

Crystal Structure and Thermal Behavior of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$

M. Touboul,*¹ N. Penin,* and G. Nowogrocki†

*Laboratoire de Réactivité et de Chimie des Solides, UPRES A 6007, 33, rue St-Leu, 80039 Amiens Cedex, France; and †Laboratoire de Cristallographie et Physicochimie du Solide, URA 452, ENSC Lille, B.P. 108, 59652 Villeneuve d'Ascq Cedex, France

Received June 4, 1999; in revised form September 15, 1999; accepted September 21, 1999

The crystal structure of synthetic $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ has been established from single-crystal X-ray diffraction data. It crystallizes in the orthorhombic space group *Pbcn* with a unit cell of dimensions $a = 11.276(5)$ Å, $b = 13.097(14)$ Å, $c = 16.751(5)$ Å; $V = 2474(3)$ Å³; $Z = 8$. The structure was determined from 1201 independent reflections and refined until $R = 0.049$ and $R_w = 0.036$; it is composed of isolated $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ polyanions separated by free water molecules and Rb^+ ions. Some of the positions of rubidium and oxygen atoms—the latter are attributed to water molecules—were localized with occupancy factors of 0.5 and 0.3. A similarity appears with the unit cell parameters of $\text{Cs}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$: $a = 8.424$ Å, $b = 11.378$ Å, $c = 13.160$ Å, $\beta = 92.06^\circ$; $V = 1260.5$ Å³; $Z = 4$; space group *P2₁/c*; in fact, the unit cell volume of rubidium borate is doubled but the symmetries of these two compounds are quite different. However, they contain identical $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ polyanions. The dehydration of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ consists of a continuous loss of water until 300°C, forming anhydrous $\text{Rb}_2\text{B}_4\text{O}_7$, which is amorphous to X-ray diffraction. $\text{Rb}_2\text{B}_4\text{O}_7$ crystallizes at about 475°C and melts at 717°C. Two forms of $\text{Rb}_2\text{B}_4\text{O}_7$ appear on the temperature resolved X-ray powder diffraction pattern. One corresponds to the triclinic form of the structure which has been solved recently; to this day, the other one has not been isolated. © 2000 Academic Press

INTRODUCTION

Over the past few years we have undertaken the study of borates in view of establishing the dehydration mechanisms of hydrated borates, and determining the better way to obtain anhydrous borates showing interesting physical properties, such as piezoelectricity for $\text{Li}_2\text{B}_4\text{O}_7$ (1) or non-linear optical behavior for LiB_3O_5 (LBO)(2), TlB_3O_5 (TBO)(3, 4), or CsB_3O_5 (CBO)(5). The present paper deals with a rubidium borate. There is little information about these compounds (6–11). Indeed, only a few papers give structural features for $\text{Rb}_3(\text{BO}_2)_3$ (12), $\text{Rb}_3[\text{B}_3\text{O}_4(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (13),

RbB_5O_8 (14), $\text{Rb}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ (15), $\text{Rb}_2\text{B}_4\text{O}_7$ (16), and two forms of RbB_3O_5 (17, 18). Until this work, the studied compound was formulated $\text{Rb}_2\text{B}_4\text{O}_7 \cdot 6\text{H}_2\text{O}$ (6) or $5\text{H}_2\text{O}$ (7, 9); it appears as a stable phase with a congruent solubility in the ternary system H_2O – Rb_2O – B_2O_3 (7, 9).

EXPERIMENTAL

Hydrated rubidium borate was obtained from an aqueous solution of Rb_2CO_3 and H_3BO_3 in stoichiometric proportions; after CO_2 release, evaporation under constant stirring and heating led to the desired compound in the form of a white powder. Chemical analyses were performed by means of the usual acid–base titration. Large single crystals can easily be obtained by slow evaporation of a diluted solution at room temperature. This compound has been characterized by X-ray powder diffraction (Siemens D5000 diffractometer; $\text{CuK}\alpha_1 = 1.5406$ Å) and by thermal analyses using a Setaram TGDTA 92 apparatus (platinum crucibles; heating rate of 10°C/mn, in air; sample amounts around 40 mg) and a Guinier–Lenné camera ($\lambda\text{CuK}\alpha = 1.5418$ Å; heating rate of 0.1°C/mn, in air, between 20 and 600°C).

STRUCTURAL STUDY

A colorless single crystal was chosen; crystal data and intensity collections are given in Table 1. Absorption corrections were made using DeMeulenaer and Tompa's analytical method (20). A great analogy to the unit cell parameters of the hydrated cesium borate $\text{Cs}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ appears (see Table 2), and in the preliminary study it was thought that the structure of the rubidium salt was simply a substructure of the cesium borate; however, the symmetries are quite different. In the first step, direct methods gave the positions of the rubidium atoms. However, for 16 Rb atoms in the unit cell, 3 positions were obtained, one on a twofold axis, with multiplicity 4, and two in general positions, with multiplicity 8. When one of these positions was affected by an occupancy factor of 1/2, the refinement, using the SHELX-76 program (21), led to $R = 0.347$ and

¹To whom correspondence should be addressed. Fax: 33 3 22827590. E-mail: marcel.touboul@sc.u-picardie.fr.

