

Synthesis and Crystal Structure of the First Fully Characterized Vanadoborate $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$

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Single crystals of synthetic $\text{Na}_3\text{VB}_6\text{O}_{13}$ were obtained by heating a mixture of Na_2CO_3 , H_2O , V_2O_5 , and H_3BO_3 ; its formula has been determined by the resolution of the structure from X-ray diffraction data. The compound is orthorhombic, space group $P2_12_12_1$; the unit cell parameters are $a = 7.723(7)$, $b = 10.155(4)$, $c = 12.505(4)$ Å, $Z = 4$. The crystal structure was solved from 1535 reflections until $R = 0.029$; it contains hexaborate units formed by three triangular BO_3 (3Δ) and three tetrahedral BO_4 ($3T$). These hexaborate groups are joined together to form sheets which are linked by VO_4 tetrahedra leading to a three-dimensional network. The shorthand notation of the vanadoborate ion is $6: \infty^3(3\Delta + 3T) + \text{VO}_4$. The sodium atoms are inside the channels that exist in the compound, whose structural formula may be written $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$. This compound melts incongruently; powder may be obtained by annealing a mixture of $\text{Na}_2\text{B}_4\text{O}_7$ and V_2O_5 at 630°C . It is the first vanadoborate for which the formula and the structure have been unambiguously established. © 2000 Academic Press

INTRODUCTION

In the past years, many papers have been published on borate materials because of their various, interesting properties. A recent review (1) reports the numerous borates that are used in nonlinear optics; three classes are distinguished: borates containing only triangular BO_3 groups, those containing BO_3 and tetrahedral BO_4 groups, and those where BO_3 groups and NbO_6 octahedra are combined. On this basis, it seemed interesting to try to obtain new materials associating borate and $M(\text{O})_x$ group ($M = \text{Mo}, \text{W}, \text{P}, \text{As}, \text{V}, \dots$) in the anion. For example, many borophosphates have been recently synthesized using hydrothermal conditions and their structures have been established (2); others have been obtained by standard solid-state reaction technique (3, 4). Few boron arsenates have been reported as

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$\text{Pb}_6(\text{AsO}_4)[\text{B}(\text{AsO}_4)_4]$ and PbAsBO_5 (5). Vanadoborates have been mentioned in studies of $\text{Na}_2\text{B}_4\text{O}_7\text{-V}_2\text{O}_5$ (6), $\text{NaBO}_2\text{-V}_2\text{O}_5$ (7), and $\text{H}_3\text{BO}_3\text{-NaVO}_3\text{-HNO}_3\text{-H}_2\text{O}$ systems (8), regarding the reaction of lithium borates with vanadium pentoxide (9) and with cesium (10). However, no structure of any hydrated or anhydrous alkaline vanadoborate has been established, which may confirm the proposed formula; only some unindexed X-ray diffraction powder patterns were given, leaving a serious doubt about their existence. The compounds Ni_2VBO_5 (11) and $\text{Ni}_5\text{VB}_2\text{O}_{10}$ (12), which belong to the ludwigite type ($M', M'' \dots$) $_3\text{O}_2\text{BO}_3$, where the metal ions ($M', M'' \dots$) can be di- or trivalent, are not considered because vanadium has an oxidation state different from five. We have undertaken the study of sodium vanadoborates starting from the results published on the $\text{NaBO}_2\text{-V}_2\text{O}_5$ binary system (7); two compounds were described: $3\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 3\text{B}_2\text{O}_3$ ($\text{Na}_3\text{V}_2\text{B}_3\text{O}_{11}$) and $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot \text{B}_2\text{O}_3$ (NaV_2BO_7) which were claimed to melt congruently at 840 and 630°C , respectively. However, we did not obtain pure phases corresponding either to these compositions or to the $2\text{Li}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{B}_2\text{O}_3$ ($\text{Li}_4\text{V}_2\text{B}_4\text{O}_{13}$) composition which was previously given (9). So, we started to explore the $\text{Na}_2\text{O-V}_2\text{O}_5\text{-B}_2\text{O}_3$ system using all the solid state methods, especially single-crystal X-ray diffraction, which permitted us to establish with certainty the existence and formula of a compound.

