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$Na_6B_{13}O_{22.5}$, a new noncentrosymmetric sodium borate

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Abstract

$Na_6B_{13}O_{22.5}$ (B/Na = 2.17) single crystals were obtained by heating, melting and appropriately cooling borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$. Its formula has been determined by the resolution of the structure from single-crystal X-ray diffraction data. The compound crystallizes in the noncentrosymmetric orthorhombic *Iba*2 space group, with the following unit cell parameters: $a = 33.359(11)$ Å, $b = 9.554(3)$ Å, $c = 10.644(4)$ Å; $V = 3392.4(19)$ Å^3; $Z = 8$. The crystal structure was solved from 3226 reflections until $R_1 = 0.0385$. It exhibits a three-dimensional framework built up from BO_3 triangles (Δ) and BO_4 tetrahedra (T). Two kinds of borate groups can be considered forming two different double B_3O_3 rings: two B_4O_9 (linkage by two boron atoms) and one B_5O_{11} (linkage by one boron atom); the shorthand notation of the new fundamental building block (FBB) existing in this compound is: 13: ∞^3 [(5: 3Δ + 2T) + 2(4: 2Δ + 2T)]. The discovery of this new borate questions the real number of $Na_2B_4O_7$ varieties. The existence of $Na_6B_{13}O_{22.5}$ (B/Na = 2.17) and of another recently discovered borate, $Na_3B_7O_{12}$ (B/Na = 2.33; FBB 7: ∞^3 [(3: 2Δ + T) + (3: Δ + 2T) + (1: Δ)], with a composition close to the long-known borate α-$Na_2B_4O_7$ (B/Na = 2; FBB 8: ∞^3 [(5: 3Δ + 2T) + (3: 2Δ + T)], may explain the very complex equilibria reported in the Na_2O–B_2O_3 phase diagram, especially in this range of composition.

Keywords: Borate; Sodium borate

1. Introduction

During the last 2 years, two new anhydrous sodium borates have been obtained, β-$Na_2B_8O_{13}$ [1] and $Na_3B_7O_{12}$ [2], although these compounds were extensively studied as main constituents of borosilicate glasses. In the successive versions of Na_2O–B_2O_3 binary phase diagram, numerous compounds with several crystalline forms were reported [3–6]. However, only some of them were clearly identified because their structures were determined: Na_3BO_3 [7], $Na_4B_2O_5$ [8], $NaBO_2$ [9], $Na_2B_4O_7$ [10], α-NaB_3O_5 [11], β-NaB_3O_5 [12], and α-$Na_2B_8O_{13}$ [13–15]. $Na_2O\cdot 2B_2O_3$ ($Na_2B_4O_7$) borate, called tetraborate, was reported to exist in three forms, which were identified by their nonindexed powder patterns [16]; only the α form, whose structure is known [10], is characterized by an indexed powder pattern [17]. However, a more recent study [18] has led to four other forms of tetraborate that were all identified by indexed X-ray diffraction powder patterns. The aim of this work was to obtain single crystals of some forms of $Na_2B_4O_7$ to solve their structures, and compare them with those of other $M_2B_4O_7$ (M monovalent element) compounds described in a recent review [19].

2. Experimental section

2.1. Synthesis

Starting with borax, $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ (analytical reagent grade, Prolabo), a dehydration was undertaken by heating until complete melting at 800 °C; then

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the mixture was slowly cooled down to 750 °C at a rate of 0.05 °C/min, and annealed at this temperature for 10 h. This process, lowering the temperature by 50 °C and annealing for 10 h, was repeated five times until the sample temperature reached 500 °C. Later, the furnace was turned off, and the mixture left to cool down to room temperature.

2.2. Single-crystal structure determination

The preparation was not very homogeneous: some fragments were noncrystalline (glass), others were polycrystalline, but all of the tested single crystals gave the same orthorhombic unit cell ($a = 33.36$ Å, $b = 9.554$ Å, $c = 10.643$ Å).

The intensity data were collected on a Bruker AXS SMART three-circle diffractometer using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å), and equipped with a CCD two-dimensional detector. Absorption corrections were made using the semi-empirical SADABS program [20].

Two space groups were compatible with the extinctions observed: *Ibam* or *Iba*2. Resolution attempts by direct methods in the centrosymmetric group did not yield any recognizable solution. Conversely, in *Iba*2 group, the resolution proceeded smoothly to $R_1 = 0.0385$ and $R_w = 0.0966$ with a formula $Na_6B_{13}O_{22.5}$, not very far from the expected composition $Na_2B_4O_7$. The Flack parameter [21] had a value of 0.13 (0.33), so the absolute configuration of the measured crystal was probably correct. With another crystal of the same preparation, the refinement leads to all of the atoms with inverse coordinates.

Considering the content of the cell (48 sodium, 104 boron and 180 oxygen atoms), it is quite evident that using the *Ibam* group (multiplicity of general position 16) would force to put at least one oxygen atom on a site with 2/*m* or 222 symmetry (multiplicity of position 4), which is quite improbable.

All of the atoms are in general positions in *Iba*2 space group, except for O(23) that lies on a twofold axis, in 4*a* Wyckoff site. Crystal data and conditions of intensity collection are given in Table 1. The structure was refined by full-matrix least-squares techniques using the SHELXTL crystallographic software package [22]. The atomic coordinates and the displacement parameters are reported in Tables 2 and 3; significant bond lengths and angles are listed in Table 4.

