High-pressure Synthesis, Crystal Structure, and Properties of the First Ternary Zirconium Borate β-ZrB_2O_5

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Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

The high-pressure phase β-ZrB_2O_5 represents the first ternary borate in the system Zr-B-O. The compound was synthesized under high-pressure / high-temperature conditions of 7.5 GPa and 1100 °C in a Walker-type multianvil apparatus. The crystal structure was determined on the basis of single crystal X-ray diffraction data, collected at room temperature. The monoclinic zirconium borate crystallizes in the space group $P2_1/c$ with the lattice parameters a = 439.04(9), b = 691.2(2), c = 896.8(2) pm, and β = 90.96(3)°. The structure is isotypic to the high-pressure phase β-HfB_2O_5, which is built up from layers of exclusively corner-sharing BO_4 tetrahedra. Between these layers, the cations are coordinated square-antiprismatically by eight oxygen atoms.

Key words: High Pressure, Crystal Structure, Multianvil, Borate, Gadolinite

Introduction

In the last years, high-pressure / high-temperature studies in the chemistry of oxoborates led to a large variety of new polymorphs like β-MB_4O_7 (M = Mn [1], Ni [1], Cu [1], Zn [2], Ca [3], Sn [4], Hg [5]), the rare-earth *meta*-oxoborates δ-$RE(BO_2)_3$ (RE = La, Ce) [6, 7], and a new non-centrosymmetric modification of bismuth triborate, δ-BiB_3O_6 [8]. New compositions could be realized in the compounds $RE_3B_5O_{12}$ (RE = Tm–Lu) [9] and $Pr_4B_{10}O_{21}$ [10]. Furthermore, the oxoborates $RE_4B_6O_{15}$ (RE = Dy, Ho) [11 – 13], α-$RE_2B_4O_9$ (RE = Sm–Ho) [14 – 16], and the recently found HP-NiB_2O_4 [17] showed, next to new compositions, the structural feature of edge-sharing BO_4 tetrahedra. In this connection, the latter compound HP-NiB_2O_4 represents the first borate in which every BO_4 tetrahedron shares one common edge with another BO_4 tetrahedron.

To our knowledge, no ternary phases are known in the system Zr-B-O, but several quaternary phases, namely $Ni_5ZrO_4(BO_3)_2$ [18], $K_2Zr(BO_3)_2$ [19], $(Co_{1.5}Zr_{0.5})(BO_3)O$ [20], $BaZr(BO_3)_2$ [21], $Zr_3V_3B_{0.384}O_{0.576}$, and $Zr_3V_3B_{0.24}O_{0.36}$ [22] have been described. We were now able to synthesize the first ternary zirconium borate, which is built up analogously to β-HfB_2O_5 [23]. Due to the fact that β-ZrB_2O_5 is a high-pressure phase, we labeled it with the Greek character "β". Attempts to synthesize the ambient-pressure zirconium diborate "α-ZrB_2O_5" are currently made. In this publication, we report the synthetic conditions, structural details, and thermal behavior of the phase β-ZrB_2O_5 in comparison to the isotypic compound β-HfB_2O_5.

Experimental Section

β-ZrB_2O_5 was synthesized under high-pressure / high-temperature conditions of 7.5 GPa and 1100 °C. According to Eq. 1, the starting reagents were monoclinic ZrO_2 (Baddeleyite) (Strem Chemicals, Newburyport, USA, 99.9 %) and B_2O_3 (Strem Chemicals, Newburyport, USA, 99+ %), which were ground together and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint® S10, Kempten, Germany) in the molar ratio $ZrO_2 : B_2O_3 = 1 : 1$.

$$ZrO_2 + B_2O_3 \xrightarrow[1100\ °C]{7.5\ GPa} \beta\text{–}ZrB_2O_5 \qquad (1)$$

The boron nitride crucible was positioned inside the center of an 18/11 assembly, which was compressed by eight tungsten carbide cubes (TSM-10 Ceratizit, Reutte, Austria).

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Table 1. Crystal data and structure refinement for β-ZrB_2O_5.

