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β -Y(BO₂)₃ – a new member of the β -Ln(BO₂)₃ (Ln = Nd, Sm, Gd–Lu) structure family

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Abstract: β -Y(BO₂)₃ was synthesized in a Walker-type multianvil module at 5.9 GPa/1000°C. The crystal structure has been elucidated through single-crystal X-ray diffraction. β -Y(BO₂)₃ crystallizes in the orthorhombic space group *Pnma* (no. 62) with the lattice parameters $a=15.886(2)$, $b=7.3860(6)$, and $c=12.2119(9)$ Å. Its crystal structure will be discussed in the context of the isotypic lanthanide borates β -Ln(BO₂)₃ (Ln = Nd, Sm, Gd–Lu).

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

1 Introduction

In the recent past, one of our main research objectives was the high-pressure synthesis and structure elucidation of novel transition metal borates. These investigations yielded a considerable amount of new phases with hitherto unknown compositions (e.g. Co₇B₂₄O₄₂(OH)₂ · 2H₂O [1]) or striking structural motifs (e.g. Mo₂B₄O₉ [2], the first borate incorporating transition metal clusters into its crystal structure). Since not all *M*-B-O(-H) (*M*=transition metal) systems have been explored via high-pressure methods as yet, our most recent studies aimed at the synthesis of novel high-pressure yttrium borates. The compounds (NH₄)YB₈O₁₄ [3] and α -Y₂B₄O₉ [4] are the first results of these investigations. Here, we report the synthesis and characterization of the third high-pressure yttrium borate β -Y(BO₂)₃ and discuss its crystal structure with regard to the isotypic lanthanide borates β -Ln(BO₂)₃ (Ln = Nd, Sm, Gd–Lu) [5–8].

To date, four modifications are known for compounds exhibiting the composition Ln(BO₂)₃ (Ln=lanthanides). They are designated with the Greek letters α , β , γ , and δ in chronological order. The first detailed description of the crystal structure of the orthorhombic β -modification was published in 2003 by Nikelski and Schleid [5], who synthesized β -Tb(BO₂)₃ in sealed platinum ampoules. Only 1 year later, Emme et al. reported the high-pressure synthesis of β -Ln(BO₂)₃ (Ln=Dy–Lu) [6]. The phases β -Ln(BO₂)₃ (Ln=Nd, Sm, Gd) [7] were also synthesized under high-pressure conditions by Emme et al. in 2007, whereas Nikelski et al. [8] showed the synthesis of β -Dy(BO₂)₃ also under normal pressure in 2008.

2 Results and discussion

2.1 Crystal structure

β -Y(BO₂)₃ crystallizes isotypically to β -Ln(BO₂)₃ (Ln=Nd, Sm, Gd–Lu) [5–8] in the orthorhombic space group *Pnma* (no. 62). The lattice parameters are $a=15.886(2)$, $b=7.3860(6)$, and $c=12.2119(9)$ Å (Table 1). The unit cell ($V=1432.8(2)$ Å³) contains $Z=16$ formula units and the asymmetric unit comprises 25 atoms (4×Y, 6×B, and 15×O) distributed over the Wyckoff positions 4c and 8d.

The anionic skeleton of the compound consists exclusively of [BO₄] tetrahedra. A central feature of the structure is a “windmill-like” structural unit built up of three tetrahedra sharing the common oxygen atom O7 (Fig. 1, top). This “windmill” is linked to a symmetry equivalent entity through the oxygen atoms O1, O2, and O3 residing on a mirror plane (Fig. 1, bottom). Along the *b* axis, these “double-windmills” are interconnected via three [B₂O₇] groups, each composed of two vertex-sharing [BO₄] tetrahedra (Fig. 2). Thus, infinite ribbons with an approximately triangular cross section are formed that run along [010]. These ribbons are interconnected through common oxygen atoms along [001] to form corrugated layers of [BO₄] tetrahedra parallel to (100) (Fig. 3). The layers are condensed by the yttrium atoms, each of which is coordinated by eight oxygen atoms (Fig. 4).

The B–O distances and O–B–O angles lie in the ranges 1.434(3)–1.532(3) Å and 102.8(2)–115.2(2)°, respectively

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Table 1: Crystal and structure refinement data for β -Y(BO₂)₃.

