High-pressure Synthesis and Crystal Structure of the Vanadium Orthoborate VBO_3

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

The vanadium orthoborate VBO_3 was synthesized under high-pressure / high-temperature conditions of 7.5 GPa and 1250 °C in a Walker-type multianvil apparatus. The crystal structure was determined on the basis of single crystal X-ray diffraction data, collected at r. t. The title compound crystallizes in the trigonal calcite structure, space group $R\bar{3}c$, with the lattice parameters $a = 462.0(1)$ and $c = 1450.9(3)$ pm. Within the trigonal planar BO_3 groups, the B–O distance is 138.8(3) pm. The vanadium atoms have a slightly distorted octahedral oxygen coordination (V–O: 202.3(2) pm).

Key words: High Pressure, Crystal Structure, Multianvil, Orthoborate, Calcite

Introduction

Over the past years, high-pressure / high-temperature studies in the chemistry of rare-earth oxoborates led to a large variety of new compositions like $RE_2B_4O_9$ (RE = Nd, Sm–Ho [1 – 3]), $RE_4B_6O_{15}$ (RE = Dy, Ho [4 – 6]), $RE_3B_5O_{12}$ (RE = Tm–Lu [7]), and $Pr_4B_{10}O_{21}$ [8]. We now focussed on the high-pressure / high-temperature synthesis of new transition metal oxoborates. These compounds often tend to form glasses, but it was possible to obtain crystalline phases under high-pressure conditions. The experiments resulted in various new compounds like β-MB_4O_7 (M = Mn [9], Ni [9], Cu [9], Zn [10], Hg [11]), β-MB_2O_5 (M = Hf [12], Zr [13]) and the recently found HP-NiB_2O_4 [14]. 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.

Until now, no high-pressure / high-temperature studies were carried out on vanadium oxoborates. Since MB_4O_7 appeared to be a very stable composition under these conditions, VO_2 and B_2O_3 in the ratio 1 : 2 were chosen as educts. Contrary to our expectations, the synthesis produced a new, still unknown vanadium oxoborate, and also vanadium orthoborate VBO_3 as a by-product, which adopts the calcite structure type (space group $R\bar{3}c$, no. 167).

Many orthoborates are known to crystallize in the trigonal calcite structure, exhibiting only isolated BO_3 units. That holds for the rare-earth (RE) orthoborates β-$REBO_3$ (RE = Lu [15] and Yb [16]) as well as for $AlBO_3$ [17] and $InBO_3$ [18]. There are also several isostructural transition metal orthoborates, including $FeBO_3$ [19], $ScBO_3$ [20], and $TiBO_3$ [21]. The synthesis and the structural characteristics of $TiBO_3$ and of the compounds $CrBO_3$ and VBO_3 were previously described by Schmid in 1964 [22]. These results were based on powder samples. To characterize this material more completely, a single-crystal structure refinement of VBO_3 is reported in the following.

Experimental Section

According to Schmid, the synthesis of VBO_3 can be carried out under ambient-pressure conditions. B_2O_3, V_2O_5, V, and VCl_2 were heated to 900 °C in a sealed quartz tube, yielding VBO_3 as hexagonal red platelets [22].

In our own study, VBO_3 was synthesized as a by-product to another still unknown vanadium borate under high-pressure / high-temperature conditions of 7.5 GPa and 1250 °C. The starting reagents were VO_2 (Merck KGaA, Darmstadt, Germany, 99+ %) and B_2O_3 (Strem Chemicals, Newburyport, USA, 99+ %), which were ground to-

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gether and filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint® S10, Kempten, Germany) in the ratio $VO_2 : B_2O_3 = 1:2$.

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). 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 [23–26]. The sample was heated to 1250 °C (cylindrical graphite furnace) in 10 min, kept at this temperature for 20 min, and cooled down to 750 °C in 60 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. VBO_3, together with the other still unknown vanadium borate, could be separated from the surrounding boron nitride. Small red brown air- and water-resistant crystals of VBO_3 were isolated near the crucible wall.

The powder diffraction pattern of the sample clearly identified VBO_3 as a product of the high-pressure synthesis. The proportion of VBO_3 in the sample amounts to approximately 30 %. Elemental analysis of the VBO_3 crystals *via* energy dispersive X-ray spectroscopy (Jeol JFM-6500F, Jeol. Ltd, Tokyo, Japan) led to 22(1) % V (20.0 %), 22(2) % B (20.0 %), and 56(2) % O (60.0 %) (theoretical values in parentheses).