EXPERIMENTAL

Single crystals of the title compound were isolated from a mixture containing reagent grades $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, V_2O_5 , and H_3BO_3 in the molar ratio 3 : 2 : 6, which was melted at 720°C , slowly cooled down to 400°C at $0.1^\circ\text{C}/\text{min}$, and then cooled down to room temperature at $1^\circ\text{C}/\text{min}$. This compound was also characterized by X-ray powder diffraction (Siemens D5000 diffractometer; $\lambda\text{CuK}\alpha_1 = 1.5406$ Å) and by thermal analysis using a Setaram TGDTA 92 apparatus (platinum crucibles; heating rate of $600^\circ\text{C}/\text{h}$, in air; sample



amounts ~40 mg). Analysis of some particles was performed by energy dispersion spectroscopy (EDS) with a Link Isis (Oxford) apparatus; only the sodium and vanadium atoms could be detected. The ratio Na/V was always equal to three.

STRUCTURAL STUDY

A colorless single crystal was chosen from the preparation, which was clearly biphased. Crystal data and conditions of intensity collections are given in Table 1. The formula corresponding to the nominal composition of the mixture was Na₃V₂B₃O₁₁ (19 atoms). However, direct methods allowed us to easily localize the positions of 21 atoms in general positions of the $P2_12_12_1$ group. The refinement with isotropic thermal parameters, using the SHELX-76 program (14), led to $R = 0.167$ and $R_w = 0.208$. The positions of two other atoms were found using Fourier difference maps, and the reliability factors got down to 0.063 and 0.059, respectively. Therefore, the studied compound had to contain 23 atoms; their chemical nature was easily determined when the oxygenated polyhedra were considered. Thus, the correct formula for the compound was found to be Na₃VB₆O₁₃. Due to the low value of the

TABLE 1
Crystal Data and Intensity Collection Conditions for Na₃[B₆O₉(VO₄)]

Formula weight (g/mol)	392.765
Space group	$P2_12_12_1$ (No. 19)
Unit cell parameters	$a = 7.723(7)$ Å; $b = 10.155(4)$ Å; $c = 12.505(4)$ Å
V ; Z	981(1) Å ³ ; 4
Density (g/cm ³)	$D_x = 2.66(1)$
Diffractometer	CAD4 (Enraf-Nonius)
Temperature	298 K
Radiation	MoK α , graphite monochromated $\lambda = 0.71069$ Å
Scattering factors	Neutral atoms (13)
Scan type	θ - 2θ
θ range (°)	2–37
Standard reflections	212; $-1-41$; $2-25$
Range in h, k, l	$-10 \leq h \leq 10$; $-14 \leq k \leq 14$; $0 \leq l \leq 17$
Maximum scan time	60 s
Period of intensity control	7200 s
Reflections collected	6045
Reflections with $I > 3\sigma(I)$	5469
Linear absorption coefficient	13.01 cm ⁻¹
Averaged reflections ($I > 3\sigma(I)$)	1535
R_{int}	0.039
Weighing scheme	$1/\sigma^2(F)$
Number of variables	209
R	0.029
R_w	0.034