Empirical formula	ZrB_2O_5
Molar mass, g·mol^{-1}	192.84
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Powder diffractometer	Stoe Stadi P
Radiation	MoK_α (λ = 71.073 pm)
Powder-diffraction data	
a, pm	440.21(2)
b, pm	693.15(3)
c, pm	899.24(3)
β, deg	90.93(1)
Volume, nm^3	0.27435(2)
Single crystal diffractometer	Enraf-Nonius Kappa CCD
Radiation	MoK_α (λ = 71.073 pm)
Single crystal data	
a, pm	439.04(9)
b, pm	691.2(2)
c, pm	896.8(2)
β, deg	90.96(3)
Volume, nm^3	0.2721(2)
Formula units per cell, *Z*	4
Temperature, K	293(2)
Calculated density, g·cm^{-3}	4.71
Crystal size, mm^3	$0.02 \times 0.02 \times 0.02$
Detector distance, mm	30.0
Absorption coefficient, mm^{-1}	3.9
$F(000)$, e	360
θ range, deg	3.7 to 34.8
Range in *hkl*	$-6/+7$, $-11/+10$, ± 14
Total no. reflections	2203
Independent reflections	1166 (R_{int} = 0.0352)
Reflections with $I \geq 2\sigma(I)$	969 (R_σ = 0.0437)
Absorption correction	multi-scan (SCALEPACK [45])
Data / parameters	1166 / 73
Goodness-of-fit (F^2)	1.027
Final *R* indices [$I \geq 2\sigma(I)$]	R_1 = 0.026 wR_2 = 0.054
R Indices (all data)	R_1 = 0.038 wR_2 = 0.058
Larg. diff. peak and hole, e·Å^{-3}	0.79 / −0.93

The assembly was compressed to 7.5 GPa in 3 h, using a multianvil device, based on a Walker-type module and a 1000 t press (both devices from the company Voggenreiter, Mainleus, Germany). A detailed description of the preparation of the assembly can be found in references [24–27]. The sample was heated to 1100 °C (cylindrical graphite furnace) in 10 min, kept at this temperature for 5 min, and cooled down to 750 °C in 15 min at constant pressure. Afterwards, the sample was quenched to r. t. by switching off the heating, followed by a decompression period of 9 h. β-ZrB_2O_5 was separated from the surrounding boron nitride and obtained as a colorless, air- and water-resistant, crystalline solid.

Next to β-ZrB_2O_5, the powder diffraction pattern of the product showed unreacted ZrO_2, whereas the corresponding B_2O_3 could not be determined by powder diffraction (X-ray amorphous).

Table 2. Atomic coordinates (Wyckoff site 4*e* for all atoms) and isotropic equivalent displacement parameters U_{eq} (Å^2) for β-ZrB_2O_5 (space group: $P2_1/c$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
Zr	0.00127(5)	0.11284(3)	0.67103(2)	0.00605(7)
B1	0.5271(6)	0.2299(4)	0.4230(3)	0.0072(5)
B2	0.4641(6)	0.0868(4)	0.1656(3)	0.0072(5)
O1	0.7861(4)	0.0902(2)	0.1790(2)	0.0076(3)
O2	0.3307(4)	0.8955(2)	0.1504(2)	0.0077(3)
O3	0.3477(4)	0.2212(2)	0.0540(2)	0.0082(3)
O4	0.3055(4)	0.1549(3)	0.3077(2)	0.0074(3)
O5	0.7689(4)	0.0974(2)	0.4674(2)	0.0080(3)

Crystal structure analysis

The powder diffraction pattern of monoclinic β-ZrB_2O_5 was collected with a Stoe Stadi P diffractometer, using monochromatized MoK_α (λ = 71.073 pm) radiation. The diffraction pattern of β-ZrB_2O_5 was indexed with the program ITO [28] on the basis of a monoclinic unit cell. The lattice parameters a = 440.21(2), b = 693.15(3), c = 899.24(2) pm, and β = 90.93(1)° (Table 1) were obtained from least-squares fits of the powder data. The correct indexing of the pattern was confirmed by intensity calculations [29], taking the atomic positions from the structure refinements of β-ZrB_2O_5 (Table 2). The lattice parameters determined from the powder and the single crystal data (a = 439.04(9), b = 691.2(2), c = 896.8(2) pm, and β = 90.96(3)°) agree well.