Empirical formula	YB ₃ O ₆
Molar mass, g · mol ⁻¹	217.34
Crystal system	orthorhombic
Space group	<i>Pnma</i> (no. 62)
Single-crystal data	
<i>T</i> , °C	24(2)
Radiation; λ , Å	MoK α_1 ; 0.71073
<i>a</i> , Å	15.886(2)
<i>b</i> , Å	7.3860(6)
<i>c</i> , Å	12.2119(9)
<i>V</i> , Å ³	1432.8(2)
<i>Z</i>	16
Calculated density, g · cm ⁻³	4.03
Absorption coeff., mm ⁻¹	16.2
<i>F</i> (000), <i>e</i>	1632
Crystal size, mm ³	0.060 × 0.025 × 0.020
θ range, deg	2.10–37.56
Range in <i>hkl</i>	±27, ±12, –18 → 20
Reflections collected	50786
Independent reflections	3996 [<i>R</i> _{int} = 0.128]
Completeness to $\theta = 25.24^\circ$, %	100.0
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/parameters	3996/196
Goodness-of-fit on <i>F</i> ²	1.051
Final <i>R</i> 1/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.034/0.065
Final <i>R</i> 1/ <i>wR</i> 2 (all data)	0.052/0.070
Largest diff. peak/hole, <i>e</i> · Å ⁻³	1.25/–1.40
Powder data	
Radiation; λ , Å	MoK α_1 ; 0.7093
<i>a</i> , Å	15.8924(5)
<i>b</i> , Å	7.3856(2)
<i>c</i> , Å	12.2131(4)
<i>V</i> , Å ³	1433.50(7)
2 θ range, deg	2.0–42.2
2 θ step width, deg	0.015
<i>R</i> _{exp} , %	2.03
<i>R</i> _{wp} , %	6.63
<i>R</i> _p , %	4.30

Fig. 1: Top: Three tetrahedra sharing a common corner to form a “windmill-like” structural unit. Bottom: “double-windmill” composed of two symmetry equivalent entities connected through common vertices.

(Tables 2 and 3). The corresponding average values (1.465–1.479 Å and 109.4–109.5°, respectively) are similar to those reported by Zobetz (1.476(35) Å/109.44(2.78)°) [9].

Each of the four crystallographically different yttrium atoms is coordinated by eight oxygen atoms. The Y–O bond lengths lie between 2.250(2) and 2.823(2) Å, where Y1 shows the largest scattering of Y–O distances (Table 4). In β -Ln(BO₂)₃ (*Ln* = Nd, Sm, Gd–Lu), the corresponding values range from ~2.21 to 2.96 Å. β -Ln(BO₂)₃ (*Ln* = Dy, Ho, Er) show *Ln*–O distances between 2.26 and 2.84 Å and thus come closest to the Y–O bond lengths in β -Y(BO₂)₃ because of the similar ionic radii of Y³⁺ (*r*(Y³⁺) = 1.215 Å for CN 9), Dy³⁺ (*r*(Dy³⁺) = 1.223 Å for CN 9), Ho³⁺ (*r*(Ho³⁺) = 1.212 Å for CN 9), and Er³⁺ (*r*(Er³⁺) = 1.202 Å for CN 9) [10].

Bond valence sums (BVS) were calculated according to the bond-length/bond-strength (BLBS) concept (Table 5) [11, 12]. The calculated values correspond well with the expected formal ionic charges.

A comparison of the lattice parameters and cell volumes of β -Y(BO₂)₃ and β -Ln(BO₂)₃ (*Ln* = Nd, Sm, Gd–Lu) is given in Table 6. The positional parameters are displayed in Table 7.

Further details on the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe,

Fig. 2: The “double-windmills” (dark blue) are interconnected by three [B₂O₇] groups (light blue) to form infinite ribbons along [010].

Fig. 3: The approximately triangular ribbons are interconnected via common vertices along [001]. This leads to the formation of corrugated layers parallel to the *bc* plane. The yttrium atoms are located between these layers.

Fig. 4: Coordination spheres of the four crystallographically independent yttrium atoms.

Table 2: Interatomic B–O distances (Å) for β -Y(BO₂)₃.