Crystal structure analysis

The powder diffraction pattern of trigonal VBO_3 was collected with a Stoe Stadi P diffractometer, using monochromatized MoK_α radiation (λ = 71.073 pm). The diffraction pattern of VBO_3 was indexed with the program ITO [27] on the basis of a hexagonal unit cell. The lattice parameters a = 462.2(1) and c = 1452.0(3) pm (Table 1) were obtained from least-squares fits of the powder data. The correct indexing of the pattern was confirmed by intensity calculations [28], taking the atomic positions from the structure refinements of VBO_3 (Table 2). The data obtained by Schmid (a = 457.3(5) and c = 1432(1) pm) [22] differ considerably. The lattice parameters, determined from the powder and single-crystal data, which we collected (a = 462.0(1) and c = 1450.9(3) pm), are in mutual agreement.

For the crystal structure analysis, small single crystals of VBO_3 were isolated by mechanical fragmentation and examined through a Buerger precession 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 red brown crystal, using an Enraf-Nonius Kappa CCD with graphite monochromatized MoK_α radiation (λ = 71.073 pm). An absorption correction was applied to the intensity data (Table 1). According to the systematic extinctions, the space groups $R3c$ (no. 161) and $R\bar{3}c$ (no. 167) were derived. Structure solution and parameter refinement with anisotropic displacement parameters for all atoms (full-matrix least-squares against F^2) were successfully performed in space group $R\bar{3}c$ (no. 167) with the SHELX-97 software suite [29, 30]. All relevant details of the data collection and evaluation are listed in Table 1. The final difference Fourier synthesis did not reveal any significant residual peaks. The positional parameters, anisotropic

Table 1. Crystal data and structure refinement for VBO_3.

Empirical formula	VBO_3
Molar mass, g · mol^{-1}	109.75
Crystal system	trigonal
Space group	$R\bar{3}c$ (no. 167)
Powder diffractometer	Stoe Stadi P
Radiation; λ, pm	MoK_α; 71.073
Powder-diffraction data	
a, pm	462.2(1)
c, pm	1452.0(3)
Volume, nm^3	0.26859(7)
Single crystal diffractometer	Enraf-Nonius Kappa CCD
Radiation; λ, pm	MoK_α; 71.073
Single-crystal data	
a, pm	462.0(1)
c, pm	1450.9(3)
Volume, nm^3	0.26824(8)
Formula units per cell, Z	6
Temperature, K	293(2)
Calculated density, g · cm^{-3}	4.08
Crystal size, mm^3	0.04 × 0.02 × 0.02
Detector distance, mm	30.0
Absorption coefficient, mm^{-1}	5.2
$F(000)$, e	312
θ range, deg.	3.13 to 37.79
Range in *hkl*	±6, ±6, ±20
Absorption correction	multi-scan (Scalepack [39])
Total no. reflections	811
Independent reflections	88
R_{int}	0.036
Reflections with $I \geq 2\sigma(I)$	87
R_σ	0.017
Data/parameters	88/11
Goodness-of-fit (F^2)	1.254
Final R_1/wR_2 [$I \geq 2\sigma(I)$]	0.041/0.112
Final R_1/wR_2 (all data)	0.042/0.112
Larg. diff. peak/hole, e · Å^{-3}	2.88/−0.49

Table 2. Atomic coordinates and anisotropic equivalent displacement parameters U_{eq} (Å^2) for VBO_3 (space group $R\bar{3}c$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff position	x	y	z	U_{eq}
V	6b	0	0	0	0.0050(8)
B	6a	0	0	1/4	0.005(2)
O	18e	0.6997(7)	x	1/4	0.0064(10)

Table 3. Anisotropic displacement parameters U_{ij} ($Å^2$) for VBO_3 (space group $R\bar{3}c$).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	0.0050(9)	0.0050(9)	0.005(1)	0	0	0.0025(4)
B	0.006(3)	0.006(3)	0.004(4)	0	0	0.003(2)
O	0.008(2)	0.008(2)	0.005(2)	0.0004(5)	−0.0004(5)	0.004(2)

Table 4. Interatomic distances (pm) and angles (deg) calculated with the single-crystal lattice parameters of VBO_3 with standard deviations in parentheses.

V–O (6×)	202.3(2)	O–V–O	92.06(5)
B–O (3×)	138.8(3)	O–V–O	87.94(5)
		O–V–O	180
O–B–O	120	V–O–V	125.7(2)

displacement parameters, and interatomic distances and angles are listed in Tables 2 – 4.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum 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-419132.

Results and Discussion

The general features of the crystal structure of VBO_3 are the same as those described for calcite, $CaCO_3$, as was predicted from powder diffraction data by Schmid [22]. The structure is composed of alternating layers of vanadium atoms and trigonal planar BO_3 units (Fig. 1). The vanadium atoms occupy distorted octahedral sites. The connectivity between the VO_6 and BO_3 groups is based only on corner sharing. Each VO_6 octahedron shares corners with three other VO_6 octahedra and with three BO_3 units. The BO_3 triangles have D_3 point symmetry and are sandwiched between the VO_6 layers (Fig. 2). All BO_3 units in a given layer of VBO_3 have an identical orientation. The alignment alternates from layer to layer by a rotation of 60° around the trigonal axis. The B–O bond length of 138.8(3) pm is slightly increased in comparison to similar calcite materials, *i. e.* $AlBO_3$ (137.96(4) pm) [17], β-$YbBO_3$ (137.8(4) pm) [16], and $FeBO_3$ (137.9(2) pm) [19]; nevertheless, it is still in a typical range for BO_3 groups.