For the crystal structure analysis, small single crystals of β-ZrB_2O_5 were isolated by mechanical fragmentation and examined using a Buerger camera, equipped with an image plate system (Fujifilm BAS-1800) in order to establish both symmetry and suitability for the collection of intensity data. Single crystal intensity data were collected at r. t. from a colorless crystal using an Enraf-Nonius Kappa CCD with graphite-monochromatized MoK_α (λ = 71.073 pm) radiation. A multi-scan absorption correction (SCALEPACK [46]) was applied to the intensity data. According to the systematic extinctions $h0l$ with $l \neq 2n$, $0k0$ with $k \neq 2n$, and $00l$ with $l \neq 2n$, the monoclinic space group $P2_1/c$ (no. 14) was derived. All relevant details of the data collections and evaluations are listed in Table 1. The starting positional parameters were taken from the structural refinement of β-HfB_2O_5 [23]. Structure solution and parameter refinement with anisotropic displacement parameters for all atoms (full-matrix least-squares against F^2) were successfully performed with the SHELXS/L-97 software suite [30, 31]. The final difference Fourier synthesis did not reveal any significant residual peaks (see Table 1). The positional parameters, anisotropic displacement parameters, interatomic distances, and angles are listed in Tables 2–5.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum

Table 3. Anisotropic displacement parameters U_{ij} (Å^2) for β-ZrB_2O_5 (space group $P2_1/c$).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr	0.0064(2)	0.0059(2)	0.0059(2)	0.00001(7)	0.00026(7)	0.00003(8)
B1	0.008(2)	0.007(2)	0.007(2)	−0.0015(8)	−0.0002(9)	−0.0001(9)
B2	0.008(2)	0.007(2)	0.007(2)	−0.0003(8)	0.0016(9)	0.0008(9)
O1	0.0071(7)	0.0084(8)	0.0071(7)	0.0013(6)	0.0001(6)	0.0000(6)
O2	0.0084(7)	0.0065(8)	0.0083(7)	0.0003(6)	0.0016(6)	0.0005(6)
O3	0.0083(7)	0.0076(8)	0.0088(7)	0.0011(6)	0.0010(6)	0.0019(6)
O4	0.0080(7)	0.0076(7)	0.0065(7)	0.0003(6)	−0.0001(6)	−0.0003(6)
O5	0.0091(7)	0.0071(8)	0.0077(7)	0.0013(6)	0.0003(6)	0.0008(6)

Table 4. Interatomic distances (pm) calculated with the single crystal lattice parameters of β-ZrB_2O_5 with standard deviations in parentheses.

Zr–O5a	207.9(2)	B1–O5	145.3(3)
Zr–O1a	214.6(2)	B1–O3	146.5(3)
Zr–O5b	217.1(2)	B1–O2	146.5(3)
Zr–O2	218.4(2)	B1–O4	150.1(3)
Zr–O3	218.7(2)		**⌀ = 147.1**
Zr–O1b	226.1(2)		
Zr–O4a	229.8(2)	B2–O1	141.7(3)
Zr–O4b	241.0(2)	B2–O2	145.2(3)
	⌀ = 221.7	B2–O3	145.2(3)
		B2–O4	153.6(3)
			⌀ = 146.4

Table 5. Interatomic angles (deg) calculated with the single crystal lattice parameters of β-ZrB_2O_5 with standard deviations in parentheses.