B1–O13	1.434(3)	B2–O12	1.449(3)	B3–O3	1.452(3)
–O10	1.440(3)	–O2	1.460(3)	–O9	1.454(3)
–O1	1.487(3)	–O14	1.472(3)	–O8	1.479(3)
–O7	1.532(3)	–O7	1.508(3)	–O7	1.519(3)
$\emptyset$	1.473	$\emptyset$	1.472	$\emptyset$	1.476
B4–O10	1.445(3)	B5–O13	1.464(3)	B6–O15	1.435(3)
–O4	1.446(3)	–O5	1.465(3)	–O9	1.443(3)
–O11	1.460(3)	–O12	1.466(3)	–O14	1.519(3)
–O8	1.518(3)	–O11	1.466(3)	–O6	1.520(3)
$\emptyset$	1.467	$\emptyset$	1.465	$\emptyset$	1.479

Average values in bold characters.

76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-mail: crysdta@fiz-karlsruhe.de) on quoting the deposition number CSD-433609 for β -Y(BO₂)₃.

2.2 X-ray powder diffraction

The result of the Rietveld refinement is shown in Fig. 5. The amorphous halo at low 2θ angles indicates the presence of considerable amounts of amorphous material. Apart from that, no crystalline phases other than β -Y(BO₂)₃ were present in the sample. More details can be found in Table 1.

2.3 Vibrational spectroscopy

Figure 6 displays the single-crystal IR and Raman spectra. Both spectra show some minor peaks at wavenumbers

Table 3: Selected bond angles (deg) for β -Y(BO₂)₃.

O10–B1–O1	106.0(2)	O12–B2–O14	106.2(2)	O9–B3–O7	107.1(2)
O13–B1–O7	107.5(2)	O12–B2–O2	107.3(2)	O9–B3–O8	107.2(2)
O10–B1–O7	108.9(2)	O2–B2–O14	110.2(2)	O3–B3–O8	107.4(2)
O13–B1–O10	109.4(2)	O14–B2–O7	110.3(2)	O3–B3–O9	110.3(2)
O13–B1–O1	112.1(2)	O2–B2–O7	110.8(2)	O8–B3–O7	111.6(2)
O1–B1–O7	112.9(2)	O12–B2–O7	111.8(2)	O3–B3–O7	113.2(2)
$\emptyset$	109.5	$\emptyset$	109.4	$\emptyset$	109.5
O4–B4–O8	102.8(2)	O5–B5–O11	106.4(2)	O14–B6–O6	105.3(2)
O10–B4–O11	106.2(2)	O12–B5–O11	109.6(2)	O15–B6–O14	107.3(2)
O10–B4–O8	106.2(2)	O13–B5–O12	109.8(2)	O15–B6–O6	107.9(2)
O4–B4–O11	112.2(2)	O13–B5–O11	110.1(2)	O9–B6–O14	109.9(2)
O11–B4–O8	114.7(2)	O13–B5–O5	110.3(2)	O9–B6–O6	110.8(2)
O10–B4–O4	114.8(2)	O5–B5–O12	110.6(2)	O15–B6–O9	115.2(2)
$\emptyset$	109.5	$\emptyset$	109.5	$\emptyset$	109.4

Average values in bold characters.

Table 4: Interatomic Y–O distances (Å) for β -Y(BO₂)₃.

Y1–O15	2.250(2)	2×	Y2–O13	2.256(2)	2×
–O9	2.264(2)	2×	–O6	2.342(2)	
–O4	2.297(2)		–O8	2.375(2)	2×
–O8	2.480(2)	2×	–O15	2.557(2)	2×
–O1	2.823(2)		–O3	2.570(2)	
$\emptyset$	2.389		$\emptyset$	2.411	
Y3–O11	2.307(2)	2×	Y4–O10	2.273(2)	2×
–O2	2.327(2)		–O5	2.376(2)	
–O12	2.354(2)	2×	–O14	2.384(2)	2×
–O14	2.536(2)	2×	–O15	2.421(2)	2×
–O6	2.627(2)		–O1	2.534(2)	
$\emptyset$	2.419		$\emptyset$	2.383	

Average values in bold characters.

Table 5: Bond valence sums in β -Y(BO₂)₃ according to BLBS.