TABLE 2
Final Atomic Coordinates and Equivalent Thermal Parameters B_{eq} (Å²) of Na₃[B₆O₉(VO₄)] with e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq}
V	0.04796(7)	0.50738(6)	0.24833(5)	0.83(1)
B(1)	-0.0317(7)	0.3698(4)	-0.0752(4)	0.6 (1)
B(2)	-0.0305(7)	0.6298(4)	-0.0743(4)	0.6 (1)
B(3)	-0.2248(4)	0.4988(5)	0.0590(3)	0.56(6)
B(4)	-0.3009(9)	0.2746(4)	-0.0054(5)	0.6 (1)
B(5)	-0.3010(9)	0.7261(4)	-0.0049(5)	0.8 (1)
B(6)	0.0961(4)	0.4998(5)	-0.2226(3)	0.68(7)
Na(1)	0.2315(3)	0.2114(2)	0.7620(2)	1.42(5)
Na(2)	0.1308(2)	0.4980(2)	0.5246(1)	1.86(4)
Na(3)	0.2639(3)	0.2208(2)	0.2617(2)	1.39(5)
O(1)	-0.1104(3)	0.5001(3)	-0.0391(2)	0.48(4)
O(2)	0.0363(5)	0.6165(2)	-0.1839(3)	0.86(7)
O(3)	0.2751(3)	0.5004(4)	0.2016(2)	0.88(5)
O(4)	-0.3388(4)	0.3844(3)	0.0542(3)	0.89(7)
O(5)	0.0309(5)	0.3829(3)	-0.1850(3)	0.89(7)
O(6)	-0.1668(5)	0.7275(3)	-0.0770(3)	0.81(7)
O(7)	0.1116(4)	0.3415(3)	-0.0045(3)	0.97(7)
O(8)	-0.1648(5)	0.2717(3)	-0.0755(3)	0.76(7)
O(9)	-0.3289(4)	0.6197(3)	0.0606(3)	0.92(7)
O(10)	0.1075(4)	0.6603(3)	-0.0019(3)	0.96(7)
O(11)	-0.1242(3)	0.4894(3)	0.1571(2)	1.33(6)
O(12)	0.0269(5)	0.6482(3)	0.3116(3)	2.36(9)
O(13)	0.0375(5)	0.3911(3)	0.3385(3)	2.26(9)

absorption factor (Table 1), no absorption corrections were made. With anisotropic thermal parameters and after secondary extinction correction, the final values of R and R_w were 0.029 and 0.034, respectively. An attempt of refinement with inversion of the signs of $\Delta f''$ led to the same results in reliability factors. The increase of the “goodness-of-fit” value from 6.858 to 6.870 is not considered significant, so the correct enantiomer cannot be chosen. The atomic coordinates and the thermal motion parameters are reported in Tables 2 and 3.

It is interesting to note that the atom pairs B(1)–B(2), B(4)–B(5), Na(1)–Na(3), O(2)–O(5), O(4)–O(9), O(6)–O(8), and O(7)–O(10) deviate by less than 0.1 Å from a mirror plane relating positions (x, y, z) and $(x, -y, z)$ (see Table 2). Only the atom pair O(12)–O(13) deviates a little more (~0.6 Å). All the remaining atoms V, B(3), B(6), Na(2), O(1), O(3), and O(11) are located within about 0.1 Å from the mirror plane at positions $(x, 1/2, z)$. A pseudo-inversion center at $(0, 1/4, 1/4)$ seems to exist. With the presence of the three screw axes 2_1 , the corresponding centrosymmetric group could be $Pcmm$ ($Pnma$ in standard orientation). However, more than 100 reflections forbidden in this space group have been measured with $I > 3\sigma(I)$; furthermore, the very good values of the reliability factors obtained (see above) also constitute strong proofs that the correct space group of this compound is $P2_12_12_1$. Significant bond lengths and angles are listed in Table 4.

TABLE 3
Anisotropic Thermal Vibration Parameters ($\times 10^4$)
(e.s.d.'s in Parentheses) for all the atoms of $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	23.4(8)	22.2(5)	16.3(3)	0.4(7)	-4.8(4)	-2.7(7)
B(1)	26(8)	8(3)	13(3)	0(4)	0(4)	-1(2)
B(2)	21(8)	6(3)	17(3)	-2(4)	4(5)	1(2)
B(3)	21(5)	10(3)	12(2)	2(5)	2(2)	0(3)
B(4)	25(9)	13(4)	12(3)	-6(5)	3(5)	-1(3)
B(5)	27(9)	15(4)	17(4)	1(5)	-4(5)	-1(3)
B(6)	18(4)	18(3)	14(2)	1(4)	0(2)	-0(3)
Na(1)	62(4)	30(1)	25(1)	3(2)	-7(2)	-2(1)
Na(2)	63(2)	62(2)	25(1)	3(3)	-1(1)	-4(2)
Na(3)	56(3)	34(1)	23(1)	-6(2)	-3(2)	-6(1)
O(1)	17(3)	6(2)	13(1)	-1(3)	4(2)	-2(2)
O(2)	42(5)	11(2)	18(2)	2(3)	15(3)	1(2)
O(3)	25(3)	26(2)	16(1)	1(3)	-5(2)	-2(2)
O(4)	34(6)	12(2)	22(2)	-9(3)	9(3)	-6(2)
O(5)	47(6)	11(2)	17(2)	-1(3)	10(3)	-2(2)
O(6)	29(6)	12(2)	19(2)	8(3)	7(3)	4(2)
O(7)	38(6)	11(2)	25(2)	9(3)	-12(3)	-4(2)
O(8)	28(6)	11(2)	19(2)	-8(3)	8(3)	-2(2)
O(9)	45(6)	12(2)	19(2)	9(3)	13(3)	2(2)
O(10)	35(6)	11(2)	26(2)	-12(3)	-12(3)	3(2)
O(11)	38(4)	52(3)	15(1)	-3(4)	-8(2)	1(2)
O(12)	47(6)	56(3)	59(3)	-7(4)	7(4)	-38(3)
O(13)	61(6)	76(4)	35(3)	-0(4)	-0(3)	30(3)