TABLE 1
Crystal Data and Intensity Collections for
 $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$

Formula weight (g/mol)	426.98
Space group	<i>Pbcn</i> (No. 60)
Unit cell parameters	$a = 11.276(5) \text{ \AA}$; $b = 13.097(14) \text{ \AA}$; $c = 16.751(5) \text{ \AA}$
V ; Z	$2474(3) \text{ \AA}^3$; 8
Density (g/cm ³)	$D_x = 2.29(1)$
Faces limiting the crystals and distances (mm) ^a	(001):0.215; (00 $\bar{1}$):0.215; (110):0.09; ($\bar{1}$ $\bar{1}$ 0):0.09; ($\bar{1}$ 10):0.025; (1 $\bar{1}$ 0):0.04; (2 $\bar{1}$ 0):0.045
Diffractometer	CAD4 (Enraf Nonius)
Temperature	298 K
Radiation	MoK α , graphite monochromated, $\lambda = 0.71069 \text{ \AA}$
Scattering factors	Neutral atoms (19)
Scan type	θ - 2θ
θ range (°)	2-30
Standard reflections	$\bar{2}2\bar{4}$; $\bar{5}22$; $\bar{1}\bar{1}\bar{1}\bar{4}$
Range in h, k, l	$-15 \leq h \leq 15$; $0 \leq k \leq 18$; $0 \leq l \leq 23$
Maximum scan time	60 s
Period of intensity control	7200 s
Reflections collected	8160
Reflections with $I > 3\sigma(I)$	2521
R_{int} before absorption correction	0.121
Linear absorption coefficient	84.2 cm^{-1}
Transmission factors	0.586-0.118
Averaged reflections ($I > 3\sigma(I)$)	1201
R_{int} after absorption correction	0.032
Weighing scheme	$1/\sigma^2(F)$
Number of variables	195
R	0.049
R_w	0.036
GOF	3.73

^aThe dimensions given are the distances from the center of the crystal to the faces of the platelet.

$R_w = 0.432$. Eleven oxygen atoms and four boron atoms were in evidence on the Fourier difference map; the reliability factors went down to 0.099 and 0.106, respectively, with anisotropic parameters. Successive Fourier difference maps then revealed four more crystallographic positions which could be attributed to the oxygen atoms of water molecules. To get reasonable thermal parameters, it was necessary to give these water molecules occupancy factors of 0.5, 0.5, 0.3, and 0.3, respectively. The final reliability factors were $R = 0.049$ and $R_w = 0.036$. Due to disorder in one rubidium atom position and in four water molecule positions, it was not possible to detect and refine the position of the hydrogen atoms. The atomic coordinates and the thermal motion parameters are reported in Tables 3 and 4; significant bond lengths and angles are listed in Table 5.

TABLE 2
Crystallographic Data for fully Hydrated Tetraborates
 $M_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot x\text{H}_2\text{O}$

M	x	Parameters (Å ; °); Z	Space group	Reference
K	2	$a = 12.899$; $b = 11.774$; $c = 6.859$; $Z = 4$	$P2_12_12_1$	(24)
Rb	3.6	$a = 11.276$; $b = 13.097$; $c = 16.751$; $Z = 8$	<i>Pbcn</i>	this work
Cs	3	$a = 8.424$; $b = 11.378$; $c = 13.160$;	$P2_1/c$	(5)
		$\beta = 92.06$; $Z = 4$		

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the crystal structure of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$. It consists of discrete borate anions separated by Rb cations and isolated water molecules. The borate polyanion is constituted of two $\text{BO}_2(\text{OH})$ groups (triangular boron, Δ) and two $\text{BO}_3(\text{OH})$ groups (tetrahedral boron, T). This isolated anion $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ has been found in a lot of hydrated borates cited in a recent paper (5) about the similar compound $\text{Cs}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ (Fig. 2); its shorthand notation, following the classification

TABLE 3
Final Atomic Coordinates and Equivalent Thermal Parameters
 B_{eq} (Å^2) of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ with e.s.d.s in Parentheses