Y1	3.26	O4	–2.11
Y2	2.93	O5	–1.93
Y3	2.85	O6	–1.95
Y4	3.06	O7	–2.00
B1	3.05	O8	–2.09
B2	3.05	O9	–2.14
B3	3.02	O10	–2.15
B4	3.09	O11	–2.02
B5	3.10	O12	–1.99
B6	3.01	O13	–2.15
O1	–1.82	O14	–2.05
O2	–2.01	O15	–1.94
O3	–1.83		

>3000 cm^{–1} which we ascribe to surface impurities or inclusions in the crystals. The broad Raman band between 2800 and 3000 cm^{–1} stems from the oil used to prepare the crystals, whereas the origin of the broad IR mode at approximately 1600 cm^{–1} is uncertain. Similar to (NH₄)YB₈O₁₄ [3], stretching vibrations of [BO₄] tetrahedra

are expected to cause vibrational bands between 1300 and 850 cm^{–1}, while bending vibrations give rise to modes in the wavenumber range ~1100–300 cm^{–1}. Between approximately 800 and 700 cm^{–1}, complex B–O–Y vibrations can be observed. Y–O stretching and bending vibrations occur between ~500–250 cm^{–1} and ~400–100 cm^{–1} [3].

3 Conclusions

β -Y(BO₂)₃ was synthesized in a high-pressure/high-temperature experiment at ~5.9 GPa/1000°C. It crystallizes isotypically to the lanthanide borates β -Ln(BO₂)₃ (Ln = Nd, Sm, Gd–Lu). The crystal structure is built up of triangular ribbons running along [010], which are interconnected along [001] to form corrugated layers. The borate layers are condensed by the yttrium atoms residing in the inter-space between these layers.

The aforementioned compounds were synthesized at quite different reaction conditions. While β -Ln(BO₂)₃ (Ln = Tb, Dy) could be obtained at ambient pressure, β -Nd(BO₂)₃ was synthesized at 3.5 GPa, β -Y(BO₂)₃ at 5.9 GPa, and β -Ln(BO₂)₃ (Ln = Sm, Gd, Ho–Lu) at 7.5 GPa.

4 Experimental section

4.1 Synthesis

β -Y(BO₂)₃ was formed in a high-pressure/high-temperature synthesis at ~5.9 GPa/1000°C using a Walker-type multi-anvil module and a 1000 t press (both Max Voggenreiter GmbH, Germany). The mixture was prepared by weighing and grinding Y₂O₃ (Sigma-Aldrich, USA, 99.99%) and

Table 6: Comparison of the lattice parameters (Å), volumes (Å³), and ionic radii (Å) (for CN 9) [10] of β -Y(BO₂)₃ and β -Ln(BO₂)₃ (Ln = Nd, Sm, Gd–Lu).

Compound	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>	<i>r</i> (M ³⁺)	Reference
β -Y(BO ₂) ₃	15.886(2)	7.3860(6)	12.2119(9)	1432.8(2)	1.215	This work
β -Nd(BO ₂) ₃	16.162(3)	7.474(2)	12.442(3)	1502.8(5)	1.303	[7]
β -Sm(BO ₂) ₃	16.125(2)	7.4602(4)	12.4087(7)	1492.7(2)	1.272	[7]
β -Gd(BO ₂) ₃	16.028(2)	7.4270(4)	12.3217(7)	1466.8(2)	1.247	[7]
β -Tb(BO ₂) ₃	15.9897(9)	7.4139(4)	12.2958(7)	1457.6(2)	1.235	[5]
β -Dy(BO ₂) ₃	15.930(2)	7.402(2)	12.264(1)	1446(1)	1.223	[6]
β -Ho(BO ₂) ₃	15.919(2)	7.395(2)	12.233(2)	1440(1)	1.212	[6]
β -Er(BO ₂) ₃	15.876(2)	7.380(2)	12.189(2)	1428(1)	1.202	[6]
β -Tm(BO ₂) ₃	15.816(2)	7.362(2)	12.162(2)	1416(1)	1.192	[6]
β -Yb(BO ₂) ₃ ^a	15.791(3)	7.352(2)	12.140(3)	1410(1)	1.182	[6]
β -Lu(BO ₂) ₃	15.767(2)	7.347(2)	12.115(2)	1403(1)	1.172	[6]

^aLattice parameters derived from powder data.

