Ingo Widmann, Klaus Wurst, Stefan Schwarzmüller and Hubert Huppertz*

High-pressure synthesis and crystal structure of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)

https://doi.org/10.1515/znb-2025-0005
Received January 20, 2025; accepted February 14, 2025;
published online April 30, 2025

Abstract: Tetragonal $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) was synthesized in a Walker-type multianvil apparatus under high-pressure/high-temperature conditions of 12.4 GPa/1,280 °C. The compound crystallizes in the space group $I4_1/acd$ (no. 142) with lattice parameters of a = 11.0884(6) and c = 21.730(2) Å. The crystal structure has been determined by single-crystal X-ray diffraction and revealed an occupation with Na^+ of about 88 % of the cuboctahedral cavity formed by condensed [BO_4] tetrahedra in the related homeotypic structure of $Ga_5B_{12}O_{25}(OH)$. The structure refinement is additionally supported by infrared spectroscopy (IR) and energy-dispersive X-ray (EDX) investigations.

Keywords: high-pressure synthesis; gallium borate; interstitial sodium; crystal structure; cuboctahedral site

1 Introduction

Black $Ti_5B_{12}O_{26}$[1] was discovered by Haberer et al. in 2009 and is the first representative of a structure class characterized by an anionic framework composed of two interpenetrating, three-dimensional networks of corner-sharing [BO_4] tetrahedra crystallizing in the space group $I4_1/acd$.[1] Subsequently, the mixed valent Ti^{3+} and Ti^{4+} cations could be replaced by triel elements with the charge of 3+ (In, Ga), accompanied by the incorporation of hydrogen cations to reach charge neutrality.[2] Surprising photocatalytic properties as well as luminescence of the Eu^{3+} activated phase $In_5B_{12}O_{25}(OH)$, reported by Vitzthum et al., are of particular interest regarding potential future applications.[2] Later on, the great structural diversity of this structure type using Al, Ga, In, V, Cr, Mn, Fe, and Co as metal cations was revealed.[2–5] Moreover, cubic structures with the same sum formula were also found, which show great similarities with the tetragonal structure type $M_5B_{12}O_{25}(OH)$.[6]

The aim of the work described in the present publication was to extend the system $M_5B_{12}O_{25}(OH)$ by structural modifications. First, we started with an optimization of the synthesis conditions and succeeded for $Ga_5B_{12}O_{25}(OH)$[2] with a powder X-ray diffraction pattern without reflections of side-phases, which is representative for the first time in the system $M_5B_{12}O_{25}(OH)$. Subsequently, we sought to modify this phase, $Ga_5B_{12}O_{25}(OH)$,[2] with an occupied cuboctahedral site. To avoid excessive distortion of the cuboctahedral site, we considered using an atom with a small ionic radius such as Na^+. As in all previously synthesized specimens, we used a multianvil press for high-pressure/high-temperature experiments. We used NaCN as Na^+ source, since we assumed from our experience that CN^- does not withstand rather extreme synthesis conditions, so it will not be present in the product.

In the following, we discuss the high-pressure/high-temperature synthesis, the crystal structure, as well as the results of infrared (IR) spectroscopy and energy-dispersive X-ray spectroscopy (EDX) of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12).

2 Experimental section

2.1 Synthesis

The synthesis of the title compound was performed under high-pressure/high-temperature conditions in a multianvil apparatus. A mixture of Ga_2O_3 (99.99 %, Tradium GmbH, Frankfurt am Main, Germany), H_3BO_3 (≥99.8 %, Carl Roth GmbH & Co KG, Karlsruhe, Germany), and NaCN (>98 %, Fluka Chemie GmbH, Buchs, Switzerland) in a molar ratio of 5:24:3 (stoichiometric ratio apart from NaCN, which was used abundantly to improve the incorporation of Na^+ compared to a previous experiment that was performed with less Na^+) was ground in an agate mortar and encapsulated in a platinum foil (0.027 mm, 99.9 %, Chem-PUR, Karlsruhe, Germany). The capsule was placed in a crucible with a lid, both made of α-BN (HeBoSint, P100, Henze Boron Nitride Products AG, Kempten, Germany) and centered in a "14/8" assembly, which was equipped with a graphite furnace (FE 254, Schunk-group GmbH, Vienna, Austria) for resistance heating. The octahedral

***Corresponding author: Hubert Huppertz**, Department of General, Inorganic, and Theoretical Chemistry, University of Innsbruck, Innrain 80–82, 6020 Innsbruck, Austria, E-mail: Hubert.Huppertz@uibk.ac.at. https://orcid.org/0000-0002-2098-6087
Ingo Widmann, Klaus Wurst and Stefan Schwarzmüller, Department of General, Inorganic, and Theoretical Chemistry, University of Innsbruck, Innrain 80–82, 6020 Innsbruck, Austria. https://orcid.org/0009-0009-8252-9891 (I. Widmann). https://orcid.org/0000-0002-8774-9051 (K. Wurst). https://orcid.org/0000-0001-7299-4874 (S. Schwarzmüller)

assembly was arranged in the center of eight beveled tungsten carbide cubes (HA-7% Co, Hawedia, Marklkofen, Germany). The synthesis was performed in a modified Walker-type multianvil device (mavo press LPR 1000-400/50, Max Voggenreiter GmbH, Mainleus, Germany). More detailed information on the experimental setup is available in the literature.[7–9] After compression of the sample to 12.4 GPa, the sample was heated to 1,280 °C within 7 min, kept constant for 5 min, then cooled to 900 °C within 30 min, before the heating was switched off. After decompression, a in most of its parts colorless sample containing crystals of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ with some additional black impurities was isolated.

2.2 X-ray structure determination

The reaction product was analyzed with a STOE Stadi P powder X-ray diffractometer (STOE & Cie GmbH, Darmstadt, Germany) equipped with a Mythen 1 K microstrip detector (Dectris, Baden-Daettwil, Switzerland). The measurement was performed with Ge(111)-monochromatized Mo-$K\alpha_1$ radiation (λ = 0.7093 Å) in transmission geometry across a 2θ range of 2.0–60.5°. Figure 1 shows the experimental powder pattern in comparison to a calculated pattern derived from the single-crystal structure data. While the great majority of reflections could be explained by the title compound, a few minor reflections are caused by an unidentified by-product.

