×	2.2081(9) 4×		O3	1.496(2)	1.511(2)
$\emptyset M2-O$		1.98	2.17	$\emptyset B2-O$		1.48	1.48
				$B3-$	O5	1.459(2)	1.469(2)
					O4	1.473(2)	1.471(2)
					O6	1.485(2)	1.483(2)
					O2	1.513(2)	1.494(2)
				$\emptyset B3-O$		1.48	1.48

compounds lie within this range and all tetrahedra show perfect angles of 109.5°. The bond valence sums (BVS) for $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ were calculated with the bond-length/bond-strength concept [28]. The deviation

between the BVS and the oxidation state is in the range of 5% for all cations except for Al2, where the calculation revealed an unexpected low BVS value of 2.45 (see Table 8). Since we could not find a suitable explanation, we compared the

Table 6: Interatomic angles (deg) in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ (standard deviations in parentheses).

$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$		$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$		$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$		$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$	
$O5-M1-O5$	83.39(6)	$82.91(4)$	$O2-M2-O2$	82.64(7) 2×	$80.07(5) 2×$	$O7-M2-O2$	89.77(3) 4×
$O5-M1-O3$	85.56(5)	$85.42(4)$	$O7-M2-O2$	90.23(3) 4×	$89.51(2) 4×$	$O2-M2-O2$	97.36(7) 2×
$O5-M1-O3$	87.26(5)	$88.20(4)$	$O2-M2-O2$	90.0	90.0	$\emptyset O-M2-O_{90}$	
$O4-M1-O1$	87.88(5)	$86.82(4)$	$\emptyset O-M2-O_{90}$				
$O5-M1-O1$	89.92(5)	$88.58(4)$					
$O6-M1-O1$	90.08(5)	$89.44(4)$	$O2-M2-O2$	179.54(5) 2×	$179.02(5) 2×$	$O7-M2-O7$	180.0
$O5-M1-O1$	90.72(5)	$90.24(4)$	$O7-M2-O7$	179.7	179.3	$\emptyset O-M2-O_{180}$	
$O6-M1-O3$	91.57(5)	$91.48(4)$	$\emptyset O-M2-O_{180}$				
$O6-M1-O5$	91.62(5)	$90.94(4)$					
$O6-M1-O4$	92.42(5)	$92.70(4)$	$O6-B2-O1$	107.7(2)	$108.4(2)$	$O6-B2-O3$	109.1(2)
$O5-M1-O4$	92.59(5)	$93.42(4)$	$O6-B2-O3$	109.1(2)	$108.5(2)$	$O2-B2-O3$	109.1(2)
$O4-M1-O3$	96.51(5)	$99.11(4)$	$O2-B2-O3$	109.4(2)	$108.2(2)$	$O6-B2-O2$	110.3(2)
$\emptyset O-M1-O_{90}$	90.0	89.9	$O6-B2-O2$	110.3(2)	$109.8(2)$	$O1-B2-O2$	111.1(2)
$O6-M1-O5$	174.95(6)	$173.85(4)$	$O1-B2-O2$	111.1(2)	$111.8(2)$	$\emptyset O-B2-O$	109.5
$O1-M1-O3$	175.24(5)	$173.94(4)$	$\emptyset O-B2-O$				
$O4-M1-O5$	175.40(5)	$174.11(4)$					
$\emptyset O-M1-O_{180}$	175.2	174.0	$O4-B3-O6$	107.5(2)	$108.4(2)$	$O5-B3-O4$	108.1(2)
$O7-B1-O3$	106.8(2)	$106.5(2)$	$O5-B3-O4$	109.3(2)	$109.2(2)$	$O5-B3-O6$	109.6(2)
$O1-B1-O4$	107.4(2)	$108.4(2)$	$O5-B3-O6$	109.6(2)	$109.8(2)$	$O4-B3-O2$	109.7(2)
$O7-B1-O4$	109.3(2)	$107.50(9)$	$O4-B3-O2$	112.6(2)	$112.7(2)$	$\emptyset O-B3-O$	109.5
$O3-B1-O1$	110.8(2)	$111.3(2)$	$\emptyset O-B3-O$				
$O7-B1-O1$	111.2(2)	$111.0(2)$					
$O3-B1-O4$	111.3(2)	$112.1(2)$					
$\emptyset O-B1-O$	109.5	109.5

Figure 4: Visualization of the hydrogen bonds in $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ (left) and $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ (right) in different orientations of the octahedral units. Only one of the four depicted hydrogen bonds is present at a time due to a site occupancy factor of 0.25 for H5.