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The main characteristic of the structure is that it contains BO_3 triangles (Δ), BO_4 tetrahedra (T), and VO_4 tetrahedra as proven by the values of angles existing in these polyhedra (Table 4). The bonds found in these polyhedra are comparable to those existing in other borates and vanadates. For the BO_3 triangles and BO_4 tetrahedra, the mean values for B-O bonds are 1.367 and 1.469 Å, respectively (Table 4), as found, for example, in the anhydrous borate TIB_5O_8 (15)

TABLE 4
Interatomic Distances (Å) and Angles ($^\circ$) in $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$

Tetrahedral VO_4			
-V-O(3)	1.849(2)	O(3)-V-O(11)	120.5(1)
O(11)	1.761(2)	O(3)-V-O(12)	106.2(2)
O(12)	1.643(4)	O(3)-V-O(13)	103.7(2)
O(13)	1.635(4)	O(11)-V-O(12)	109.1(2)
		O(11)-V-O(13)	109.6(2)
Mean	1.722	O(12)-V-O(13)	107.0(2)
Tetrahedral BO_4			
-B(1)-O(1)	1.525(5)	O(1)-B(1)-O(5)	109.3(3)
-O(5)	1.462(6)	O(1)-B(1)-O(7)	107.3(3)
-O(7)	1.444(6)	O(1)-B(1)-O(8)	108.6(3)
-O(8)	1.431(6)	O(5)-B(1)-O(7)	109.9(3)
		O(5)-B(1)-O(8)	107.4(3)
Mean	1.466	O(7)-B(1)-O(8)	114.4(3)