Atom	Occ.	x	y	z	B_{eq}
Rb(1)	1.0	0.0536(1)	0.5259(1)	0.1327(1)	2.98(3)
Rb(2)	1.0	0	0.9090(1)	0.25	4.52(7)
Rb(3)	0.5	0.4278(2)	0.7401(2)	0.2464(2)	3.60(8)
B(1)	1.0	0.8691(13)	0.3105(9)	0.0499(7)	1.3(4)
B(2)	1.0	0.6501(12)	0.3088(10)	0.0534(7)	1.3(4)
B(3)	1.0	0.6331(13)	0.4316(10)	-0.0601(7)	1.8(4)
B(4)	1.0	0.7515(14)	0.2725(10)	-0.0713(6)	1.7(4)
O(1)	1.0	0.6660(6)	0.2363(5)	-0.0121(4)	1.2(2)
O(2)	1.0	0.6080(6)	0.4090(5)	0.0169(4)	1.3(2)
O(3)	1.0	0.9732(6)	0.3139(5)	0.0898(3)	1.7(2)
O(4)	1.0	0.7664(6)	0.3282(5)	0.0923(3)	1.3(2)
O(5)	1.0	0.5885(6)	0.5204(5)	-0.0944(3)	2.3(2)
O(6)	1.0	0.7081(6)	0.3715(5)	-0.1056(4)	1.4(2)
O(7)	1.0	0.5672(6)	0.2761(5)	0.1115(3)	1.4(2)
O(8)	1.0	0.7696(6)	0.2026(5)	-0.1376(4)	1.5(2)
O(9)	1.0	0.8679(6)	0.2909(5)	-0.0303(4)	1.3(2)
Ow(1)	1.0	0.6583(7)	0.0403(5)	0.0325(4)	3.4(3)
Ow(2)	1.0	0.6513(8)	0.1651(6)	0.2348(5)	5.0(3)
Ow(3)	0.5	0.7968(21)	0.4548(14)	0.2206(10)	5.2(8)
Ow(4)	0.5	0.8573(17)	0.3914(13)	0.2428(10)	3.5(6)
Ow(5)	0.3	0.6485(29)	0.5581(23)	0.1765(15)	4(1)
Ow(6)	0.3	0.6356(26)	0.6037(20)	0.2224(18)	4(1)

TABLE 4

Anisotropic Thermal Vibration Parameters ($\times 10^4$) (e.s.d.s in parentheses) for All the Atoms of Rb₂[B₄O₅(OH)₄] · 3.6H₂O Except the Hydrogen Atoms

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb(1)	68(1)	41(1)	24(1)	-18(1)	-2(1)	1(1)
Rb(2)	161(3)	42(1)	22(1)	0	19(1)	0
Rb(3)	87(3)	55(2)	23(1)	-10(2)	-12(2)	-0(1)
B(1)	51(17)	2(8)	9(5)	-6(9)	-0(7)	6(5)
B(2)	28(16)	23(9)	8(4)	19(10)	-0(6)	-3(5)
B(3)	24(15)	35(11)	15(5)	-2(10)	-5(7)	-4(6)
B(4)	32(14)	25(9)	15(4)	13(10)	-0(8)	5(7)
O(1)	22(8)	16(5)	12(3)	-8(5)	0(4)	5(3)
O(2)	21(8)	21(5)	12(3)	6(5)	-1(4)	4(3)
O(3)	25(9)	31(5)	15(3)	6(5)	-13(4)	-7(3)
O(4)	18(8)	23(5)	12(3)	-3(6)	-1(4)	-5(3)
O(5)	50(9)	32(5)	19(3)	21(6)	-2(4)	16(4)
O(6)	20(8)	27(6)	12(3)	6(5)	1(4)	2(3)
O(7)	25(7)	21(5)	13(2)	-4(6)	7(4)	4(3)
O(8)	27(8)	22(6)	13(3)	4(5)	1(4)	-5(3)
O(9)	19(8)	21(5)	12(3)	0(5)	-0(4)	3(3)
Ow(1)	78(10)	23(6)	41(4)	10(7)	22(5)	7(4)
Ow(2)	145(13)	49(7)	39(4)	-24(8)	-33(7)	20(5)
Ow(3)	183(39)	49(17)	26(8)	-52(20)	9(13)	5(10)
Ow(4)	86(24)	60(16)	19(7)	-28(17)	14(11)	-6(9)
Ow(5)	68(39)	68(30)	39(14)	-68(28)	31(17)	-45(15)
Ow(6)	30(31)	16(20)	74(20)	0(22)	24(21)	-12(16)

proposed by Heller (22) and Christ and Clark (23), is $4:2\Delta + 2T$. The B–O bonds are similar in these two compounds: in the triangular borons, the B–O bonds go from 1.352 to 1.391 Å in the rubidium compound, and from 1.361 to 1.379 Å in the cesium compound; the mean values for B–O bonds are 1.366 to 1.376 Å for the first borate, and 1.368 and 1.367 Å for the second. For the tetrahedral borons, the mean values of the B–O bonds are 1.472 and 1.479 Å in the rubidium compound, and 1.474 and 1.473 Å in the cesium compound. The Rb⁺ ions and the isolated water molecules are disposed between [B₄O₅(OH)₄]²⁻ anions. The oxygenated environment of rubidium atoms (see Table 5) is classical: there are eight and nine oxygen atoms around the rubidium ions between 2.844 and 3.284 Å.