Table 1
Crystal data and structure refinement for $Na_6B_{13}O_{22.5}$

Formula weight (g/mol)	638.47
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Iba*2 (No. 45)
Unit cell dimensions (Å)	$a = 33.359(11)$
	$b = 9.554(3)$
	$c = 10.644(4)$
Volume (Å^3)	3392.4(19)
Z	8
Density, Dx (g/cm^3)	2.500
Absorption coefficient (mm^{-1})	0.357
F (000)	2488
Crystal size (mm^3)	$0.45 \times 0.28 \times 0.15$
θ range for data collection (deg)	2.22–28.05
Index ranges	$-43 \leqslant h \leqslant 41$
	$-12 \leqslant k \leqslant 12$
	$-13 \leqslant l \leqslant 13$
Reflections collected	12663
Independent reflections	3733
Independent reflections [$I > 2\sigma(I)$]	3226
R_{int}	0.0362
Refinement method	Full-matrix least-squares on F^2
Number of variables	375
Goodness-of-fit on F^2	1.095
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0385$
	w$R_2 = 0.0925$
Final R indices (all data)	$R_1 = 0.0456$
	w$R_2 = 0.0966$
Largest difference map peak and hole (e/Å^3)	0.354 and −0.313

3. Description of the crystal structure and discussion

3.1. Borate anion

The borate anion found in $Na_6B_{13}O_{22.5}$ is formed by a complex association of BO_3 triangles (Δ) and BO_4 tetrahedra (T) linked together by the vertices. All of the oxygen atoms are common to two triangles, two tetrahedra, or to one triangle and one tetrahedron. The B–O distances in this borate anion are comparable with those existing in other borates with shorter distances in BO_3 triangles (from 1.338 to 1.400 Å) than in BO_4 tetrahedra (from 1.420 to 1.517 Å) (Table 4). A bond valence analysis [23] of the structure of $Na_6B_{13}O_{22.5}$ is performed, and included in Table 4; it is interesting to note that the values of the valence sums corresponding to boron atoms are around 3, ranging from 2.958 for B(13) to 3.052 for B(1).

The structure of this sodium borate can be described from a three-dimensional association of new complex anions with 13 boron atoms; it is formed by two linked tetraborate groups (B_4O_9) bonded to a pentaborate group (B_5O_{11}) (Fig. 1). These tetraborate and pentaborate groups were often met in complex borates as reported in a recent review [19]. The first tetraborate group is formed of two BO_3 triangles (B(1) and B(2)) and two BO_4 tetrahedra (B(3) and B(4)); the second tetraborate group also contains two BO_3 triangles (B(5) and B(8)) and two BO_4 tetrahedra (B(6) and B(7)); the pentaborate group consists of three BO_3 triangles (B(10, B(12) and B(13)) and two BO_4 tetrahedra (B(9) and

Table 2
Atomic coordinates ($\times 10^5$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) for $Na_6B_{13}O_{22.5}$ with e.s.d.'s in parentheses

Atoms	x	y	z	U_{eq}[a]
Na(1)	54509(5)	93450(13)	14581(15)	283(4)
Na(2)	69979(4)	60529(13)	254(13)	241(3)
Na(3)	54450(4)	142049(14)	−26660(14)	290(4)
Na(4)	62350(4)	34421(14)	5176(14)	275(3)
Na(5)	70318(4)	111348(14)	−13085(13)	260(3)
Na(6)	62768(4)	87666(15)	82859(14)	318(3)
O(1)	71411(6)	42260(20)	12480(20)	166(5)
O(2)	72755(6)	19160(20)	5250(20)	149(4)
O(3)	74698(7)	39464(18)	−6490(30)	189(4)
O(4)	72595(6)	30060(20)	32270(20)	161(5)
O(5)	71862(6)	6780(20)	24840(20)	158(4)
O(6)	67026(5)	23810(20)	18710(20)	151(4)
O(7)	67664(6)	1870(20)	6860(20)	174(5)
O(8)	67182(6)	45740(20)	30580(20)	177(5)
O(9)	64179(7)	80630(20)	3840(30)	186(5)
O(10)	64487(6)	91090(20)	24310(20)	179(5)
O(11)	59130(5)	75180(20)	19380(30)	148(4)
O(12)	64364(7)	68010(20)	34000(20)	190(5)
O(13)	59742(7)	86140(20)	40020(20)	201(5)
O(14)	63936(6)	57550(20)	13670(20)	175(5)
O(15)	58950(7)	63760(20)	−740(20)	200(5)
O(16)	56703(7)	82810(20)	59940(20)	200(5)
O(17)	54887(6)	67140(20)	43030(20)	191(5)
O(18)	52766(7)	90860(20)	42090(30)	291(6)
O(19)	57029(7)	69140(20)	78700(20)	202(5)
O(20)	53435(7)	79150(20)	95750(20)	223(5)
O(21)	52130(7)	63060(20)	63330(20)	184(5)
O(22)	51326(7)	84510(20)	74800(20)	215(5)
O(23)	50000	50000	45280(30)	195(6)
B(1)	72979(10)	33380(40)	3910(30)	147(7)
B(2)	73240(10)	16100(30)	33370(40)	152(7)
B(3)	69697(10)	12800(40)	14120(40)	152(7)
B(4)	69439(10)	35530(40)	23320(40)	147(7)
B(5)	65404(10)	91320(40)	11640(40)	168(7)
B(6)	61729(10)	79980(40)	29570(50)	140(7)
B(7)	61446(11)	69480(40)	9170(30)	158(7)
B(8)	65136(10)	57070(40)	26090(30)	149(7)
B(9)	56186(10)	81910(30)	46300(30)	158(7)
B(10)	56467(11)	70480(30)	91260(40)	163(7)
B(11)	54361(8)	75220(40)	68890(40)	150(6)
B(12)	52397(11)	60360(40)	50790(40)	196(7)
B(13)	50684(11)	85350(40)	87530(30)	205(8)