A colorless single-crystal of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) was measured with a Bruker D8 Quest Photon III C14 diffractometer (Bruker Corporation, Billerica, Massachusetts, U.S.).

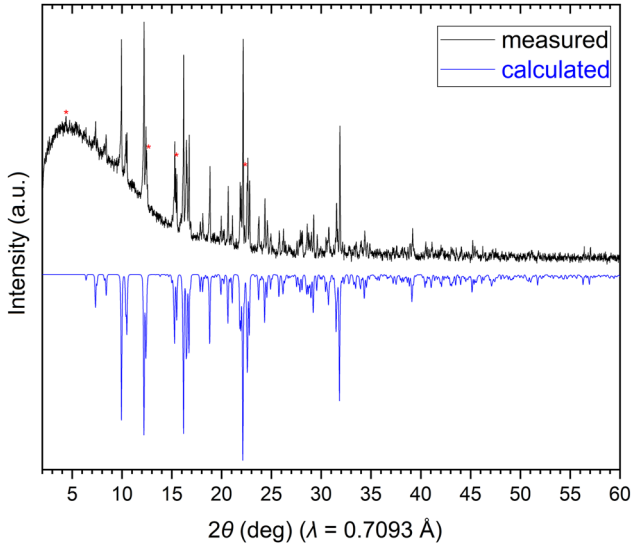

Figure 1: Experimental powder pattern (black) of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ compared to a calculated powder pattern based on single-crystal structure data of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) (colored blue, inverted). The asterisk-marked reflections refer to an unidentified byproduct.

For data collection and processing, the programs Saint (v8.40 B)[10] and Apex4 (v2021.4.0)[11] were used and a multi-scan absorption correction was performed by the program Sadabs (2016/2).[12] For structure solution and parameter refinement, the software tools Shelxt (2018/2)[13] and Shelxl (2018/3)[14] implemented in the program Olex2-1.5[15] were applied. All atoms could be refined anisotropically, except the hydrogen atom, which could not be located.

Details of the data collection are specified in the synoptical Table 1. Tables 2 and 3 show the positional and displacement parameters, the Wyckoff positions, and the site occupancy factors (S.O.F.).

CSD-2376207 contains the supplementary crystallographic data of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) 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.

2.3 Infrared spectroscopy

The transmission FT-IR spectrum of a single-crystal of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) was measured with a Vertex 70

Table 1: Single-crystal data and structure refinement of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12). Standard deviations are given in parentheses and refer to the last decimal place.

Empirical formula	$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)
Molar mass, g mol^{-1}	914.59
Crystal system	Tetragonal
Space group	$I4_1/acd$
Single-crystal diffractometer	Bruker D8 Quest
Radiation/wavelength λ, Å	Mo-$K\alpha$/0.71073
Single-crystal data	
a, Å	11.0884(6)
c, Å	21.730(2)
V, Å^3	2,671.8(4)
Formula units per cell Z	8
Calculated density, g cm^{-3}	4.55
Crystal size, mm^3	0.12 × 0.09 × 0.05
Temperature, K	183(2)
Absorption coefficient, mm^{-1}	10.2
F(000), e	3462
θ range, deg	3.20–41.14
Range in hkl	±20; ±20; ±40
Reflections total/independent	168,453/2,226
R_{int}	0.0553
Reflections with $I \geq 2\,\sigma(I)$	2,192
R_σ	0.0124
Data/ref. parameters	2,226/103
Absorption correction	Multi-scan
Final R_1/wR_2 [$I \geq 2\,\sigma(I)$]	0.0144/0.0309
Final R_1/wR_2 (all data)	0.0147/0.0310
Goodness-of-fit on F^2	1.229
Largest diff. peak/hole, e Å^{-3}	0.58/−0.63

Table 2: Wyckoff positions, atomic coordinates, equivalent isotropic displacement parameters U_{eq} (Å^2) and site occupancy factors (S.O.F.) for $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) in comparison to published data for the homeotypic structure $Ga_5B_{12}O_{25}(OH)$.[2] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses).

Atom	Wyckoff position	x	y	z	U_{eq} (U_{iso} for H3)	S.O.F.
$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) (present study)						
Ga1	32*g*	0.31774(2)	0.09362(2)	0.20586(2)	0.00191(2)	1
Ga2	8*b*	0	1/4	1/8	0.00379(3)	1
B1	32*g*	0.07346(7)	0.16230(7)	0.25065(4)	0.0023(2)	1
B2	32*g*	0.25211(7)	0.18300(7)	0.08247(3)	0.0025(2)	1
B3	32*g*	0.40466(7)	0.00994(7)	0.08122(3)	0.0026(2)	1
O1	32*g*	0.16059(5)	0.23023(5)	0.29120(2)	0.00238(7)	1
O2	32*g*	0.16263(5)	0.11545(5)	0.04513(2)	0.00231(7)	1
O3	32*g*	0.18955(5)	0.26360(5)	0.12638(2)	0.00245(7)	1
O4	32*g*	0.31404(5)	0.08062(5)	0.29302(2)	0.00261(7)	1
O5	32*g*	0.32734(5)	0.09587(5)	0.11782(2)	0.00239(7)	1
O6	32*g*	0.33790(5)	0.25072(5)	0.04312(2)	0.00243(7)	1
O7	16*d*	0	1/4	0.03339(3)	0.0024(2)	1
Na1	8*a*	1/2	1/4	1/8	0.0046(2)	0.876(4)
$Ga_5B_{12}O_{25}(OH)$[2]						
Ga1	32*g*	0.32036(2)	0.09695(2)	0.20509(2)	0.00502(5)	1
Ga2	16*f*	0.01270(4)	0.26270(4)	1/8	0.0094(2)	0.5
B1	32*g*	0.0735(2)	0.1622(2)	0.25051(6)	0.0040(2)	1
B2	32*g*	0.2540(2)	0.1824(2)	0.08195(6)	0.0040(2)	1
B3	32*g*	0.4054(2)	0.0138(2)	0.08154(6)	0.0055(2)	1
O1	32*g*	0.16120(8)	0.22924(8)	0.29014(4)	0.0044(2)	1
O2	32*g*	0.16229(8)	0.11458(8)	0.04561(4)	0.0044(2)	1
O3	32*g*	0.19235(8)	0.26479(8)	0.12568(4)	0.0048(2)	1
O4	32*g*	0.31426(8)	0.08075(8)	0.29334(4)	0.0047(2)	1
O5	32*g*	0.32661(8)	0.09573(8)	0.11742(4)	0.0042(2)	1
O6	32*g*	0.33698(8)	0.25057(8)	0.04185(4)	0.0040(2)	1
O7	16*d*	0	1/4	0.03408(6)	0.0042(2)	1
H3	32*g*	0.38(2)	0.08(2)	0.31(2)	0.2(2)	0.25