TABLE 4—Continued

Tetrahedral BO_4			
-B(2)-O(1)	1.520(5)	O(1)-B(2)-O(2)	109.4(3)
-O(2)	1.470(6)	O(1)-B(2)-O(6)	107.8(3)
-O(6)	1.447(6)	O(1)-B(2)-O(10)	107.8(3)
-O(10)	1.432(6)	O(2)-B(2)-O(6)	107.3(3)
		O(2)-B(2)-O(10)	110.4(3)
Mean	1.467	O(6)-B(2)-O(10)	114.1(3)
-B(3)-O(1)	1.511(4)	O(1)-B(3)-O(4)	109.0(3)
-O(4)	1.459(5)	O(1)-B(3)-O(9)	108.9(3)
-O(9)	1.467(5)	O(1)-B(3)-O(11)	111.9(2)
-O(11)	1.456(4)	O(4)-B(3)-O(9)	109.7(3)
		O(4)-B(3)-O(11)	107.7(3)
Mean	1.473	O(9)-B(3)-O(11)	109.6(3)
Triangular BO_3			
-B(4)-O(4)	1.373(6)	O(4)-B(4)-O(7 ⁱ)	123.1(4)
-O(7 ⁱ)	1.364(6)	O(4)-B(4)-O(8)	121.9(4)
-O(8)	1.368(7)	O(7 ⁱ)-B(4)-O(8)	114.9(4)
Mean	1.368		
-B(5)-O(6)	1.373(8)	O(6)-B(5)-O(9)	121.2(4)
-O(9)	1.373(6)	O(6)-B(5)-O(10 ⁱⁱ)	115.2(4)
-O(10 ⁱⁱ)	1.355(6)	O(9)-B(5)-O(10 ⁱⁱ)	123.4(4)
Mean	1.367		
-B(6)-O(2)	1.361(5)	O(2)-B(6)-O(3 ⁱⁱⁱ)	119.4(3)
-O(3 ⁱⁱⁱ)	1.374(4)	O(2)-B(6)-O(5)	120.5(3)
-O(5)	1.372(5)	O(3 ⁱⁱⁱ)-B(6)-O(5)	120.1(3)
Mean	1.369		
B-O-B angles inside a hexaborate unit			
B(1)-O(1)-B(2)	120.3(4)	B(1)-O(5)-B(6)	121.5(4)
B(1)-O(1)-B(3)	117.8(4)	B(1)-O(8)-B(4)	122.3(5)
B(2)-O(1)-B(3)	118.7(4)	B(2)-O(2)-B(6)	122.0(4)
B(2)-O(6)-B(5)	121.8(5)	B(3)-O(4)-B(4)	122.7(4)
B(3)-O(9)-B(5)	124.3(4)		
Angles between hexaborate units			
B(1)-O(7)-B(4 ^v)	127.3(5)	B(2)-O(10 ^{xi})-B(5)	127.7(5)
Angles between hexaborate unit and tetrahedral VO_4			
V-O(3)-B(6 ^{viii})	117.9(2)	V-O(11)-B(3)	160.4(2)
Na-O bonds (< 3 Å)			
Na(1)-O(6 ^{iv})	2.373(4)	Na(2)-O(3 ^{viii})	2.330(3)
-O(5 ^{vi})	2.423(4)	-O(4 ^{viii})	2.578(4)
-O(12 ^{viii})	2.428(4)	-O(7 ^{vii})	2.597(4)
-O(2 ^{iv})	2.481(4)	-O(10 ^{vii})	2.603(4)
-O(11 ^v)	2.535(4)	-O(9 ^{vii})	2.658(4)
-O(4 ^v)	2.554(4)	-O(13)	2.666(4)
-O(13 ^v)	2.872(5)	-O(6 ^{iv})	2.838(4)
		-O(8 ^{ix})	2.863(4)
Na(3)-O(2 ^{vii})	2.360(4)	Na(3)-O(12 ^{iv})	2.534(4)
-O(8 ^x)	2.394(4)	-O(13)	2.640(4)
-O(9 ^{iv})	2.499(4)	-O(11 ^{iv})	2.778(4)
-O(5 ^x)	2.506(4)	-O(3)	2.938(4)
Na-B distances (< 3 Å)			
Na(1)-B(2 ^{iv})	2.933(6)	Na(3)-B(1 ^x)	2.963(6)

Note. Symmetry code: (i): $x - 1/2, 1/2 - y, -z$; (ii): $x - 1/2, 1.5 - y, -z$; (iii): $1/2 - x, 1 - y, z - 1/2$; (iv): $-x, y - 1/2, 1/2 - z$; (v): $1/2 + x, 1/2 - y, 1 - z$; (vi): $x, y, 1 + z$; (vii): $1/2 - x, 1 - y, 1/2 + z$; (viii): $x - 1/2, 1 - y, 1/2 + z$; (ix): $-x, 1/2 + y, 1/2 - z$; (x): $1/2 + x, 1/2 - y, -z$; (xi): $1/2 + x, 1.5 - y, -z$.