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

Table 3
Anisotropic displacement parameters ($Å^2 \times 10^4$) (e.s.d.'s in parentheses) for all of the atoms of $Na_6B_{13}O_{22.5}$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	256(7)	209(7)	383(10)	−32(6)	51(6)	2(5)
Na(2)	306(7)	235(7)	182(7)	60(6)	18(6)	−14(6)
Na(3)	323(8)	298(7)	249(9)	57(6)	10(6)	115(6)
Na(4)	243(7)	351(8)	230(8)	−37(6)	−29(6)	−10(6)
Na(5)	303(7)	253(7)	224(8)	−75(6)	−27(6)	−19(6)
Na(6)	330(8)	333(8)	292(9)	72(6)	95(7)	6(6)
O(1)	192(10)	151(10)	155(12)	4(9)	24(10)	4(8)
O(2)	161(10)	136(10)	150(12)	7(8)	11(9)	−15(8)
O(3)	263(11)	137(9)	167(9)	3(10)	83(8)	1(10)
O(4)	182(11)	145(10)	155(12)	−11(9)	−26(10)	9(8)
O(5)	217(11)	150(10)	107(11)	2(8)	−21(9)	−2(8)
O(6)	144(9)	159(9)	149(9)	1(7)	7(10)	−5(9)
O(7)	219(10)	184(11)	119(11)	−1(8)	1(9)	−74(9)
O(8)	218(11)	167(11)	146(11)	7(9)	3(9)	65(8)
O(9)	243(12)	182(11)	134(12)	1(8)	19(9)	−71(9)
O(10)	200(11)	206(11)	130(12)	−6(9)	1(9)	−69(9)
O(11)	137(9)	148(9)	159(9)	−5(7)	−10(10)	4(9)
O(12)	249(12)	170(11)	152(12)	−28(9)	−49(10)	56(9)
O(13)	205(11)	206(12)	191(13)	−30(9)	60(9)	−31(9)
O(14)	217(11)	174(11)	135(12)	−30(9)	−28(9)	49(9)
O(15)	230(12)	171(11)	199(12)	−48(9)	−89(10)	31(9)
O(16)	279(12)	180(11)	140(12)	1(8)	6(9)	−64(9)
O(17)	248(11)	166(10)	159(11)	−40(8)	41(9)	−41(9)
O(18)	220(11)	196(12)	458(15)	26(11)	−133(11)	−5(9)
O(19)	195(11)	271(12)	139(12)	−4(9)	−13(9)	64(9)
O(20)	264(12)	264(13)	140(11)	−13(9)	6(9)	92(10)
O(21)	237(11)	174(10)	143(12)	−1(8)	18(9)	−33(9)
O(22)	243(12)	193(11)	207(13)	−28(9)	−16(10)	69(9)
O(23)	228(14)	199(14)	158(15)	0	0	−42(13)
B(1)	140(15)	158(16)	144(19)	6(14)	1(14)	0(13)
B(2)	149(16)	149(15)	159(19)	24(14)	19(14)	−15(13)
B(3)	132(16)	171(17)	150(20)	39(13)	−3(14)	−28(12)
B(4)	141(15)	163(17)	136(19)	−19(13)	23(14)	23(13)
B(5)	160(16)	172(17)	173(19)	0(13)	8(15)	−6(13)
B(6)	132(16)	122(16)	167(17)	26(12)	11(13)	−5(13)
B(7)	171(17)	160(17)	143(18)	28(12)	−31(13)	−20(13)
B(8)	162(15)	120(15)	164(18)	−32(13)	19(15)	−10(12)
B(9)	161(16)	150(17)	162(18)	6(13)	−3(13)	−5(13)
B(10)	165(16)	134(17)	191(18)	−23(13)	−7(14)	−25(13)
B(11)	163(13)	171(14)	115(13)	−19(11)	−17(15)	−11(15)
B(12)	225(18)	142(17)	222(18)	18(14)	−19(16)	−13(14)
B(13)	188(18)	181(17)	246(19)	24(14)	−6(14)	−33(14)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^*U_{11}+\cdots)$.

B(11)) (Fig. 2). Each borate anion with 13 boron atoms is linked to nine other similar groups to form a three-dimensional network (Fig. 3). Following the crystal chemical classification of borates proposed by Christ and Clark [24], Heller [25], and slightly modified [19], the shorthand notation of this new complex association of BO_3 triangles (Δ) and BO_4 tetrahedra (T) can be written with the fundamental building block (FBB): 13: ∞^3 [(5: 3Δ + 2T) + 2(4: 2Δ + 2T)]. It is interesting to note that this new FBB with 13 boron atoms completes the list of FBBs described in the recent review concerning crystal chemistry of alkaline and pseudo-alkaline (Ag^+, Tl^+, NH_4^+) borates [19], between those with 12 boron atoms, 12: 2[(6: 3Δ + 3T)] or 12: [(7: 4Δ + 3T) + (5: 2Δ + 3T)] and FBB with 14 boron atoms, 14: [2(5: 3Δ + 2T) + (3: 2Δ + T) + (1: T)]. Note the good agreement with the calculation of the ratio of BO_3 triangles to BO_4 tetrahedra from the Parthé formula [26].