Table 3: Anisotropic displacement parameters U_{ij} (Å^2) of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga1	0.00232(3)	0.00193(3)	0.00148(3)	−0.00007(2)	−0.00005(2)	0.00005(2)
Ga2	0.00476(4)	0.00476(4)	0.00186(5)	0.00181(5)	0	0
B1	0.0022(2)	0.0023(2)	0.0024(2)	0.0002(2)	−0.0002(2)	0.0000(2)
B2	0.0029(2)	0.0021(2)	0.0024(2)	0.0001(2)	0.0001(2)	0.0000(2)
B3	0.0024(2)	0.0029(2)	0.0025(2)	0.0001(2)	0.0002(2)	0.0003(2)
O1	0.0027(2)	0.0018(2)	0.0027(2)	−0.0001(2)	−0.0011(2)	0.0003(2)
O2	0.0023(2)	0.0019(2)	0.0027(2)	0.0001(2)	−0.0012(2)	0.0002(2)
O3	0.0023(2)	0.0023(2)	0.0028(2)	−0.0000(2)	−0.0001(2)	−0.0012(2)
O4	0.0035(2)	0.0021(2)	0.0022 (2)	0.0005(2)	0.0003(2)	−0.0003(2)
O5	0.0027(2)	0.0026(2)	0.0019(2)	0.0011(2)	−0.0002(2)	−0.0000(2)
O6	0.0026(2)	0.0017(2)	0.0029(2)	−0.0001(2)	0.0014(2)	−0.0002(2)
O7	0.0029(2)	0.0025(2)	0.0017(2)	0.0008(2)	0	0
Na	0.0047(2)	0.0047(2)	0.0044(3)	0	0	0

FT-IR spectrometer (spectral resolution 4 cm^{-1}, 15 × IR objective as focus), which was equipped with a KBr beam splitter, a liquid nitrogen cooled mercury cadmium telluride detector and attached to a Hyperion 3,000 microscope (Bruker Corporation, Billerica, Massachusetts, U.S.A.). As a mid-infrared source, a Globar (silicon carbide) rod was applied. During the measurement, the sample was placed on a BaF_2 window. 320 scans were recorded in a spectral range of 600–4,000 cm^{-1}. Atmospheric influences were corrected with the software Opus 7.2.[16]

2.4 Energy-dispersive X-ray spectroscopy

The chemical composition of the title compound was further investigated with a field emission gun scanning electron microscope (FEG-SEM) Clara Ultra High Resolution (UHR) from TESCAN equipped with an energy-dispersive X-ray spectroscopy (EDX) detector Ultim Max, 65 mm^2 from OXFORD. Grinded sample material was prepared on a carbon sticker on an aluminum stub. Imaging and EDX measurements were performed in analysis mode at an acceleration voltage of 20 keV and a beam current of 3 nA at a working distance of 9 mm. For EDX, preferably flat and horizontally aligned surfaces of single crystals or crystalline aggregates were selected.

3 Results and discussion

3.1 Crystal structure

$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) crystallizes in the tetragonal space group $I4_1/acd$ (no. 142) with eight formula units (Z = 8) and the lattice parameters a = 11.0884(6), c = 21.730(2) Å, and V = 2,671.8(4) $Å^3$. The structure is homeotypic to $M_5B_{12}O_{25}(OH)$ (M = Al, Cr, Ga, Ga/In, V),[2–4] $In_5B_{12}O_{25}(OH):Eu^{3+}$,[2] $Ti_5B_{12}O_{26}$,[1] $Mn_5MnB_{12}O_{22}(OH)_4$,[4] $Mn_5Mn_{0.83}B_{12}O_{26}$,[4] $Fe_5Fe_{0.14}B_{12}O_{24.3}(OH)_{1.7}$[4] and $V_{1.36}Co_{3.64}Co_{0.53}[B_{12}O_{24}(OH)_2]$.[5] Details of the single-crystal data and structure refinement are given in Table 1, the positional and displacement parameters and site occupancy factors in Table 2 and 3. $Ga_5B_{12}O_{25}(OH)$[2] seemed to be most suited for a comparison, which contains the same elements, apart from the vacant cuboctahedral void and a slightly shifted Ga2, which leads to a different site of Ga2.

$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) has two different sites for Ga in octahedral, one for Na in cuboctahedral and three different sites for B in tetrahedral coordination (see Table 2). Furthermore, there is a hydrogen site required for charge neutrality, but this could not be exactly assigned in the structure refinement and the situation discussed below. As compared in Table 2, all atoms have the same Wyckoff position as in $Ga_5B_{12}O_{25}(OH)$,[2] apart from Na1, which is not present in $Ga_5B_{12}O_{25}(OH)$,[2] hydrogen, which could not be refined in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12), and Ga2, which is directly located on a special site in the title compound and has therefore a higher site symmetry. In $Ga_5B_{12}O_{25}(OH)$,[2] this positional shift at Ga2 is presumably caused in a distortion of the borate network due to a strong hydrogen bond to O3 (see Figure 4).[2] Since there is only a small amount of hydrogen in the title compound, the influence of this hydrogen bond is inferior and did not lead to a shift of the position of Ga2. Figure 2 depicts the arrangement of the metal cation polyhedra in the unit cell. The green and orange edge-sharing units are crystallographically identical, but are differently colored in order to distinguish paired units. Thereby, two [Ga1O_6] octahedra are linked with a common edge, forming a [$Ga1_2O_{10}$] unit. Along the crystallographic c axis, every second unit is either rotated by 90° or shifted along the b axis relative to the adjacent unit. The Ga2 atoms are surrounded by six O atoms forming single [Ga2O_6] octahedra and are located in the holes along the $\bar{4}$ inversion