O2–B1–O4	103.7(2)	O2–B2–O4	99.8(2)
O3–B1–O4	106.3(2)	O3–B2–O4	102.5(2)
O5–B1–O2	107.5(2)	O2–B2–O3	112.4(2)
O5–B1–O3	109.0(2)	O1–B2–O3	112.8(2)
O2–B1–O3	114.8(2)	O1–B2–O4	113.0(2)
O5–B1–O4	115.7(2)	O1–B2–O2	115.0(2)
	⌀ = 109.5		**⌀ = 109.3**

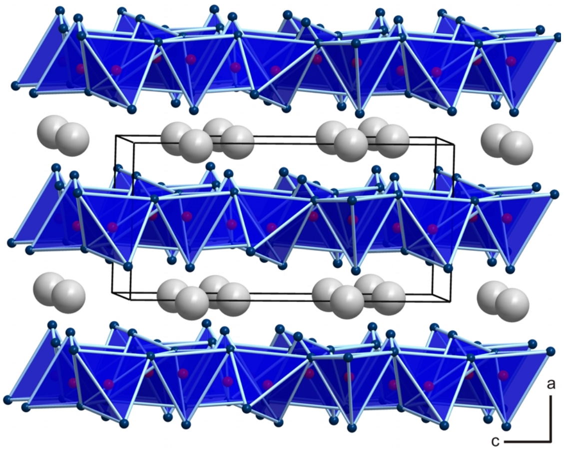

Fig. 1 (color online). A view of the crystal structure of β-ZrB_2O_5 along [010], exhibiting layers of BO_4 tetrahedra and Zr^{4+} ions.

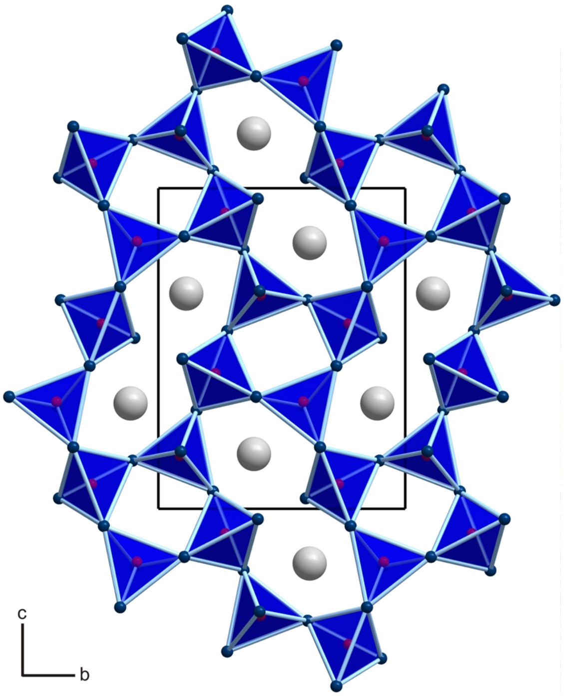

Fig. 2. (color online). Top view along [100] of one borate layer in β-ZrB_2O_5.

Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-418931.

Results and Discussion

The crystal structure of β-ZrB_2O_5 is built up exclusively from corner-sharing BO_4 tetrahedra (Q^3), forming layers separated by zirconium cations (Fig. 1). Fig. 2 gives a view of the crystal structure along [100], showing eight-membered rings, occupied by the Zr^{4+} ions and four-membered rings remaining empty. These rings are interconnected to layers, that spread out in the *bc* plane. Fig. 3 gives a view of the coordination of the Zr^{4+} ions, which are surrounded by eight oxygen atoms forming a square antiprism. Inside the framework of BO_4 tetrahedra, the B–O dis-

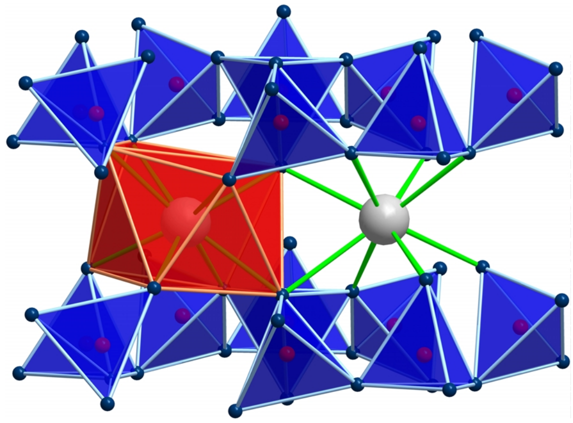

Fig. 3. (color online). Zr^{4+} ions in β-ZrB_2O_5 in a distorted square-antiprismatic coordination.