To our knowledge, only three other compounds with 13 boron atoms were reported. The first one is a new potassium manganese borate recently solvothermally synthesized [27]; its structural formula is $K_7\{(BO_3)Mn[B_{12}O_{18}(OH)_6]\}\cdot H_2O$ with only six and a half crystallographically independent boron atoms. The

Table 4
Interatomic distances (Å), angles (°), and bond valence analysis* in $Na_6B_{13}O_{22.5}$

BO_3 triangles				
		s		
B(1)–O(1)	1.351(4)	1.055	O(1)–B(1)–O(2)	122.1(3)
B(1)–O(2)	1.368(4)	1.008	O(1)–B(1)–O(3)	116.0(3)
B(1)–O(3)	1.375(4)	0.989	O(2)–B(1)–O(3)	121.8(3)
Mean	1.365(4)	$\Sigma s = 3.052$	Mean	120.0(3)
B(2)–O(5)	1.353(4)	1.050	O(5)–B(2)–O(4)	122.4(3)
B(2)–O(4)	1.356(4)	1.041	O(5)–B(2)–O(3)[a]	116.0(3)
B(2)–O(3)[a]	1.386(4)	0.960	O(4)–B(2)–O(3)[a]	121.5(3)
Mean	1.365(4)	$\Sigma s = 3.051$	Mean	120.0(3)
B(5)–O(7)[b]	1.358(4)	1.036	O(7)[b]–B(5)–O(9)	119.3(3)
B(5)–O(9)	1.378(4)	0.981	O(7)[b]–B(5)–O(10)	120.0(3)
B(5)–O(10)	1.382(4)	0.971	O(9)–B(5)–O(10)	120.6(3)
Mean	1.373(4)	$\Sigma s = 2.988$	Mean	120.0(3)
B(8)–O(8)	1.366(4)	1.014	O(8)–B(8)–O(12)	119.0(3)
B(8)–O(12)	1.367(4)	1.011	O(8)–B(8)–O(14)	120.4(3)
B(8)–O(14)	1.382(4)	0.971	O(12)–B(8)–O(14)	120.6(3)
Mean	1.372(4)	$\Sigma s = 2.996$	Mean	120.0(3)
B(10)–O(15)[c]	1.351(4)	1.055	O(15)[c]–B(10)–O(19)	119.4(3)
B(10)–O(19)	1.356(5)	1.041	O(15)[c]–B(10)–O(20)	120.8(3)
B(10)–O(20)	1.392(4)	0.945	O(19)–B(10)–O(20)	119.7(3)
Mean	1.366(4)	$\Sigma s = 3.041$	Mean	119.9(3)
B(12)–O(17)	1.338(4)	1.093	O(17)–B(12)–O(21)	123.6(3)
B(12)–O(21)	1.363(4)	1.022	O(17)–B(12)–O(23)	116.0(3)
B(12)–O(23)	1.401(4)	0.922	O(21)–B(12)–O(23)	120.4(3)
Mean	1.367(4)	$\Sigma s = 3.037$	Mean	120.0(3)
B(13)–O(18)[d]	1.356(4)	1.041	O(18)[d]–B(13)–O(22)	120.6(3)
B(13)–O(22)	1.374(4)	0.992	O(18)[d]–B(13)–O(20)	119.8(3)
B(13)–O(20)	1.400(4)	0.925	O(22)–B(13)–O(20)	119.3(3)
Mean	1.377(4)	$\Sigma s = 2.958$	Mean	119.9(3)
BO_4 tetrahedra				
		s		
B(3)–O(6)	1.463(4)	0.780	O(6)–B(3)–O(7)	114.0(2)
B(3)–O(7)	1.465(4)	0.776	O(6)–B(3)–O(5)	108.8(3)
B(3)–O(5)	1.467(4)	0.771	O(6)–B(3)–O(2)	109.2(2)
B(3)–O(2)	1.517(4)	0.674	O(7)–B(3)–O(5)	111.0(3)
Mean	1.478(4)	$\Sigma s = 3.001$	O(7)–B(3)–O(2)	105.6(3)
			O(5)–B(3)–O(2)	108.1(2)
			Mean	109.4(3)
B(4)–O(8)	1.454(4)	0.799	O(8)–B(4)–O(6)	114.0(2)
B(4)–O(6)	1.464(4)	0.778	O(8)–B(4)–O(1)	110.7(3)
B(4)–O(1)	1.476(4)	0.753	O(8)–B(4)–O(4)	104.9(3)
B(4)–O(4)	1.513(4)	0.681	O(6)–B(4)–O(1)	108.5(3)
Mean	1.477(4)	$\Sigma s = 3.011$	O(6)–B(4)–O(4)	109.2(3)
			O(1)–B(4)–O(4)	109.4(2)
			Mean	109.4(3)
B(6)–O(13)	1.422(4)	0.871	O(13)–B(6)–O(11)	115.7(3)
B(6)–O(11)	1.462(4)	0.782	O(13)–B(6)–O(10)	106.4(3)
B(6)–O(10)	1.512(4)	0.683	O(13)–B(6)–O(12)	109.9(3)
B(6)–O(12)	1.517(4)	0.674	O(11)–B(6)–O(10)	107.8(3)
Mean	1.478(4)	$\Sigma s = 3.010$	O(11)–B(6)–O(12)	109.7(3)
			O(10)–B(6)–O(12)	106.9(2)
			Mean	109.4(3)
B(7)–O(11)	1.440(4)	0.830	O(11)–B(7)–O(15)	112.5(3)
B(7)–O(15)	1.451(4)	0.806	O(11)–B(7)–O(14)	110.2(3)
B(7)–O(14)	1.490(4)	0.725	O(11)–B(7)–O(9)	109.9(3)
B(7)–O(9)	1.513(4)	0.681	O(15)–B(7)–O(14)	105.4(3)
Mean	1.474(4)	$\Sigma s = 3.042$	O(15)–B(7)–O(9)	109.8(3)
			O(14)–B(7)–O(9)	108.9(3)
			Mean	109.4(3)