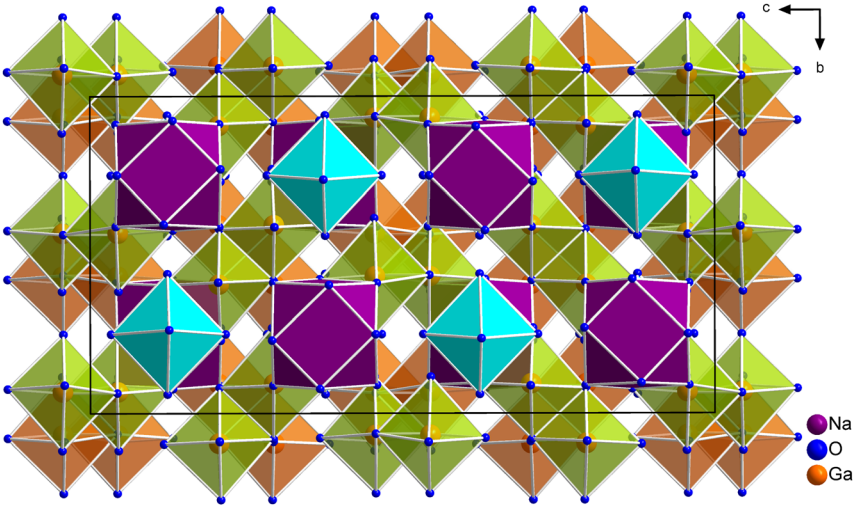

Figure 2: Visualization of the arrangement of [GaO_6] octahedra (orange, green or cyan) and [NaO_{12}] cuboctahedra (purple) in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) in viewing direction [100]. To better distinguish the crystallographically identical [Ga_2O_{10}] units, they were colored orange and green.

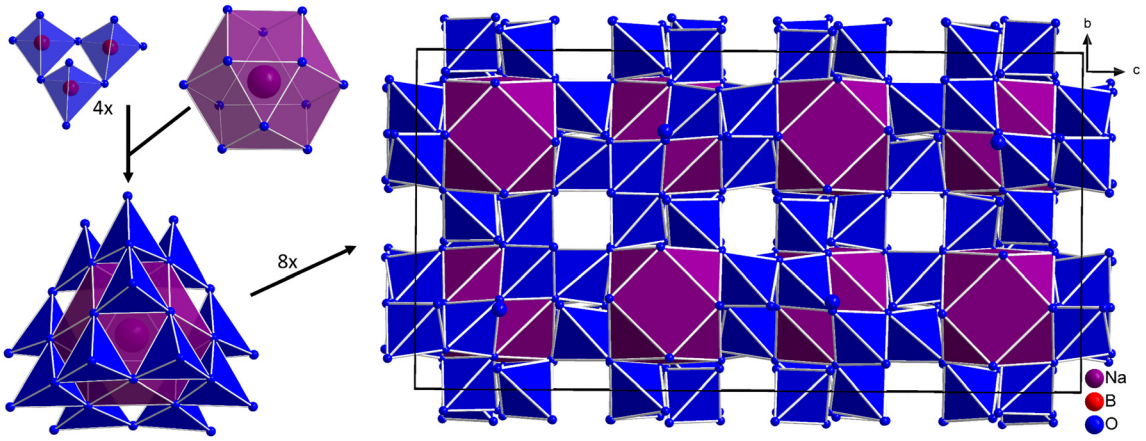

Figure 3: Formation of the network built of $[BO_4]$ tetrahedra in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) in viewing direction [100]. Four tetrahedrally arranged $[B_3O_9]$ units form a $[Na1O_{12}]$ cuboctahedron, which is repeated eight times per unit cell.

axis (colored cyan in Figure 2). The $[Na1O_{12}]$ cuboctahedra are alternating (checkered) with the $[Ga2O_6]$ octahedra. However, Na1 has a site occupancy factor (S.O.F.) of 0.876(4), and so not all theoretically possible sites are occupied. Therefore, we considered hydrogen atoms for charge neutrality reasons and this could also be confirmed by infrared spectroscopy (see below). Since a site for H could not be assigned in the structure refinement, we compared the title compound with $Ga_5B_{12}O_{25}(OH)$.[2] As depicted in Figure 4, Vitzthum et al. could locate hydrogen bonds formed by O4 as the donor atom and O3, O7, and O6 as the acceptor atoms in their structure refinement.[2] To account for charge neutrality, and considering the obvious similarities of the title compound to $Ga_5B_{12}O_{25}(OH)$,[2] in particular the same distortion of the Ga2 octahedra, we assume that the H atom is also connected to O4.

The B–O network has a complex arrangement of 96 corner-sharing $[BO_4]$ tetrahedra. Four tetrahedrally arranged $[B_3O_9]$ units form a $[B_{12}O_{30}]$ unit and a cave is formed