Table 7: Hydrogen bonds (Å, deg) in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ (standard deviations in parentheses).

	$d(\text{D} \cdots \text{H})$	$d(\text{H} \cdots \text{A})$	$d(\text{D} \cdots \text{A})$	$\angle(\text{D} \cdots \text{H} \cdots \text{A})$
$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$				
$\text{O5} \cdots \text{H5} \cdots \text{O2}$	0.84(2)	1.78(5)	2.591(2)	161(15)
$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$				
$\text{O5} \cdots \text{H5} \cdots \text{O2}$	0.83(2)	2.0(2)	2.648(2)	130(11)

results with the BVS of the atoms on the same crystallographic position in $\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ti}_5\text{B}_{12}\text{O}_{26}$ and observed with values of 2.37 for Ga2, 2.14 for In2, and 2.43 for Ti2 the same abnormality. It seems that a

Figure 5: Formation of $\text{B}_{12}\text{O}_{30}$ clusters (upper right) by tetrahedrally connecting four B_3O_9 dreier rings (upper left) and the cluster arrangement in the unit cell of $\text{M}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{In}, \text{Ga}, \text{Al}, \text{Ga}/\text{In}$) (bottom). The color code is for illustrative purposes only, all clusters are equivalent.

low BVS for the cations building up isolated octahedra is characteristic for this structure type with the only exception of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$, in which this position is taken by a different element (in that case indium) than the other cation position forming octahedral double units. In a second coordination sphere, Al2 and In are surrounded by eight additional oxygen atoms forming a slightly distorted cubic coordination (Figure 7). If we take into account their

Figure 6: Simplified visualization of the connectivity pattern of $\text{B}_{12}\text{O}_{30}$ clusters in $\text{M}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{In}, \text{Ga}, \text{Al}, \text{In}/\text{Ga}$). Each cluster (gray) is tetrahedrally connected to four more clusters (green bonds). The red bonds mark dreier rings belonging to adjacent clusters. The yellow octahedron represents the isolated metal-centered octahedra in $\text{M}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{In}, \text{Ga}, \text{Al}, \text{Ga}/\text{In}$) filling the holes shaped by $\text{B}_{12}\text{O}_{30}$ clusters.

Table 8: Comparison of the charge distribution in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$, $\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, $\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$, and $\text{Ti}_5\text{B}_{12}\text{O}_{26}$ [6], calculated with the bond-length/bond-strength concept.

$\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$		$\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$		$\text{Ga}_5\text{B}_{12}\text{O}_{25}(\text{OH})$		$\text{In}_5\text{B}_{12}\text{O}_{25}(\text{OH})$		$\text{Ti}_5\text{B}_{12}\text{O}_{26}$ [6]	
Al1	3.13	Ga	3.04	Ga1	3.14	In1	3.08	Ti1	3.31
Al2	2.45	In	2.93	Ga2	2.37	In2	2.14	Ti2	2.43
B1	2.99	B1	3.02	B1	2.94	B1	2.98	B1	3.00
B2	2.96	B2	2.96	B2	2.93	B2	2.96	B2	2.97
B3	2.96	B3	2.99	B3	3.02	B3	3.02	B3	2.93
O1	−1.99	O1	−2.00	O1	−1.99	O1	−1.96	O1	−2.03
O2	−1.79	O2	−1.90	O2	−1.87	O2	−1.92	O2	−2.06
O3	−1.90	O3	−1.80	O3	−1.88	O3	−1.86	O3	−2.10
O4	−2.03	O4	−2.01	O4*	−1.87	O4	−1.93	O4	−1.88
O5*	−1.87	O5*	−1.84	O5	−2.09	O5	−2.18	O5	−1.85
O6	−2.09	O6	−2.09	O6	−1.96	O6	−1.96	O6	−2.04
O7	−2.00	O7	−2.20	O7	−1.98	O7	−2.01	O7	−1.80
H**	0.91	H**	0.85	H**	0.93				