Table 7: Atomic coordinates and equivalent isotropic displacement parameters U_{eq} (Å²) for β -Y(BO₂)₃.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Y1	4 <i>c</i>	0.37889(2)	1/4	0.00853(3)	0.00449(6)
Y2	4 <i>c</i>	0.17226(2)	1/4	0.43438(3)	0.00451(6)
Y3	4 <i>c</i>	0.04822(2)	1/4	0.08873(3)	0.00488(6)
Y4	4 <i>c</i>	0.37252(2)	1/4	0.73155(3)	0.00446(6)
B1	8 <i>d</i>	0.2175(2)	0.0704(3)	0.8147(2)	0.0047(4)
B2	8 <i>d</i>	0.0569(2)	0.0734(3)	0.8457(2)	0.0042(4)
B3	8 <i>d</i>	0.1099(2)	0.0768(3)	0.6432(2)	0.0041(4)
B4	8 <i>d</i>	0.2417(2)	0.0689(3)	0.1284(2)	0.0043(4)
B5	8 <i>d</i>	0.3476(2)	0.0775(3)	0.4827(2)	0.0044(4)
B6	8 <i>d</i>	0.0319(2)	0.0598(3)	0.3227(2)	0.0045(4)
O1	4 <i>c</i>	0.2451(2)	1/4	0.8564(2)	0.0053(4)
O2	4 <i>c</i>	0.0482(2)	1/4	0.8982(2)	0.0054(4)
O3	4 <i>c</i>	0.0779(2)	1/4	0.6053(2)	0.0053(4)
O4	4 <i>c</i>	0.2752(2)	1/4	0.1396(2)	0.0056(4)
O5	4 <i>c</i>	0.3411(2)	1/4	0.5413(2)	0.0037(4)
O6	4 <i>c</i>	0.0651(2)	1/4	0.3027(2)	0.0060(4)
O7	8 <i>d</i>	0.1289(2)	0.0742(2)	0.7652(2)	0.0045(3)
O8	8 <i>d</i>	0.1854(2)	0.0340(2)	0.5774(2)	0.0040(3)
O9	8 <i>d</i>	0.4514(2)	0.0655(2)	0.1227(2)	0.0048(3)
O10	8 <i>d</i>	0.2768(1)	0.0213(2)	0.7306(2)	0.0052(3)
O11	8 <i>d</i>	0.1639(2)	0.0653(2)	0.0648(2)	0.0051(3)
O12	8 <i>d</i>	0.4306(2)	0.0589(2)	0.4317(2)	0.0047(3)
O13	8 <i>d</i>	0.2820(2)	0.0650(2)	0.3989(2)	0.0047(3)
O14	8 <i>d</i>	0.4780(2)	0.0233(2)	0.7097(2)	0.0051(3)
O15	8 <i>d</i>	0.4039(2)	0.0408(2)	0.8787(2)	0.0053(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

H₃BO₃ (Carl Roth, Germany, ≥99.8%) in a stoichiometric ratio of 1:6 in an agate mortar under ambient conditions. Subsequently, the starting mixture was filled into a crucible and closed with a lid (both made of α -BN; Henze Boron Nitride Products AG, Germany), before it was placed in

Fig. 5: Rietveld refinement plot.

Fig. 6: Single-crystal IR (red) and Raman (black) spectrum of β -Y(BO₂)₃.

an 18/11 assembly. For a more detailed description of the experimental setup, the reader is referred to the corresponding literature [13–15].

The pressure of ~5.9 GPa was reached within 150 min. Afterwards, the sample was heated to 1000°C over 10 min. This temperature was maintained for 30 min before it was reduced to 400°C during the following 20 min. Subsequently, the heating was switched off and the 16 h lasting process of decompression started. The colorless reaction product was mechanically separated from the BN crucible as well as possible.

4.2 Single-crystal structure analysis

A Bruker D8 Quest Kappa diffractometer equipped with a Photon 100 detector was employed to collect the single-crystal intensity data. An Incoatec microfocus X-ray tube and a multilayer optic were used to generate monochromatized MoK $_{\alpha}$ radiation ($\lambda = 0.7107$ Å). The absorption correction was carried out with SADABS [16] before the structure was solved with SHELXT (version 2014/4) [17] and further refined with SHELXL (version 2016/6) [18] as implemented in the WINGX suite (version 2013/3) [19]. Atom labels were chosen according to β -Tb(BO₂)₃ [5].