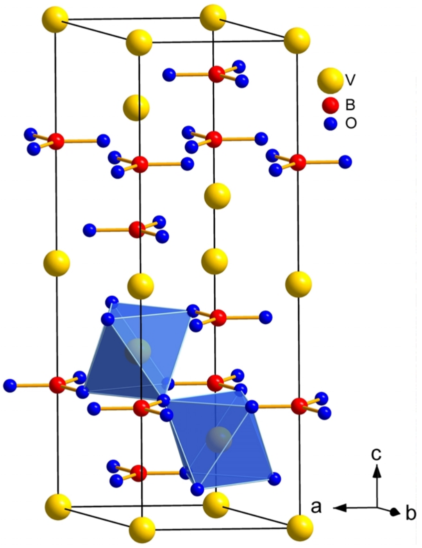

Fig. 1 (color online). Schematic drawing of the unit cell of VBO_3, depicting the VO_6 octahedra and the trigonal planar BO_3 units.

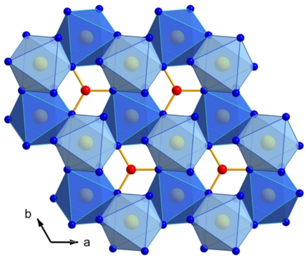

Fig. 2 (color online). View along the [001] axis of VBO_3, illustrating the connection of the layers. Down the *c* axis, the dark-blue octahedra represent the first layer, the BO_3 units the second one, and the light-blue octahedra generate the lowest layer in the diagram.

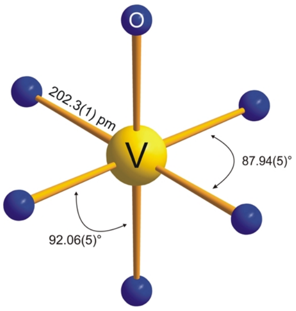

Fig. 3 (color online). Distortion of the VO_6 octahedron in VBO_3.

The VO_6 octahedron is elongated along the *c* axis leading to O–V–O angles of 92.1(1)° and 87.9(1)° (Fig. 3). This deviation from O_h symmetry occurs in other isostructural borates as well, *i. e.* in $ScBO_3$ (92.3(1)°) [20], in $FeBO_3$ (91.8(1)°) [19], and in β-$YbBO_3$ (92.9(1)°) [16].

As expected from the smaller ionic radius of octahedrally coordinated V^{3+} (78 pm) in comparison to Sc^{3+} (88.5 pm) and Yb^{3+} (100.8 pm), the V–O distance of 202.3(2) pm is noticeably shorter than the distances in the corresponding ytterbium and scandium orthoborates (Yb–O: 224.4(2) pm, Sc–O: 212.0(1) pm) [16,20]. The ionic radius of Fe^{3+} (78.5 pm) is nearly identical to that of V^{3+}, which leads to a comparable Fe–O distance of 202.8(1) pm in $FeBO_3$ [19].

The calculation of bond valence sums for VBO_3 with the bond-length/bond-strength (BLBS) [31,32] and CHARDI concept (*char*ge *di*stribution in solids according to Hoppe [33]) confirmed the formal ionic charges, resulting from the single crystal structure analysis [ΣV (BLBS): +2.82 (V), +2.87 (B), −1.89 (O) and ΣQ (CHARDI): +3.00 (V), +3.00 (B), −2.00 (O)].

Furthermore, we calculated the MAPLE value (*ma*delung *p*art of *l*attice *e*nergy according to Hoppe [34–36]) of VBO_3 in order to compare it with the sum of the MAPLE values for the binary components V_2O_3 (Karelianite) [37] and the high-pressure modification B_2O_3-II [38] [0.5 V_2O_3 (17289 $kJ\,mol^{-1}$) + 0.5 B_2O_3-II (21938 $kJ\,mol^{-1}$)]. The calculated value (19531 $kJ\,mol^{-1}$) for VBO_3 and the MAPLE value obtained from the sum of the binary oxides (19614 $kJ\,mol^{-1}$) tally well (deviation 0.4 %).

Conclusions

Under high-pressure/high-temperature conditions VO_2 and B_2O_3 react to give crystals of VBO_3, from which single crystal diffraction data could be collected. By contrast under normal-pressure conditions, the products of reactions in oxoborate chemistry are often glasses. As demonstrated in this work, high-pressure/high-temperature conditions can force the formation of a crystalline product, allowing for the first single-crystal structure determination of VBO_3. The second product of the reaction is as yet unidentified.

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