Table 4 (*continued*)

B(9)–O(13)	1.420(4)	0.876	O(13)–B(9)–O(16)	110.6(3)	
B(9)–O(16)	1.464(4)	0.778	O(13)–B(9)–O(18)	109.5(3)	
B(9)–O(18)	1.494(4)	0.717	O(13)–B(9)–O(17)	113.3(3)	
B(9)–O(17)	1.517(4)	0.674	O(16)–B(9)–O(18)	110.7(3)	
Mean	1.474(4)	$\Sigma s = 3.045$	O(16)–B(9)–O(17)	108.4(3)	
			O(18)–B(9)–O(17)	104.2(3)	
			Mean	109.4(3)	
B(11)–O(16)	1.430(5)	0.853	O(16)–B(11)–O(22)	110.6(3)	
B(11)–O(22)	1.486(4)	0.733	O(16)–B(11)–O(19)	109.8(2)	
B(11)–O(19)	1.490(4)	0.725	O(16)–B(11)–O(21)	113.6(3)	
B(11)–O(21)	1.501(4)	0.704	O(22)–B(11)–O(19)	110.1(3)	
Mean	1.477(4)	$\Sigma s = 3.015$	O(22)–B(11)–O(21)	106.9(2)	
			O(19)–B(11)–O(21)	105.7(3)	
			Mean	109.4(3)	
Environment of sodium atoms (< 3.00 Å)					
		s			*s*
Na(1)–O(11)	2.384(2)	0.208	Na(4)–O(6)	2.353(3)	0.226
Na(1)–O(22)[e]	2.388(3)	0.206	Na(4)–O(12)[h]	2.364(3)	0.220
Na(1)–O(16)[f]	2.434(3)	0.182	Na(4)–O(14)	2.445(3)	0.176
Na(1)–O(20)[g]	2.452(3)	0.173	Na(4)–O(16)[h]	2.553(3)	0.132
Na(1)–O(22)[f]	2.597(3)	0.117	Na(4)–O(13)[h]	2.687(3)	0.092
Na(1)–O(18)[f]	2.883(3)	0.054			$\Sigma s = 0.846$
Na(1)–O(18)	2.996(3)	0.040	Na(4)–B(9)[h]	2.749(4)	
		$\Sigma s = 0.980$	Na(4)–O(17)[h]	2.809(3)	
Na(2)–O(1)	2.229(3)	0.316	Na(5)–O(5)[h]	2.217(3)	0.327
Na(2)–O(4)[h]	2.288(3)	0.270	Na(5)–O(2)[b]	2.242(3)	0.305
Na(2)–O(8)[h]	2.370(3)	0.216	Na(5)–O(10)[f]	2.375(3)	0.213
Na(2)–O(14)	2.487(3)	0.157	Na(5)–O(7)[b]	2.472(3)	0.164
Na(2)–O(2)[i]	2.615(3)	0.111	Na(5)–O(4)[l]	2.551(3)	0.132
Na(2)–O(3)	2.654(2)	0.100	Na(5)–O(3)[i]	2.762(2)	0.075
Na(2)–O(9)	2.753(3)	0.077	Na(5)–O(12)[f]	2.816(3)	0.065
		$\Sigma s = 1.247$			$\Sigma s = 1.281$
Na(2)–B(1)	2.808(4)		Na(5)–B(2)[h]	2.823(4)	
Na(2)–B(4)[h]	2.897(4)		Na(5)–B(3)[b]	2.907(4)	
			Na(5)–B(1)[b]	2.914(4)	
Na(3)–O(17)[f]	2.277(3)	0.278	Na(6)–O(10)[m]	2.298(3)	0.262
Na(3)–O(11)[f]	2.307(2)	0.256	Na(6)–O(6)[n]	2.343(3)	0.232
Na(3)–O(21)[j]	2.401(3)	0.199	Na(6)–O(9)[c]	2.379(3)	0.211
Na(3)–O(21)[k]	2.488(3)	0.157	Na(6)–O(19)	2.644(3)	0.103
Na(3)–O(19)[j]	2.787(3)	0.070	Na(6)–O(13)[m]	2.804(3)	0.067
Na(3)–O(23)[f]	2.869(3)	0.056			$\Sigma s = 0.875$
		$\Sigma s = 1.016$	Na(6)–B(10)	2.813(4)	
Na(3)–B(7)[f]	2.989(4)				

Symmetry code:
[a] $-x+1.5, -y+0.5, z+0.5$.
[b] $x, y+1, z$.
[c] $x, y, z+1$.
[d] $-x+1, y, z+0.5$.
[e] $-x+1, y, z-0.5$.
[f] $x, -y+2, z-0.5$.
[g] $x, y, z-1$.
[h] $x, -y+1, z-0.5$.
[i] $-x+1.5, y+0.5, z$.
[j] $x, y+1, z-1$.
[k] $-x-1, -y+2, z+1$.
[l] $-x+1.5, -y+1.5, z-0.5$.
[m] $x, -y+2, z+0.5$.
[n] $x, -y+1, z+0.5$.
[*] The results refer to the equation $s = \exp[(r_0-r)/B]$ with $r_0 = 1.371$ Å and 1.803 Å for B–O and Na–O bonds, respectively, and $B = 0.37$ [23].