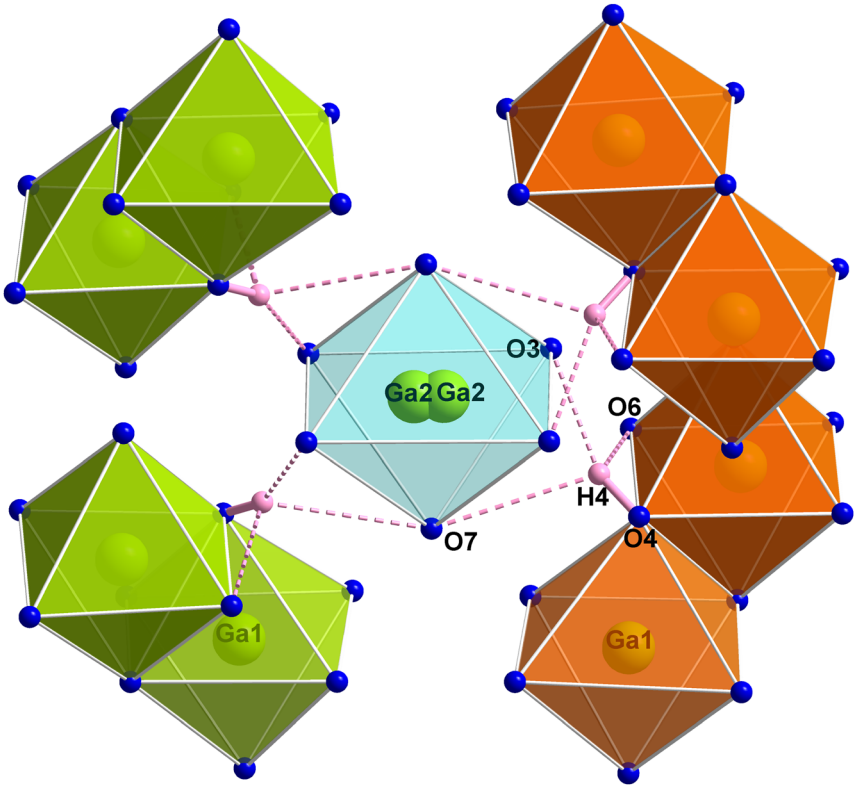

Figure 4: Visualization of the hydrogen bonds in the homeotypic structure $Ga_5B_{12}O_{25}(OH)$,[2] which may be similarly arranged in the title compound. O4 represents the donor atom and O3, O6, and O7 the acceptor atoms. Statistically only about 12 % of the four hydrogen bonds and one of the two Ga2 atoms depicted are present at the same time. The same color code as in Figure 2 is used.

within three- and six-membered rings containing the Na^+ cation in its centre, the assembly thus featuring a [Na1O_{12}] cuboctahedron (see Figure 3).

The Ga1–O distances of the edge-sharing double-octahedra are in the range between 1.9163(5) and 2.0326(6) Å (see Figure 5(a)) with an average value of 1.96 Å, which is in accordance with typical Ga–O distances in borates.[2,17–19] However, the Ga2–O bond lengths, which are ranging from 1.9908(8) to 2.1066(7) Å (see Figure 5(b)) with an average value of 2.07 Å, are peculiarly long. Nevertheless, extraordinarily long *M*2–O distances have been observed in all the other known homeotypic phases[1–5] with the exception of $Ga_4InB_{12}O_{25}(OH)$,[3] where the larger In atom shows common In–O bond lengths. Furthermore, in Table 4 the comparison of the distances to the values of the previously published homeotypic structure $Ga_5B_{12}O_{25}(OH)$ [2] shows that they are in good agreement. The majority of the values as well as the lattice parameters of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) are slightly shorter than those of $Ga_5B_{12}O_{25}(OH)$,[2] which may be due to the lower measurement temperature (see Table 1). The Na–O distances are in the range between 2.5292(5) and 2.5711(6) Å (see Figure 5(c)) with a mean value of 2.55 Å, which corresponds to values in the literature of 2.65 Å for $NaMn_7O_{12}$[20] and 2.94 Å for $NaTi_8O_{13}$,[21] if one considers that the size of the cuboctahedral void predominantly depends on the surrounding framework. The effective ionic radius for Na^+ in 12-fold coordination was estimated at 1.53 Å by Shannon in 1976.[22] Compared to the smallest diameter of the cuboctahedral void of the title compound of about 5.1 Å between two O atoms, there is sufficient space for Na^+, giving rise to only in a minimal distortion. The B–O distances are in the range between 1.4624(9) and 1.5099(9) Å with average values of 1.48 Å for B1–O and B2–O, and 1.49 Å for B3–O. These values are in accordance with the mean value of 1.476(35) Å for B–O distances in BO_4 tetrahedra[23] and with values commonly found in borates.[24–26]

The angles can be found in Table 5, where they are compared to those in $Ga_5B_{12}O_{25}(OH)$,[2] where very similar values have been observed. Furthermore, the mean values for the octahedra show only a minimal deviation from the regular values of 90°, 180°, and those for the Na1 cuboctahedron with 60° and 120°. Individual angle values deviate within acceptable limits.

To further confirm the structure refinement, calculations of the bond-length/bond-strength values[27] (BLBS, see Table 6), and the charge distribution[28] (CHARDI, see Table 6) were performed. For this purpose, a full occupation of Na1 had to be set, because at a specific position inside the structure there is only the possibility of a full Na atom or

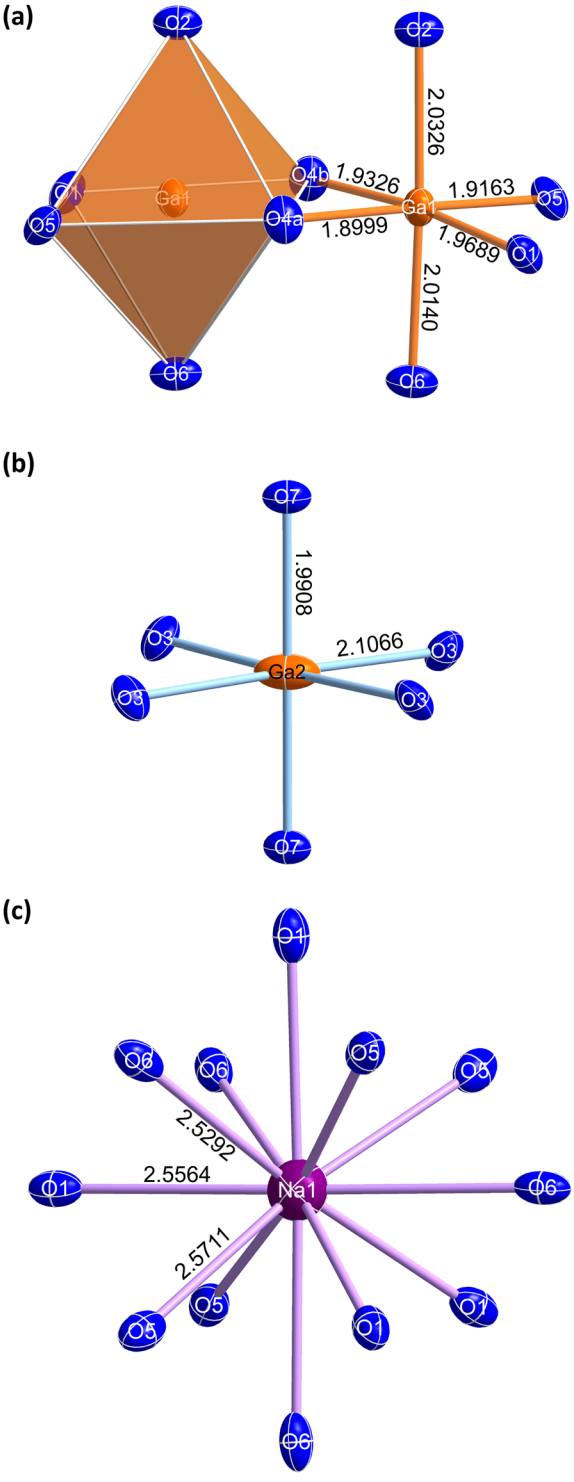

Figure 5: Oak Ridge Thermal Ellipsoid Plot Diagram (ORTEP)-type representation of [Ga1$_2$O$_{10}$] (a) and [Ga2O$_6$] octahedra (b) and [Na1O$_{12}$] cuboctahedra (c) in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) with displacement ellipsoids at the 99.99 % probability level. Bond lengths are depicted in Å. The values are shown here without standard deviation, but can be completely found in Table 4.