1.368 and 1.471 Å, respectively. A similar result concerns the VO_4 tetrahedra, where the mean value 1.722 Å (Table 4) corresponds to the mean values found in vanadates such as Li_3VO_4 , 1.724 Å (16); CrVO_4 , 1.725 Å (17); InVO_4 , 1.710 and 1.726 Å (18,19); or $\text{In}_{0.6}\text{Li}_{1.2}\text{VO}_4$, 1.722 Å (20). However, the interesting point is the linkage of these different polyhedra. The three BO_3 and three BO_4 polyhedra form a compact hexaborate unit. It is characterized by an oxygen atom O(1) which is shared by three BO_4 tetrahedra (Fig. 1); this oxygen atom is just a little (0.159(2) Å) off the mean plane defined by the three tetrahedral boron atoms; the O(1)-boron bonds are longer than the three other B-O distances in each of the three BO_4 tetrahedra. Such a group, formed by three six-membered B-O rings, each made up of two tetrahedra and one triangle, has been described in several hydrated borates, where it exists isolated, in chains and in sheets (21, 22). To our knowledge, it appears that such a group has never been found in any anhydrous borate. In the studied compound, these hexaborate units are linked together by terminal oxygens O(7) and O(10) belonging to BO_3 and BO_4 polyhedra (Fig. 1) to form sheets parallel to (001) (Fig. 2). A three-dimensional framework is formed by VO_4 tetrahedra which, with oxygen atoms O(3) and O(11), link these sheets along [001]; the atom O(3) belongs to a BO_3 triangle of a hexaborate unit and the atom O(11) belongs to a BO_4 tetrahedron of another hexaborate unit. The two other oxygen atoms O(12) and O(13) of VO_4 tetrahedron stay free; it is noticeable that the value of their B_{eq} (Table 2) are larger than those of the other oxygen atoms. The presence of these oxygen atoms, which do not belong to the borate ion, is probably responsible of the noncentrosymmetry of this structure. Following the crystal

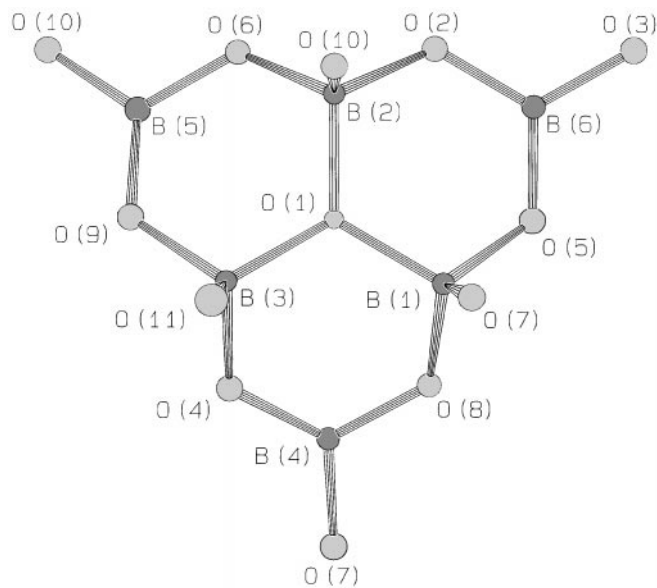


FIG. 1. Representation of the hexaborate group in $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$.

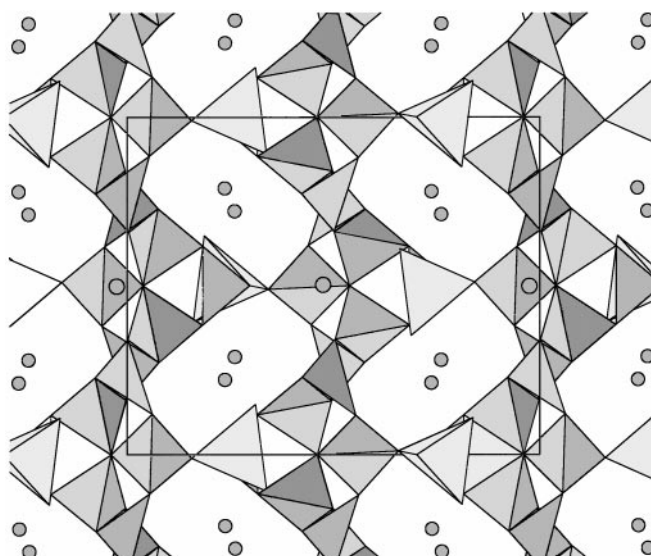


FIG. 2. Projection of the structure of $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$ in the (001) plane; VO_4 tetrahedra are white, the circles represent sodium atoms.

chemical classification of borates proposed by Christ and Clark (21) and Heller (22), the shorthand notation of this vanadoborate anion is: $6: \infty^3(3\Delta + 3T) + \text{VO}_4$.