* This oxygen atom is the donor atom of the hydrogen bond. The bond valence sum was calculated without the consideration of the hydrogen atom because it would get disproportionately high if calculated with a full contribution of the proton as it only has a site occupancy factor of 0.25.

** To calculate the valence sum of the hydrogen atom, a distance of 0.97 Å to the donor oxygen atom was assumed and on the basis of that the distance to the acceptor atom(s) was determined via a second refinement process.

contribution to the BVS, the values increase to 2.63 for Al2 and 3.28 for In. Regarding the BVS of the oxygen atoms in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$, most of them show only a slight deviation from the oxidation state of −2. Clearly, the BVS for the oxygen atoms functioning as donors in the hydrogen bonds are too low as we calculated them without the contribution of the hydrogen atom (see note in Table 8). Furthermore, O2 in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ as well as O3 and O7 in $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ show a deviation of ~10% from the −2 oxidation state. The value of O2 can be improved from −1.79 to −1.85 when considering the contribution of Al1 as an additional bonding partner.

4000 cm^{-1} . In the broad band in the range 600–1400 cm^{-1} many different vibrations of M–O and B–O bonds overlap. The position of the O–H stretching vibration depends on the strength of the hydrogen bond. Hammer et al. classify $R_{\text{O} \cdots \text{O}}$ distances between 2.5 and 2.7 Å as strong hydrogen bonds which result in IR bands between 1600 and 3200 cm^{-1} [29]. Apparently, this is the case for the hydrogen bonds in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($R_{\text{O5} \cdots \text{O2}} = 2.59$ Å) and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ ($R_{\text{O5} \cdots \text{O2}} = 2.65$ Å). Besides this strong hydrogen bond in both structures, H5 presumably is also engaged in other hydrogen bonds to e. g. O1 and O7. While those $R_{\text{O} \cdots \text{O}}$ distances are only slightly longer in $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($R_{\text{O5} \cdots \text{O1}} = 2.69$ Å and

3.2 IR spectroscopy

Figure 8 displays the single-crystal IR spectra of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ and $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ in the spectral region of 600–

Figure 7: Visualization of the distorted cubic second coordination sphere of the metal cations on the Wyckoff position 8b. **Figure 8:** Single-crystal IR spectra of $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ and $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ in the range of 600–4000 cm^{-1} .

$R_{O5...O7} = 2.72 \text{ \AA}$) and therefore in the crossover between strong and weak hydrogen bonds, they should clearly be classified as weak in $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ ($R_{O5...O1} = 2.80 \text{ \AA}$ and $R_{O5...O7} = 2.85 \text{ \AA}$). The strong band for $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ near 3500 cm^{-1} and the jump near 3200 cm^{-1} thus indicate both poor hydrogen bonding (non-contacted hydroxyl groups) along with stronger hydrogen bonding. The latter prevails for $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ (Figure 8).

4 Conclusion

The isotopic compounds $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$ were synthesized in high-pressure/high-temperature experiments in a multianvil press. Both structures could be determined from single-crystal data and comprise a complex network of BO_4 tetrahedra with single- and double-octahedral units centered by the metal cations. IR spectroscopic studies confirmed the presence of hydroxyl groups in both borates. With $\text{Al}_5\text{B}_{12}\text{O}_{25}(\text{OH})$ and $\text{Ga}_4\text{InB}_{12}\text{O}_{25}(\text{OH})$, two new representatives of the structure type $M_5\text{B}_{12}\text{O}_{25}(\text{OH})$ ($M = \text{Ga}, \text{In}$) could be discovered. Whether this structure type is also stable with other metal cations remains to be investigated in future experiments.