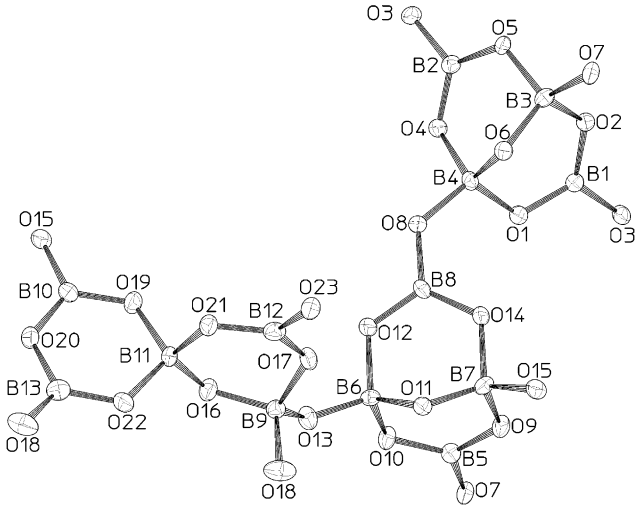

Fig. 1. Representation of the ($B_{13}O_{27}$) borate group existing in $Na_6B_{13}O_{22.5}$. It consists of the association of one pentaborate group (B_5O_{11}) and two tetraborate groups (B_4O_9); the linkage is made by O13 and O8 oxygen atoms. Atoms are represented by 50% ellipsoids.

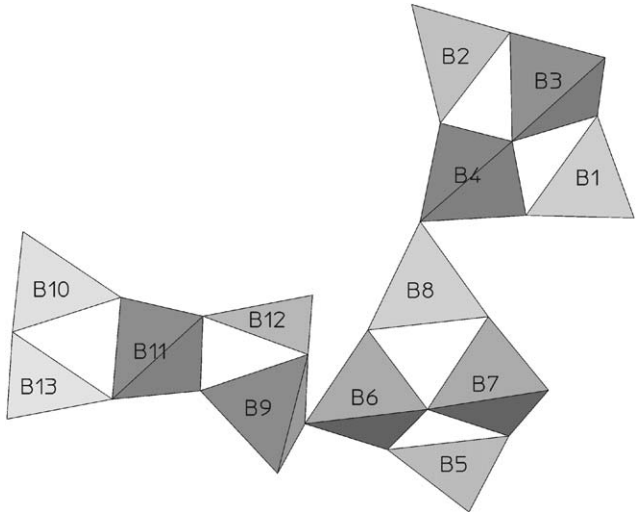

Fig. 2. Representation of ($B_{13}O_{27}$) borate group existing in $Na_6B_{13}O_{22.5}$. BO_3 triangles are in light and BO_4 tetrahedra in dark. Only the boron atoms are labelled.

shorthand notation of the corresponding FBB can be written 13: 2[6(3Δ + 3T) + 0.5(1: Δ)] following the rules of the classification of borates [19,24,25]. Even if there is the same number of BO_3 triangles (seven) and BO_4 tetrahedra (six) as in the studied borate, its structure is completely different; it consists of a distorted O_2MnO_3 square pyramid embedded between $[B_{12}O_{18}(OH)_6]$ and BO_3 units. The $[B_{12}O_{18}(OH)_6]$ cluster is identical to the one existing in a hydrated sodium borate $Na_8[B_{12}O_{20}(OH)_4]$ [28] with the FBB at the above-mentioned 12 boron atoms [19]. Another borate contains 13 boron atoms; this is a mineral named walkerite, the structure of which was recently solved; this is a complex hydrated chloro-borate with the formula: $Ca_{16}Mg[B_{13}O_{17}(OH)_{12}]_4Cl_6(H_2O)_{28}$ [29]. The structure contains 13 crystallographically independent boron atoms with six BO_3 triangles and seven BO_4 tetrahedra, different from the studied borate. Another borate with 13 boron atoms is reported in a recent review [30] but it contains 12 BO_3 triangles and one BO_4 tetrahedron. Therefore, the FBB found in $Na_6B_{13}O_{22.5}$ really corresponds to a new association of BO_3 triangles and BO_4 tetrahedra.

3.2. Sodium atom environments

The sodium atoms are located in six crystallographically independent positions. The Na–O distances show a considerable variation, ranging from 2.217 Å for Na(5)–O(5) to 2.996 Å for Na(1)–O(18) (Table 4). These values are close to the ones found in the other anhydrous sodium borates of known structures (Table 5) [1,2,7–15]. However, some Na–B distances were inferior to the longest Na–O bond, like Na(4)–B(9), 2.749 Å. The bond valence analysis [23] of $Na_6B_{13}O_{22.5}$ structure cannot permit to obtain a more precise value of coordination number of the sodium atoms (Table 4); the values of the valence sums range from 0.846 for Na(4) to 1.281 for Na(5).

To complete the valence bond analysis (Table 4), it is interesting to note that the valence sum values concerning oxygen atoms are around 2, from 1.852 for O(18) to 2.148 for O(5).