The sodium atoms are situated inside channels that exist in the three-dimensional framework as shown in Fig. 2; the oxygenated environment of the sodium is not well defined (see Table 4). The structural formula of this compound may be written $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$.

The DTA performed on single crystals of $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$ shows, upon heating, two endothermic phenomena at 684 (very strong) and 704°C (weak); therefore, this compound is an incongruently melting phase.

It is interesting to note that crystals of the α form of NaVO_3 (23, 24) are the second component of the initial mixture along with crystals of $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$. This result is well explained with the analysis of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{V}_2\text{O}_5$ ternary system (Fig. 3), where the initial composition of the mixture, $\text{Na}_3\text{V}_2\text{B}_3\text{O}_{11}$ on the $\text{NaBO}_2-\text{V}_2\text{O}_5$ line, belongs to the $\text{NaB}_3\text{O}_5-\text{NaVO}_3$ pseudo-binary system. The sodium vanadoborate also belongs to two other pseudo-binary systems: $\text{Na}_3\text{VO}_4-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{B}_4\text{O}_7-\text{V}_2\text{O}_5$; because these two compounds are commercial, we have undertaken the synthesis of the sodium vanadoborate by ceramic route. When a mixture with the suitable composition was melted around 700°C, sodium vanadoborate was not obtained, but we could identify $\alpha\text{-NaVO}_3$ (23, 24) and NaB_3O_5 (25, 26) in the solid; this result is consistent with Fig. 3. By heating the mixture at a temperature below the incongruent-melting point, at 630°C for 48 h, with intermediate grindings, a powder of sodium vanadoborate was obtained with very good purity as proven by the excellent experimental powder pattern.

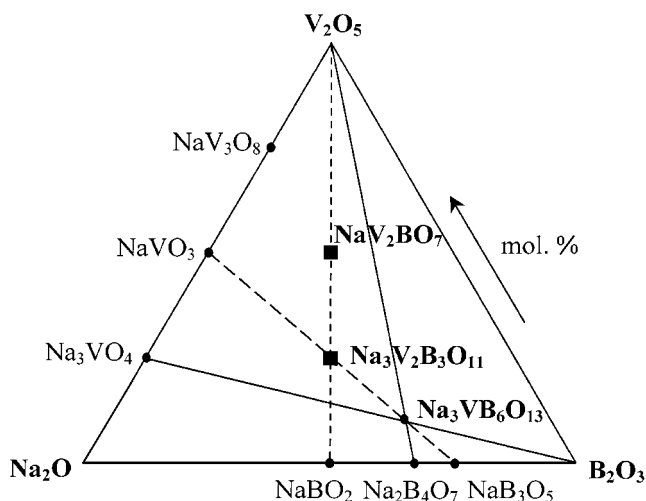


FIG. 3. Ternary system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{V}_2\text{O}_5$, where the position of $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$ is reported.

The question of the name of this compound may be asked: is it a mixed borate of sodium and vanadium $\text{Na}_3\text{V}(\text{B}_6\text{O}_{13})$, a sodium borovanadate or a sodium vanadoborate? The first proposition must be excluded because the size of bonds in BO_4 and VO_4 tetrahedra is relatively near compared to the Na–O bonds (Table 4), and the network of the structure must be formed by boron and vanadium oxygenated polyhedra as described above. For the second proposition, a comparison with the known numerous anhydrous borophosphates can be made. In these compounds, the values of the B/P ratio, 1 (2, 4), 0.66 (2), 0.5 (3), and 0.33 (2), are very different from the value of the B/V ratio in $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$, which is 6. Moreover, the main characteristic of the found structure is the presence of the hexaborate units which allow us to consider this compound a vanadoborate.