Acknowledgments: We thank Assoc. Univ. Prof. Dr. Gunter Heymann for the recording of the single-crystal data, Freia Ruegenberg for the IR measurements and Univ. Prof. Dr. Roland Stalder for giving us access to the single-crystal IR spectrometer.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- Vitzthum D., Wurst K., Pann J. M., Brüggeller P., Seibald M., Huppertz H. *Angew. Chem. Int. Ed.* 2018, 57, 11451–11455.
- Vitzthum D., Wurst K., Pann J. M., Brüggeller P., Seibald M., Huppertz H. *Angew. Chem.* 2018, 130, 11622–11626.
- Bither T. A., Young H. S. *J. Solid State Chem.* 1973, 6, 502–508.
- Cox J. R., Keszler D. A. *Acta Crystallogr.* 1994, C50, 1857–1859.
- Vitzthum D., Huppertz H. *Z. Naturforsch.* 2019, 74b, 357–363.
- Haberer A., Huppertz H. *J. Solid State Chem.* 2009, 182, 484–490.
- Marchuk A., Neudert L., Oeckler O., Schnick W. *Eur. J. Inorg. Chem.* 2014, 2014, 3427–3434.
- Huppertz H. *Z. Kristallogr.* 2004, 219, 330–338.
- Walker D., Carpenter M. A., Hitch C. M. *Am. Mineral.* 1990, 75, 1020–1028.
- Walker D. *Am. Mineral.* 1991, 76, 1092–1100.
- SADABS-2014/5; Bruker AXS Inc.: Madison, Wisconsin, USA, 2014.
- Sheldrick G. M., SHELXS-2013/1; University of Göttingen: Göttingen, Germany, 2013.
- Sheldrick G. M. *Acta Crystallogr.* 2008, A64, 112–122.
- Sheldrick G. M. *Acta Crystallogr.* 2015, C71, 3–8.
- Farrugia L. J. *J. Appl. Crystallogr.* 2012, 45, 849–854.
- Gelato L., Parthé E. *J. Appl. Crystallogr.* 1987, 20, 139–143.
- Spek A. J. *J. Appl. Crystallogr.* 2003, 36, 7–13.
- Ju J., Yang T., Li G., Liao F., Wang Y., You L., Lin J. *Chem. Eur. J.* 2004, 10, 3901–3906.
- Vegas A., Cano F., García-Blanco S. *Acta Crystallogr.* 1977, B33, 3607–3609.
- Fischer R. X., Kahlenberg V., Voll D., MacKenzie K. J., Smith M. E., Schnetger B., Brumsack H. J., Schneider H. *Am. Mineral.* 2008, 93, 918–927.
- Cong R., Yang T., Li K., Li H., You L., Liao F., Wang Y., Lin J. *Acta Crystallogr.* 2010, B66, 141–150.
- Vitzthum D., Schauperl M., Strabler C. M., Brüggeller P., Liedl K. R., Griesser U. J., Huppertz H. *Inorg. Chem.* 2016, 55, 676–681.
- Vitzthum D., Hering S. A., Perfler L., Huppertz H. *Z. Naturforsch.* 2015, 70b, 207–214.
- Vitzthum D., Bayarjargal L., Winkler B., Huppertz H. *Inorg. Chem.* 2018, 57, 5554–5559.
- Vitzthum D., Wurst K., Prock J., Brüggeller P., Huppertz H. *Inorg. Chem.* 2016, 55, 11473–11478.
- Liebau F. *Structural Chemistry of Silicates*; Springer-Verlag: Berlin, 1985.
- Zobetz E. *Z. Kristallogr.* 1990, 191, 45–57.
- Brown I. D., Altermatt D. *Acta Crystallogr.* 1985, B41, 244–247.
- Hammer V. M., Libowitzky E., Rossman G. R. *Am. Mineral.* 1998, 83, 569–576.
- Shannon R. T. *Acta Crystallogr.* 1976, A32, 751–767.
- Shannon R. T., Prewitt C. T. *Acta Crystallogr.* 1969, B25, 925–946.