3.3. Phase transformations of $Na_2B_4O_7$ and $Na_6B_{13}O_{22.5}$ formation

As for other hydrated alkaline tetraborates [31–34], the thermal decomposition of borax leads to an anhydrous amorphous phase [35]. By annealing this solid for different times and at different temperatures, nonindexed X-ray diffraction patterns were obtained, and attributed to three forms of sodium tetraborate [16]. In a more recent detailed study on "Dependence of crystallization behavior of $Na_2B_4O_7$ on its glass structure and the characteristics of phase transformation" [18], four forms were obtained and identified by their indexed powder patterns; they all crystallize in monoclinic system, while the form with the known structure ([10,17], see Table 5) named α, is triclinic. The following results were published [18], and the Smith and Snyder figures of merit [36] were calculated in Powder Diffraction File [37]: β-$Na_2B_4O_7$: $a = 14.395$ Å, $b = 16.59$ Å, $c = 5.596$ Å, $\beta = 95.09°$, $V = 1331.13$ Å^3, $Z = 10$, $F(30) = 7(0.037, 120)$; γ-$Na_2B_4O_7$: $a = 18.311$ Å, $b = 4.786$ Å, $c = 12.37$ Å, $\beta = 104.48°$, $V = 1049.63$ Å^3, $Z = 8$, $F(30) = 6(0.044, 117)$; δ-$Na_2B_4O_7$: $a = 12.636$ Å, $b = 15.387$ Å, $c = 5.812$ Å, $\beta = 106.98°$, $V = 1080.77$ Å^3, $Z = 8$, $F(30) = 6(0.044,$

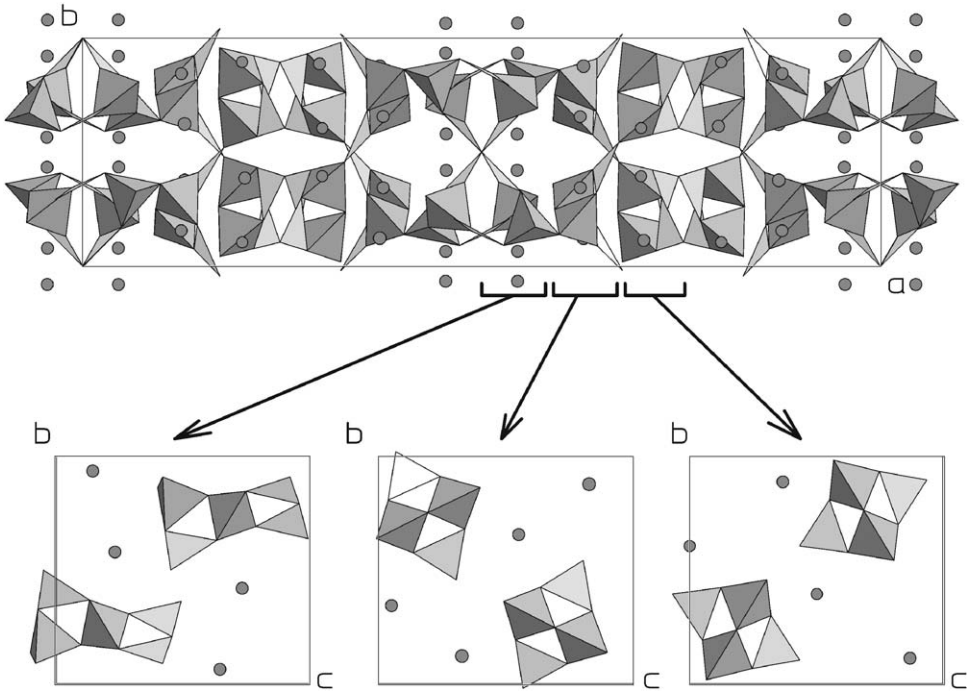

Fig. 3. Schematic representation of the content of the cell. Upper part: whole cell projected on *ab* plane; lower part: contents of the slices $0.5<x<0.6$, $0.6<x<0.675$ and $0.675<x<0.75$, respectively. Black circles represent sodium atoms.

Table 5
Crystallographic and structural data of anhydrous sodium borates

Formula	B/Na	Parameters (Å, deg); V (Å^3); Z	Space group	Borate anion	Ref.
Na_3BO_3	0.33	$a = 5.687$, $b = 7.530$, $c = 9.993$, $\beta = 127.15$; $V = 341.1$; $Z = 4$.	$P2_1/c$	1: [(1: Δ)]	[7]
$Na_4B_2O_5$	0.5	$a = 10.618$, $b = 8.015$, $c = 6.287$, $\beta = 110.1$; $V = 502.46$; $Z = 4$.	$C2/c$	2: [(2: 2Δ)]	[8]
$NaBO_2$ ($Na_3B_3O_6$)	1	$a = 11.925$, $c = 6.439$; $V = 793$; $Z = 6$.	$R-3c$	3: [(3: 3Δ)]	[9]
α-$Na_2B_4O_7$ ($Na_4B_8O_{14}$)	2	$a = 6.5445$, $b = 8.6205$, $c = 10.4855$, $\alpha = 93.279$, $\beta = 94.870$, $\gamma = 90.843$; $V = 588.3$; $Z = 2$.	$P-1$	8: ∞^3 [(5: 3Δ + 2T) + (3: 2Δ + T)]	[10]
$Na_6B_{13}O_{22.5}$	2.17	$a = 33.359$, $b = 9.554$, $c = 10.644$; $V = 3392.4$; $Z = 8$.	*Iba*2	13: ∞^3 [(5: 3Δ + 2T) + 2(4: 2Δ + 2T)]	This work
$Na_3B_7O_{12}$	2.33	$a = 6.638$, $b = 8.249$, $c = 8.836$, $\alpha = 95.875$,	$P-1$	7: ∞^3 [(3: 2Δ + T) + (3: Δ + 2T) + (1: Δ)]	[2]

Table 5 (*continued*)