Table 4: Interatomic distances (Å) in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12; present study) compared to published data of the homeotypic structure $Ga_5B_{12}O_{25}(OH)$[2] (standard deviations in parentheses). O4a and O4b, as well as O3a and O3b, respectively, are crystallographically identical, but are distinguished in this table, if the distances are different.

		$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)		$Ga_5B_{12}O_{25}(OH)$[2]			$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)	$Ga_5B_{12}O_{25}(OH)$[2]
Ga1–	O1	1.9689(6)		1.952(2)	B1–	O1	1.5091(9)	1.503(2)
	O2	2.0326(6)		2.065(2)		O2	1.4624(9)	1.475(2)
	O4a	1.8999(6)		1.930(2)		O6	1.4863(9)	1.481(2)
	O4b	1.9326(5)		1.983(2)		O7	1.4684(8)	1.482(2)
	O5	1.9163(5)		1.909(2)	**ØB1–O**		**1.48**	**1.49**
	O6	2.0140(6)		2.001(2)				
ØGa1–O		**1.96**		**1.97**	B2–	O2	1.4845(9)	1.497(2)
						O3	1.4799(9)	1.490(2)
Ga2–	O3	2.1066(7) 4 ×	O3a	2.003(2) 2 ×		O5	1.4898(9)	1.478(2)
			O3b	2.307(2) 2 ×		O6	1.4832(9)	1.482(2)
	O7	1.9908(8) 2 ×		1.988(2) 2 ×	**ØB2–O**		**1.48**	**1.49**
ØGa2–O		**2.07**		**2.10**				
					B3–	O1	1.4950(9)	1.480(2)
Na1–	O1	2.5564(5) 4 ×				O3	1.5099(9)	1.514(2)
	O5	2.5711(6) 4 ×				O4	1.4269(9)	1.463(2)
	O6	2.5292(5) 4 ×				O5	1.5084(9)	1.489(2)
ØNa1–O		**2.55**			**ØB3–O**		**1.49**	**1.49**

Mean values of distances are written in bold.

Table 5: Interatomic angles (deg) in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12; present study) compared to reported data of the homeotypic structure $Ga_5B_{12}O_{25}(OH)$.[2] Standard deviations are specified in parentheses. Atoms labeled a, b, c, and d are crystallographically identical, but are distinguished in this table, if the angles are different.

	$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)	$Ga_5B_{12}O_{25}(OH)$[2]		$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)	$Ga_5B_{12}O_{25}(OH)$[2]
O1–Ga1–O2	98.98(2)	98.92(4)	O2–B2–O3	110.11(6)	109.5(2)
O1–Ga1–O4a	92.61(2)	92.51(4)	O2–B2–O5	109.20(6)	108.6(2)
O1–Ga1–O5	90.73(2)	93.23(4)	O2–B2–O6	111.65(6)	112.0(2)
O1–Ga1–O6	84.78(2)	87.04(4)	O3–B2–O5	108.77(6)	108.8(2)
O2–Ga1–O4b	86.84(2)	85.18(4)	O3–B2–O6	111.50(6)	110.4(2)
O2–Ga1–O4a	89.22(2)	88.14(4)	O5–B2–O6	105.45(6)	107.5(2)
O2–Ga1–O5	92.60(2)	91.64(4)	**ØO–B2–O**	**109.4**	**109.5**
O4a–Ga1–O4b	84.90(2)	83.57(4)			
O4b–Ga1–O5	91.53(2)	90.65(4)	O1–B3–O3	108.86(6)	110.1(2)
O4b–Ga1–O6	89.40(2)	88.75(4)	O1–B3–O4	108.85(6)	107.9(2)
O4a–Ga1–O6	90.47(2)	89.82(4)	O1–B3–O5	104.66(5)	107.5(2)
O5–Ga1–O6	87.47(2)	89.80(4)	O3–B3–O4	113.78(6)	111.8(2)
ØO–Ga1–O_{90}	**90.0**	**89.9**	O3–B3–O5	110.24(5)	110.3(2)
			O4–B3–O5	110.05(6)	109.1(2)
O1–Ga1–O4b	173.66(2)	174.26(4)	**ØO–B3–O**	**109.4**	**109.5**
O2–Ga1–O6	176.24(2)	173.78(4)			
O4a–Ga1–O5	175.90(2)	174.22(4)	O1–Na1–O1	89.15(2) 2 ×	
ØO–Ga1–O_{180}	**175.3**	**174.1**	O1–Na1–O6	90.33(2) 4 ×	
			O5–Na1–O5	90.211(1) 4 ×	
O3a–Ga2–O3b	81.80(3) 2 ×	88.67(6)	O6–Na1–O6	90.59(2) 2 ×	
O3c–Ga2–O3d		74.73(5)	**ØO–Na1–O_{90}**	**90.1**	
O3b–Ga2–O3c	98.22(3) 2 ×	98.31(5) 2 ×			
O3a–Ga2–O7	90.81(2) 4 ×	94.55(3) 2 ×	O1–Na1–O1	120.49(2) 4 ×	
O3b–Ga2–O7		93.71(3) 2 ×	O1–Na1–O5a	118.92(2) 4 ×	
O3c–Ga2–O7	89.19(2) 4 ×	85.78(3) 2 ×	O1–Na1–O5b	120.33(2) 4 ×	
O3d–Ga2–O7		85.04(3) 2 ×	O5–Na1–O6a	118.97(2) 2 ×	
ØO–Ga2–O_{90}	**90.0**	**89.8**	O5–Na1–O6b	118.98(2) 2 ×	
			O5–Na1–O6c	121.16(2) 4 ×	