CONCLUSION

A new compound has been synthesized and well characterized from its structure. The compound consists in an original, three-dimensional network formed by sheets of hexaborate units linked by VO_4 tetrahedra. The sodium atoms occupy channels that exist in this compound whose structural formula is $\text{Na}_3[\text{B}_6\text{O}_9(\text{VO}_4)]$. At the present time, we are trying to exchange sodium cations by other cations or protons. Experiments in nonlinear optics are also scheduled to evaluate the influence of the presence of the pseudo-

symmetry center in this structure, and its performance will be compared with those of borates of the same space group $P2_12_12_1$, but with a very different structure (27, 28). It is interesting to note that Xia *et al.* (29) have not calculated microscopic second harmonic generation (SHG) coefficients for the hexaborate anion because it was considered to be unable to promote a noncentrosymmetric structure.

REFERENCES

1. P. Becker, *Adv. Mater.* **10**, 979 (1998).
2. R. Kniep, H. Engelhardt, and C. Hauf, *Chem. Mater.* **10**, 2930 (1998).
3. Y. Shi, J. Liang, H. Zhang, J. Yang, W. Zhuang, and G. Rao, *J. Solid State Chem.* **129**, 45 (1997).
4. S. Yu. Stefanovich, V. N. Sigaev, A. V. Dechev, and A. V. Mosunov, *Russ. J. Inorg. Chem.* **40**, 1667 (1995).
5. K. Bluhm and C.-H. Park, *Z. Naturforsch. B: Chem. Sci.* **51**, 313 (1996).
6. B. Nador, *Nature* **201**, 921 (1964).
7. N. T. Buludov, F. D. Mamedaliev, Z. Sh. Karaev, and G. K. Abdullaev, *Russ. J. Inorg. Chem.* **30**, 1032 (1985).
8. I. V. Ditrach and A. P. Nakhodnova, *Russ. J. Inorg. Chem.* **37**, 1097 (1992).
9. S. A. Kulieva, P. F. Rza-Zade, K. L. Ganf, and N. P. Luzhnaya, *Izv. Akad. Nauk SSSR, Neorgan. Mater.* **10**, 2013 (1974).
10. A. Nakhodnova, I. Listratenko, and R. Makarova, *Ukr. Khim. Zh. (Russ. Ed.)* **53**, 899 (1987).
11. R. Norrestam, M. Kritikos, K. Nielsen, I. Sotofte, and N. Thorup, *J. Solid State Chem.* **111**, 217 (1994).
12. K. Bluhm and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **579**, 111 (1989).
13. "International Tables for X-Ray Crystallography," Vol. IV. Kynoch Press, Birmingham, UK, 1974. [Also published by Kluwer Academic, Dordrecht, The Netherlands]
14. G. M. Sheldrick, "SHELX-76: A program for Crystal Structure Determination." University of Cambridge, 1976.
15. M. Touboul and G. Nowogrocki, *J. Solid State Chem.* **136**, 216 (1998).
16. D. Shannon and C. Calvo, *J. Solid State Chem.* **6**, 538 (1973).
17. M. Touboul, S. Denis, and L. Seguin, *Eur. J. Solid State Inorg. Chem.* **32**, 577 (1995).
18. M. Touboul, K. Melghit, P. Bénard, and D. Loüer, *J. Solid State Chem.* **118**, 93 (1995).
19. M. Touboul and P. Tolédano, *Acta Crystallogr. Sect. B* **36**, 240 (1980).
20. M. Touboul and P. Tolédano, *J. Solid State Chem.* **38**, 386 (1981).
21. C. L. Christ and J. R. Clark, *Phys. Chem. Miner.* **2**, 59 (1977).
22. G. Heller, *Topics Curr. Chem.* **131**, 39 (1986).
23. F. Marumo, M. Isobe, and S. I. Iwai, *Acta Crystallogr. Sect. B* **30**, 1628 (1974).
24. PDF No. 32-1197.
25. J. Krogh-Moë, *Acta Crystallogr. Sect. B* **28**, 1751 (1972).
26. PDF No. 22-1347.
27. M. Touboul, E. Bétourné, and G. Nowogrocki, *J. Solid State Chem.* **131**, 370 (1997).
28. M. Touboul, N. Penin, A. Kahn-Harari, and J. Godard, in "First International Conference on Inorganic Materials," Versailles, France, Sept. 1998.
29. Y. Xia, C. Chen, D. Tang, and B. Wu, *Adv. Mater.* **7**, 79 (1995).