tances of the two crystallographically distinguishable BO_4 groups vary between 142 and 154 pm (Table 4). The average B–O bond length of 146.8 pm corresponds to the known average value of 147.6 pm for boron-oxygen distances in BO_4 tetrahedra [32, 33]. The O–B–O bond angles range from 99.8 to 115.7° with a mean value of 109.4°. The application of Liebau's nomenclature for silicates [34] to the arrangement of tetrahedra in the structure of β-ZrB_2O_5 leads to the formula $\mathrm{Zr}\{\mathrm{uB},1^2_\infty\}[^4\mathrm{B_2O_5}]$, representing an unbranched "Vierer" single layer. The Zr–O distances vary from 208 to 241 pm with an average value of 221.7 pm. This is slightly longer than the average Zr–O distance of 219.8 pm in zirconia ($ZrSiO_4$) [35] or of 219.5 pm in $ZrMo_2O_8$ [36], which both exhibit zirconium in eight-fold coordination as well.

A comparison of β-ZrB_2O_5 to the isotypic phase β-HfB_2O_5 shows that the bond lengths and angles of the two phases are nearly identical. This is in accord with the similar ionic radii of Zr^{4+} (98 pm) and Hf^{4+} (97 pm) in an eightfold oxygen-coordination. Accordingly, the lattice parameters of β-ZrB_2O_5 (a = 439.04(9), b = 691.2(2), c = 896.8(2) pm, and β = 90.96(3)°) are nearly equal to those of β-HfB_2O_5 (a = 438.48(9), b = 690.60(2), c = 897.60(2) pm, and β = 90.76(3)°).

A close comparison of the arrangement of the BO_4 tetrahedra in the isotypic phases β-MB_2O_5 (M = Zr, Hf) with other structures show that in minerals of the gadolinite group the topology of the tetrahedra is virtually identical. A more detailed description, including a discussion of the related structures, can be found in reference [23].

Table 6. Charge distribution in β-ZrB_2O_5, calculated with the bond length / bond strength (ΣV) [37, 38] and the CHARDI concept (ΣQ) [39].

	Zr	B1	B2	O1	O2	O3	O4	O5
ΣQ	+3.87	+3.06	+3.13	−1.87	−2.09	−2.09	−2.00	−2.02
ΣV	+4.01	+2.97	+3.02	−1.93	−2.10	−2.09	−1.81	−2.07

The calculation of bond valence sums for β-ZrB_2O_5 using the bond length / bond strength [37, 38] and the CHARDI concept (*char*ge *di*stribution in solids according to Hoppe [39]) confirmed the formal ionic charges resulting from the single crystal structure analysis. Table 6 shows the values for each atom, which are in agreement within the limits of both concepts.

Furthermore, we calculated the MAPLE value (*Ma*delung *P*art of *L*attice *E*nergy according to Hoppe [40 – 42]) of β-ZrB_2O_5 in order to compare it with the sum of the MAPLE values for the binary components ZrO_2 (Baddeleyite) [43] and the high-pressure modification B_2O_3-II [44] [ZrO_2 (12713 kJ mol^{-1}) + B_2O_3-II (21938 kJ mol^{-1})]. The calculated value (34651 kJ mol^{-1}) for β-ZrB_2O_5 and the MAPLE value obtained from the sum of the binary oxides (34661 kJ mol^{-1}) tally well (deviation 0.03 %).