Table 5: (continued)

	$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)	$Ga_5B_{12}O_{25}(OH)$[2]		$Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12)	$Ga_5B_{12}O_{25}(OH)$[2]
O3a–Ga2–O3c	178.37(3)	172.99(3)	O6–Na1–O6	119.66(2) 4 ×	
O3b–Ga2–O3d	178.37(3)	172.99(3)			
O7–Ga2–O7	180.0	168.44(4)	**ØO–Na1–O_{120}**	**119.9**	
ØO–Ga2–O_{180}	**178.9**	**171.5**			
			O1–Na1–O5a	55.24(2) 4 ×	
O1–B1–O2	112.59(6)	111.4(2)	O1–Na1–O5b	65.26(2) 4 ×	
O1–B1–O6	105.60(6)	107.2(2)	O1–Na1–O6a	55.96(2) 4 ×	
O1–B1–O7	108.58(5)	108.81(9)	O1–Na1–O6b	63.74(2) 4 ×	
O2–B1–O6	111.31(6)	110.8(2)	O5–Na1–O6a	55.26(2) 3 ×	
O2–B1–O7	106.89(6)	106.6(2)	O5–Na1–O6b	55.27(2)	
O6–B1–O7	111.92(5)	112.0(2)	O5–Na1–O6c	64.40(2) 4 ×	
ØO–B1–O	**109.5**	**109.5**	**ØO–Na1–O_{60}**	**60.0**	
			O1–Na1–O6	175.17(2) 4 ×	
			O5–Na1–O5	173.04(2) 2 ×	
			ØO–Na1–O_{180}	**174.5**	

Angle mean values are written in bold.

Table 6: Charge distribution in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) according to the bond-length/bond-strength[27] (ΣV) and CHARDI[28] (ΣQ) concept. Values with a deviation from the regular values >±8 % are written in italics.

	Ga1	Ga2	B1	B2	B3	O1	O2	O3	O4	O5	O6	O7	Na1
ΣV	3.24	*2.43*	2.97	2.94	2.95	−2.06	−1.96	−1.79	−2.07	−2.15	−2.08	−2.03	*1.59*
ΣQ	2.97	3.00	2.97	3.05	3.01	−2.01	−2.00	−1.99	−2.00	−2.00	−2.00	−2.00	1.00

none. According to the CHARDI-concept,[28] only minimal deviations (<±1.7 %) of the calculated values compared to the regular values of +3 for Ga and B, +1 for Na, and −2 for O were observed. According to the BLBS-concept,[27] most values also have only a slight deviation from the regular values (≤±8 %), but Ga2 and Na1 do not fit well, because of comparatively long bond lengths. However, compared to the homeotypic compounds, the long Ga2–O distances are indeed to be expected to be characteristic for this structure type[1–5] and the Na1–O distances may depend on the surrounding framework. Therefore, the very good values according to the CHARDI[28] concept may be more crucial, due to its consideration of the spatial arrangement of atoms and their electron configuration.

3.2 IR spectroscopy

Figure 6 shows a FT-IR spectrum of a single crystal of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) in comparison to published data of the homeotypic phase $Ga_5B_{12}O_{25}(OH)$[2] in the spectral region of 600–4,000 cm^{-1}. In the fingerprint region up to ~1,400 cm^{-1}, the peaks can be explained by vibrations of M–O, B–O or various overlapping combinations. Specifically, the stretching modes of [BO_4] tetrahedra are typically observed between 850 and 1,100 cm^{-1},[29] the characteristic frequencies of [AlO_6] octahedra between 750 and 400 cm^{-1},[30] which are

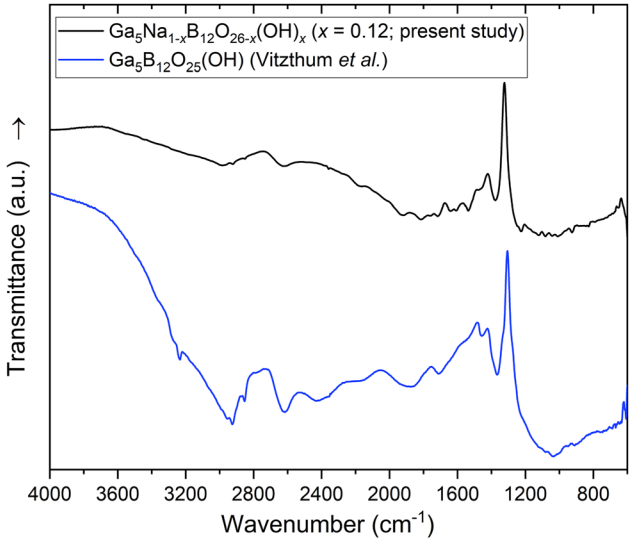

Figure 6: Single-crystal IR spectrum of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) (black) compared to published data of the homeotypic structure $Ga_5B_{12}O_{25}(OH)$[2] (blue) in the spectral region of 600–4,000 cm^{-1} (both experimental data).

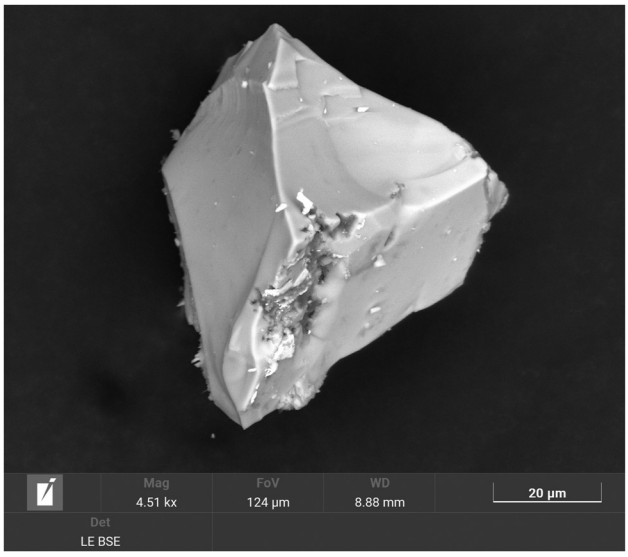

Figure 7: Scanning electron microscope (SEM) image of a representative crystal of $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$.

both present in the experimental spectrum. The position of an O–H stretching vibration was observed in the homeotypic structure $Ga_5B_{12}O_{25}(OH)$[2] at around 3,000 cm^{-1}. If we consider the small amount of O–H in $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) based on the single-crystal data, only a weak peak is expected, which seems to be present in the FT-IR spectrum.