4.3 X-ray powder diffraction

A STOE Stadi P was used to investigate the reaction product *via* X-ray powder diffraction. The flat sample was irradiated with Ge(111)-monochromatized MoK $_{\alpha}$ radiation ($\lambda = 0.7093$ Å). A Dectris Mythen 1K detector was employed to collect the diffracted radiation. Because of the strong fluorescence of yttrium caused by molybdenum radiation, a horizontal background line was subtracted from the original diffractogram before the Rietveld refinement was accomplished with TOPAS 4.2 [20].

4.4 Vibrational spectroscopy

The single-crystal IR spectrum was recorded on a Bruker Vertex 70 FT-IR spectrometer (spectral resolution 4 cm⁻¹) equipped with a Globar mid-IR source and a KBr beam splitter. The spectrometer was equipped with a mercury cadmium telluride (MCT) detector and coupled to a Bruker Hyperion 3000 microscope. The measurement covered the wavenumber range 600–4000 cm⁻¹ and was carried out in transmittance mode using a BaF₂ window and a 15× IR

objective lens. 320 scans of the sample were recorded. Data processing was accomplished with OPUS [21].

A Horiba Jobin Yvon Labram-HR-800 spectrometer was used to acquire the Raman spectrum of an arbitrarily oriented single-crystal. An area of approximately 5 μ m in diameter was excited using a 532 nm frequency-doubled Nd:YAG laser. A 50× objective lens, a 100 μ m slit, a 1000 μ m pinhole, and an optical grating with 1800 lines mm⁻¹ were used for the measurement. The scattered radiation was detected with a 1024 × 256 Andor CCD detector in the wavenumber range 100–3700 cm⁻¹. Two spectra with an acquisition time of 70 s each were averaged with LABSPEC (version 5.93.20) [22].

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References

- [1] S. C. Neumair, R. Kaindl, H. Huppertz, *J. Solid State Chem.* **2012**, *185*, 1.
- [2] M. K. Schmitt, O. Janka, R. Pöttgen, C. Benndorf, M. de Oliveira, H. Eckert, F. Pielhofer, A.-S. Tragl, R. Weihrich, B. Joachim, D. Johrendt, H. Huppertz, *Angew. Chem. Int. Ed.* **2017**, *56*, 6449.
- [3] M. K. Schmitt, H. Huppertz, *Inorg. Chem.* **2017**, *56*, DOI: 10.1021/acs.inorgchem.7b02402.
- [4] M. K. Schmitt, H. Huppertz, *Z. Naturforsch. B.* in press.
- [5] T. Nikelski, Th. Schleid, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1017.
- [6] H. Emme, T. Nikelski, Th. Schleid, R. Pöttgen, M. H. Möller, H. Huppertz, *Z. Naturforsch.* **2004**, *59b*, 202.
- [7] H. Emme, G. Heymann, A. Haberer, H. Huppertz, *Z. Naturforsch.* **2007**, *62b*, 765.
- [8] T. Nikelski, M. C. Schäfer, H. Huppertz, Th. Schleid, *Z. Kristallogr. NCS* **2008**, *223*, 177.
- [9] E. Zobetz, *Z. Kristallogr.* **1990**, *191*, 45.
- [10] A. F. Holleman, N. Wiberg, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102nd edition, De Gruyter, Berlin, **2007**.
- [11] I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244.
- [12] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192.
- [13] H. Huppertz, *Z. Kristallogr.* **2004**, *219*, 330.
- [14] D. Walker, *Am. Mineral.* **1991**, *76*, 1092.
- [15] D. Walker, M. A. Carpenter, C. M. Hitch, *Am. Mineral.* **1990**, *75*, 1020.
- [16] G. M. Sheldrick, SADABS, Bruker AXS Inc., Madison, WI (USA) **2001**.
- [17] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3.
- [18] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3.
- [19] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.
- [20] TOPAS, Bruker AXS Inc., Madison, Wisconsin (USA) **2009**.
- [21] OPUS, Bruker, Billerica, Massachusetts (USA) **2008**.
- [22] LABSPEC, Horiba Jobin Yvon GmbH, Bensheim (Germany) **2005**.