Thermal behavior of β-ZrB₂O₅

In situ temperature-programmed X-ray powder diffraction experiments were carried out on a Stoe Stadi P powder diffractometer (MoK_α radiation, λ = 71.073 pm) with a computer controlled Stoe furnace. The sample was enclosed in a quartz glass capillary and heated from r. t. up to 500 °C in steps of 100 °C, and from 500 to 1100 °C and back to 500 °C in steps of 50 °C. Below 500 °C, the temperature shift per range was again 100 °C. The heating rate was set

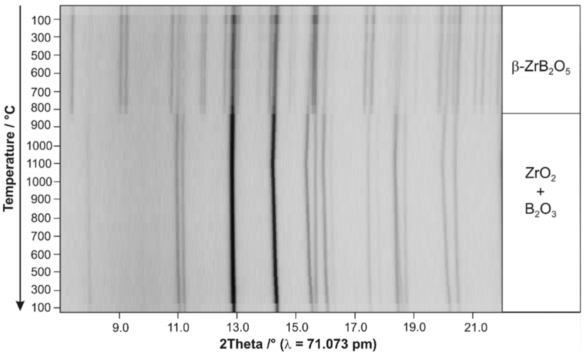

Fig. 4. Temperature-programmed X-ray powder diffraction patterns following the decomposition of β-ZrB_2O_5.

to 50 °C/min. After each step, a diffraction pattern was recorded over the angular range $7° \leq 2\theta \leq 22°$. Fig. 4 shows that β-ZrB_2O_5 is stable up to 800 °C and decomposes into monoclinic ZrO_2 (Baddeleyite) and presumably B_2O_3 beyond this temperature. This behavior was also observed for the isotypic hafnium borate β-HfB_2O_5, which decomposed into HfO_2 and B_2O_3 at a temperature of 800 – 850 °C [23].

Conclusions

High-pressure / high-temperature conditions led to the formation of the first ternary compound β-ZrB_2O_5 in the system Zr-B-O. Under normal pressure conditions, glasses are often the favored products of reactions in oxoborate chemistry. As demonstrated in this work, high-pressure / high-temperature conditions can force the formation of a crystalline product. This is supported by further examples like the synthesis of β-SnB_4O_7 [4], the first crystalline borate in the system Sn-B-O, for which previously only glasses were known. To our knowledge, no crystalline or glassy compound is known in the system Zr-B-O until now. Thus, β-ZrB_2O_5 represents the first ternary zirconium borate. In earlier work, the high-pressure / high-temperature strategy was successful in the system Hf-B-O, for which no ternary phases had been known [23]. Through this approach, we hope to get access to other systems in oxoborate chemistry, for which no or only glass-forming compounds exist until now.

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[1] J.S. Knyrim, J. Friedrichs, S. Neumair, F. Roeßner, Y. Floredo, S. Jakob, D. Johrendt, R. Glaum, H. Huppertz, *Solid State Sci.* **2008**, *10*, 168.

[2] H. Huppertz, G. Heymann, *Solid State Sci.* **2003**, *5*, 281.

[3] H. Huppertz, *Z. Naturforsch.* **2003**, *58b*, 257.

[4] J.S. Knyrim, F.M. Schappacher, R. Pöttgen, J. Schmedt auf der Günne, D. Johrendt, H. Huppertz, *Chem. Mater.* **2007**, *19*, 254.

[5] H. Emme, M. Weil, H. Huppertz, *Z. Naturforsch.* **2005**, *60b*, 815.

[6] G. Heymann, T. Soltner, H. Huppertz, *Solid State Sci.* **2006**, *8*, 821.

[7] A. Haberer, G. Heymann, H. Huppertz, *Z. Naturforsch.* **2007**, *62b*, 759.

[8] J.S. Knyrim, P. Becker, D. Johrendt, H. Huppertz, *Angew. Chem.* **2006**, *118*, 8419; *Angew. Chem. Int. Ed.* **2006**, *45*, 8239.

[9] H. Emme, M. Valldor, R. Pöttgen, H. Huppertz, *Chem. Mater.* **2005**, *17*, 2707.

[10] A. Haberer, G. Heymann, H. Huppertz, *J. Solid State Chem.* **2007**, *180*, 1595.

[11] H. Huppertz, B. von der Eltz, *J. Am. Chem. Soc.* **2002**, *124*, 9376.

[12] H. Huppertz, *Z. Naturforsch.* **2003**, *58b*, 278.

[13] H. Huppertz, H. Emme, *J. Phys.: Condens. Matter* **2004**, *16*, 1283.