3.3 Energy-dispersive X-ray spectroscopy

The results of a semi-quantitative energy-dispersive X-ray (EDX) spectroscopy study confirmed the presence and approximate quantity (within 3 standard deviations or less) of all the elements identified by single-crystal X-ray diffraction with the exception of H, which cannot be detected with this method. Especially the measured sodium content of 1.9(3) at% (averaged from 14 point measurements) is in good agreement with the expected value of 2.0 at%. Figure 7 shows a representative crystal of the title compound, which was obtained by a scanning electron microscope (SEM).

4 Conclusions

Tetragonal $Ga_5Na_{1-x}B_{12}O_{26-x}(OH)_x$ (x = 0.12) was synthesized in a high-pressure/high-temperature experiment in a multianvil press. Its structure could be determined by single-crystal X-ray diffraction, which revealed single- and double-octahedral and cuboctahedral units centered by the metal cations and a complex network of $[BO_4]$ tetrahedra. The presence of hydroxyl groups could be confirmed by IR spectroscopy. EDX investigations confirmed the presence of the elements Ga, B, O, and Na.

Acknowledgements: The authors thank Assoc.-Prof. Dr. Gunter Heymann for recording of the single-crystal data and Dr. Daniela Vitzthum for the IR data of $Ga_5B_{12}O_{25}(OH)$. I. W. gratefully acknowledges the Vice Rector for Research for the grant of a doctoral fellowship at the University of Innsbruck.
Research ethics: Not applicable.
Informed consent: Not applicable.
Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission.
Use of Large Language Models, AI and Machine Learning Tools: ChatGPT and Google Translate were used to improve language when required.
Conflict of interest: The authors state no conflict of interest.
Research funding: None declared.
Data availability: The raw data can be obtained on request from the corresponding author. CSD-2376207 contains 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.

References

1. Haberer, A.; Huppertz, H. *J. Solid State Chem.* **2009**, *182*, 484–490.
2. Vitzthum, D.; Wurst, K.; Pann, J. M.; Brüggeller, P.; Seibald, M.; Huppertz, H. *Angew. Chem. Int. Ed.* **2018**, *57*, 11451–11455.
3. Vitzthum, D.; Wimmer, D. S.; Widmann, I.; Huppertz, H. *Z. Naturforsch.* **2020**, *75b*, 605–613.
4. Pasqualini, L. C.; Tribus, M.; Huppertz, H. *Z. Naturforsch.* **2024**, *79b*, 39–49.
5. Somasundaram, J. D.; Pasqualini, L. C.; Krivosudský, L.; Huppertz, H. *Z. Naturforsch.* **2024**, *79b*, 497–505.
6. Vitzthum, D.; Widmann, I.; Wimmer, D. S.; Wurst, K.; Joachim-Mrosko, B.; Huppertz, H. *Eur. J. Inorg. Chem.* **2021**, 1165–1174; https://doi.org/10.1002/ejic.202001136.
7. Huppertz, H. *Z. Kristallogr.* **2004**, *219*, 330–338.
8. Walker, D.; Carpenter, M. A.; Hitch, C. M. *Am. Mineral.* **1990**, *75*, 1020–1028.
9. Walker, D. *Am. Mineral.* **1991**, *76*, 1092–1100.
10. Saint, *Area Detector Control and Integration Software*, Bruker AXS Inc.: Madison, Wisconsin (USA), 2021.
11. Apex4 *Data Reduction and Frame Integration Program for the CCD Area-Detector System*; Bruker AXS Inc.: Madison, Wisconsin (USA), 2021.
12. Sheldrick, G. M. Sadabs (version 2016). Bruker AXS Inc.: Madison, Wisconsin (USA), 2016.
13. Sheldrick, G. M. *Acta Crystallogr.* **2015**, *A71*, 3–8.
14. Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.
15. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

16. Opus, Bruker Corporation: Billerica, Massachusetts (USA), 2012.
17. Vitzthum, D.; Schauperl, M.; Strabler, C. M.; Brüggeller, P.; Liedl, K. R.; Griesser, U. J.; Huppertz, H. *Inorg. Chem.* **2016**, *55*, 676–681.
18. Vitzthum, D.; Hering, S. A.; Perfler, L.; Huppertz, H. *Z. Naturforsch.* **2015**, *70b*, 207–214.
19. Gao, W.; Jing, Y.; Yang, J.; Zhou, Z.; Yang, D.; Sun, J.; Lin, J.; Cong, R.; Yang, T. *Inorg. Chem.* **2014**, *53*, 2364–2366.
20. Marezio, M.; Dernier, P. D.; Chenavas, J.; Joubert, J. C. *J. Solid State Chem.* **1973**, *6*, 16–20.
21. Akimoto, J.; Takei, H. *J. Solid State Chem.* **1991**, *90*, 147–154.
22. Shannon, R. *Acta Crystallogr.* **1976**, *A32*, 751–767.
23. Zobetz, E. *Z. Kristallogr.* **1990**, *191*, 45–57.
24. Widmann, I.; Kinik, G.; Jähnig, M.; Glaum, R.; Schwarz, M.; Wüstefeld, C.; Johrendt, D.; Tribus, M.; Hejny, C.; Bayarjargal, L.; Dubrovinsky, L.; Heymann, G.; Suta, M.; Huppertz, H. *Adv. Funct. Mater.* **2024**, *34* (9), 2400054.
25. Vitzthum, D.; Widmann, I.; Plank, M.; Joachim-Mrosko, B.; Huppertz, H. *Z. Naturforsch.* **2020**, *75b*, 975–981.
26. Teichtmeister, T. A.; Widmann, I.; Bayarjargal, L.; Tribus, M.; Heymann, G.; Wurst, K.; Huppertz, H. *Eur. J. Inorg. Chem.* **2024**, *27*, e202300555.
27. Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244–247.
28. Hoppe, R. *Z. Kristallogr.* **1979**, *150*, 23–52.
29. Ross, S. D. *Spectrochim. Acta, Part A* **1972**, *28*, 1555–1561.
30. Tarte, P. *Spectrochim. Acta, Part A* **1967**, *23*, 2127–2143.