Formula	B/Na	Parameters (Å, deg); V (Å^3); Z	Space group	Borate anion	Ref.
		$\beta = 100.680$, $\gamma = 99.688$; $V = 464.2$; $Z = 2$.			
α-NaB_3O_5 ($Na_3B_9O_{15}$)	3	$a = 10.085$, $b = 11.363$, $c = 10.845$, $\beta = 104.48$; $V = 1203.3$; $Z = 2$.	$P2_1/c$	9: ∞^3 [(5: 4Δ + T) + (4: 2Δ + 2T)]	[11]
β-NaB_3O_5($Na_3B_9O_{15}$)	3	$a = 8.990$, $b = 11.033$, $c = 12.107$, $\beta = 90.50$; $V = 1200.8$; $Z = 2$.	$P2_1/c$	9: ∞^3 [(5: 4Δ + T) + (3: 2Δ + T) + (1: T)]	[12]
α-$Na_2B_8O_{13}$	4	$a = 6.507$, $b = 17.796$, $c = 8.377$, $\beta = 96.57$; $V = 964$; $Z = 4$.	$P2_1/a$	8: ∞^3 [(5: 4Δ + T) + (3: 2Δ + T)]	[13–15]
β-$Na_2B_8O_{13}$	4	$a = 11.731$, $b = 7.880$, $c = 10.410$, $\beta = 99.883$; $V = 948$; $Z = 4$.	$P2_1/c$	8: ∞^3 [(5: 4Δ + T) + (3: 2Δ + T)]	[1]

115); ε-$Na_2B_4O_7$: $a = 18.862$ Å, $b = 5.856$ Å, $c = 8.839$ Å, $\beta = 93.82°$, $V = 974.15$ Å^3, $Z = 6$, $F(30) = 4(0.046, 171)$. It is worth noting that the results of automatic indexation of powder patterns are of poor quality. Moreover, all these unit cell parameters are completely different from those of α-$Na_2B_4O_7$ and $Na_6B_{13}O_{22.5}$ (Table 5). However, almost all of the reflections reported for the β form can be indexed with $Na_6B_{13}O_{22.5}$ unit cell parameters. It seems that out of the five forms reported for $Na_2B_4O_7$ [18], only two species, whose structures were solved, were clearly determined: triclinic α-$Na_2B_4O_7$, and the new orthorhombic borate $Na_6B_{13}O_{22.5}$, which probably corresponds to the so-called β-$Na_2B_4O_7$. Other experiments of crystal growth are necessary to try to obtain single crystals of the other forms, γ, δ and ε of $Na_2B_4O_7$, to verify the correct formula by the resolution of their structures.

3.4. Discussion

For the past 2 years, three new sodium borates have been found: β-$Na_2B_8O_{13}$ [1], $Na_3B_7O_{12}$ [2] and $Na_6B_{13}O_{22.5}$. Table 5 reports the main crystallographic and structural data of the anhydrous sodium borates whose structures were determined. Most of them participate in the complex equilibria existing in the Na_2O–B_2O_3 binary phase diagram [3–6]. In a recent paper [2], we pointed out that probably $Na_3B_7O_{12}$ (B/Na = 2.33) replaces $Na_2B_5O_{8.5}$ (B/Na = 2.5) in the phase diagram. However, with the discovery of the new borate $Na_6B_{13}O_{22.5}$ (B/Na = 2.17), it was difficult to state that none of the formulas proposed in the phase diagram exist. In a recent work about $Na_2B_4O_7$ [6], to explain the complexity of the Na_2O–B_2O_3 phase diagram around this composition, several thermal analyses were performed on samples preliminary annealed at different temperatures and for different periods. From the results, a small domain of solid solution under the melting point and another form of $Na_2B_4O_7$ (named β) were pointed out without any identification from X-ray powder diffraction [6]. However, the discovery of the new borate $Na_6B_{13}O_{22.5}$ (68.5 mol% B_2O_3) close to $Na_2B_4O_7$ (66.7 mol% B_2O_3) and some experiments to grow single crystals suggests that this last compound melts incongruently while the new borate melts congruently around 740 °C. The Na_2O–B_2O_3 phase diagram must be corrected to integrate this result as well as the presence of $Na_3B_7O_{12}$ [2].

As in other M_2O–B_2O_3 binary systems (M monovalent element), several possibilities may arise with B/M ratio, and not only with integer values; e.g., in the Cs_2O–B_2O_3 system several new cesium borates were found that led to the following B/Cs ratios: 1, 2, 2.33, 3, 4.33, 5, 9 [38]. So, it appears that, from the association of BO_3 triangles and BO_4 tetrahedra, any complex

anions may exist as, e.g., in $K_5B_{19}O_{31}$ [39] or $Rb_5B_{19}O_{31}$ [40] (B/K and B/Rb = 3.8), in $Cs_3B_{13}O_{21}$ (B/Cs = 4.33) (this compound has in fact 26 independent boron atoms) [41], in $Cs_3B_7O_{12}$ (B/Cs = 2.33) [42], and in the studied borate $Na_6B_{12}O_{22.5}$ (B/Na = 2.17) with following complex FBBs: 19: ∞^3 2[(5: 4Δ + T) + (3: 2Δ + T) + (1: Δ) + 0.5(1: T)], 26: ∞^2 [2(5: 4Δ + T) + 4(3: 2Δ + T) + 4(1: Δ)], 63: ∞^2 [(7: 3Δ + 4T) + 10(5: 3Δ + 2T) + ((5: 2Δ + 3T) + (1: T) or (5: 3Δ + 2T) + (1: Δ))], and 13: ∞^3 [(5: 3Δ + 2T) + 2(4: 2Δ + 2T))].

Experiments are in progress to study the nonlinear optical properties of this new noncentrosymmetric borate on powder and single crystal.

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