[14] H. Emme, H. Huppertz, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2165.

[15] H. Emme, H. Huppertz, *Chem. Eur. J.* **2003**, *9*, 3623.

[16] H. Emme, H. Huppertz, *Acta Crystallogr.* **2005**, *C61*, i29.

[17] J. S. Knyrim, F. Roeßner, S. Jakob, D. Johrendt, I. Kinski, R. Glaum, H. Huppertz, *Angew. Chem.* **2007**, *119*, 9256; *Angew. Chem. Int. Ed.* **2007**, *46*, 9097.

[18] K. Bluhm, Hk. Müller-Buschbaum, *J. Less-Common Met.* **1989**, *147*, 133.

[19] A. Akella, D. A. Keszler, *Inorg. Chem.* **1994**, *33*, 1554.

[20] A. Utzolino, K. Bluhm, *Z. Naturforsch.* **1995**, *50b*, 1653.

[21] V. Hornebecq; P. Gravereau, J.P. Chaminade, E. Lebraud, *Mater. Res. Bull.* **2002**, *37*, 2165.

[22] A. B. Riabov, V. A. Yartys’, B. C. Hauback, P. W. Guegan, G. Wiesinger, I. R. Harris, *J. Alloys Compd.* **1999**, *293*, 93.

[23] J. S. Knyrim, H. Huppertz, *J. Solid State Chem.* **2007**, *180*, 742.

[24] V. F. Ross, J. O. Edwards, *The Structural Chemistry of the Borates*, Wiley, New York **1967**.

[25] D. Walker, M. A. Carpenter, C. M. Hitch, *Am. Mineral.* **1990**, *75*, 1020.

[26] D. Walker, *Am. Mineral.* **1991**, *76*, 1092.

[27] H. Huppertz, *Z. Kristallogr.* **2004**, *219*, 330.

[28] J. W. Visser, *J. Appl. Crystallogr.* **1969**, *2*, 89.

[29] Stoe & CIE GmbH, WinX^{POW} Software, Darmstadt (Germany) **1998**.

[30] G. M. Sheldrick, SHELXS-97 and SHELXL-97 – Program Suite for the Solution and Refinement of Crystal Structures; University of Göttingen, Göttingen (Germany) **1997**.

[31] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[32] E. Zobetz, *Z. Kristallogr.* **1990**, *191*, 45.

[33] F. C. Hawthorne, P. C. Burns, J. D. Grice in: *Boron: Mineralogy, Petrology and Geochemistry*, 2nd ed., (Eds.: E. S. Grew, L. M. Anovitz), Mineralogical Society of America, Washington **1996**, Vol. 33, pp 41.

[34] F. Liebau, *Structural Chemistry of Silicates*, Springer, Berlin **1985**.

[35] L. W. Finger, *Carnegie Institution of Washington: Yearbook* **1974**, *73*, 544.

[36] R. F. Klevtsova, L. A. Glinskaya, E. S. Zolotova, P. V. Klevtsov, *Sov. Phys. Dokl.* **1989**, *34*, 185.

[37] I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244.

[38] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B47*, 192.

[39] R. Hoppe, S. Voigt, H. Glaum, J. Kissel, H. P. Müller, K. J. Bernet, *J. Less-Common Met.* **1989**, *156*, 105.

[40] R. Hoppe, *Angew. Chem.* **1966**, *78*, 52.

[41] R. Hoppe, *Angew. Chem.* **1970**, *82*, 7.

[42] R. Hübenthal, MAPLE, program for the calculation of MAPLE values (version 4) University of Gießen, Gießen (Germany) **1993**.

[43] F. J. Torres, J. M. Amigo, J. Alarcon, *J. Solid State Chem.* **2003**, *173*, 40.

[44] C. T. Prewitt, R. D. Shannon, *Acta Crystallogr.* **1968**, *B41*, 244.

[45] Z. Otwinowski, W. Minor, *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A (Eds.: C. W. Carter Jr, R. M. Sweet), Academic Press, New York **1997**, pp. 307.