Comparison of rubidium and cesium borates shows great similarities between them (see Fig. 1 and 2). It is only the orientation of half of the [B₄O₅(OH)₄] groups which imposes the doubling of one of the parameters in the rubidium salt ($c = 16.751$ Å instead of $a = 8.424$ Å, Table 2). The disorder in rubidium ions and water molecules is another striking difference. Very often the rubidium and potassium compounds are isotypic due to the same size of the K⁺ and Rb⁺ cations. However, the synthetic fully hydrated alkaline (K, Rb, and Cs) tetraborates are not similar as shown in Table 2; the cesium compound is monoclinic and the

TABLE 5
Interatomic Distances (Å) and Angles (°) in Rb₂[B₄O₅(OH)₄] · 3.6H₂O

Triangular borons			
B(1)–O(3)	1.352(15)	O(3)–B(1)–O(4)	118.0(8)
–O(4)	1.378(15)	O(3)–B(1)–O(9)	120.0(8)
–O(9)	1.368(14)	O(4)–B(1)–O(9)	122.0(8)
mean	1.366	mean	120
B(3)–O(2)	1.353(14)	O(2)–B(3)–O(5)	120.1(8)
–O(5)	1.391(15)	O(2)–B(3)–O(6)	121.9(9)
–O(6)	1.384(15)	O(5)–B(3)–O(6)	118.0(8)
mean	1.376	mean	120
Tetrahedral borons			
B(2)–O(1)	1.462(14)	O(1)–B(2)–O(2)	107.2(7)
–O(2)	1.524(15)	O(1)–B(2)–O(4)	109.4(7)
–O(4)	1.486(15)	O(1)–B(2)–O(7)	113.6(7)
–O(7)	1.416(14)	O(2)–B(2)–O(4)	107.7(7)
mean	1.472	O(2)–B(2)–O(7)	109.3(7)
		O(4)–B(2)–O(7)	109.5(7)
		mean	109.5
B(4)–O(1)	1.462(15)	O(1)–B(4)–O(6)	109.0(7)
–O(6)	1.500(15)	O(1)–B(4)–O(8)	114.0(7)
–O(8)	1.454(13)	O(1)–B(4)–O(9)	108.6(8)
–O(9)	1.501(16)	O(6)–B(4)–O(8)	107.3(7)
mean	1.479	O(6)–B(4)–O(9)	108.8(8)
		O(8)–B(4)–O(9)	109.1(8)
		mean	109.5
B–O–B angles inside the B ₄ O ₅ unit			
B(2)–O(1)–B(4)	112.3(9)	B(3)–O(6)–B(4)	119(1)
B(2)–O(2)–B(3)	120(1)	B(1)–O(9)–B(4)	119(1)
B(1)–O(4)–B(2)	119(1)		
Rb–O bonds (< 3.50 Å)			
Rb(1)–Ow(4 ⁱ)	2.909(17)	Rb(2)–Ow(5 ^v)	2.852(30)
–Ow(1 ⁱⁱ)	2.926(8)	–Ow(5 ⁱⁱ)	2.852(30)
–O(3 ⁱⁱⁱ)	3.008(7)	–O(5 ^{vii})	2.940(5)
–O(6 ^{iv})	3.038(7)	–O(5 ^{viii})	2.940(5)
–Ow(2 ^v)	3.076(8)	–O(7 ^v)	2.998(6)
–O(9 ^{iv})	3.079(7)	–O(7 ⁱⁱ)	2.998(6)
–Ow(3 ⁱ)	3.123(19)	–Ow(6 ^v)	3.009(27)
–Ow(1 ^{vi})	3.131(7)	–Ow(6 ⁱⁱ)	3.009(27)
–Ow(4 ⁱⁱⁱ)	3.377(18)	–Ow(3 ^v)	3.436(23)
–Ow(3 ⁱⁱⁱ)	3.379(22)	–Ow(3 ⁱⁱ)	3.436(23)
–Ow(2 ⁱⁱ)	3.404(9)		
Rb(3)–Ow(5 ⁱ)	2.844(30)		
–O(3 ^v)	2.954(6)		
–O(8 ^{iv})	2.973(7)		
–Ow(6)	2.974(28)		
–O(3 ^{ix})	3.010(6)		
–Ow(4 ^{ix})	3.131(18)		
–O(6 ^{iv})	3.170(7)		
–Ow(3 ^v)	3.224(20)		
–Ow(2 ^v)	3.284(9)		
–O(4 ^v)	3.456(6)		

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

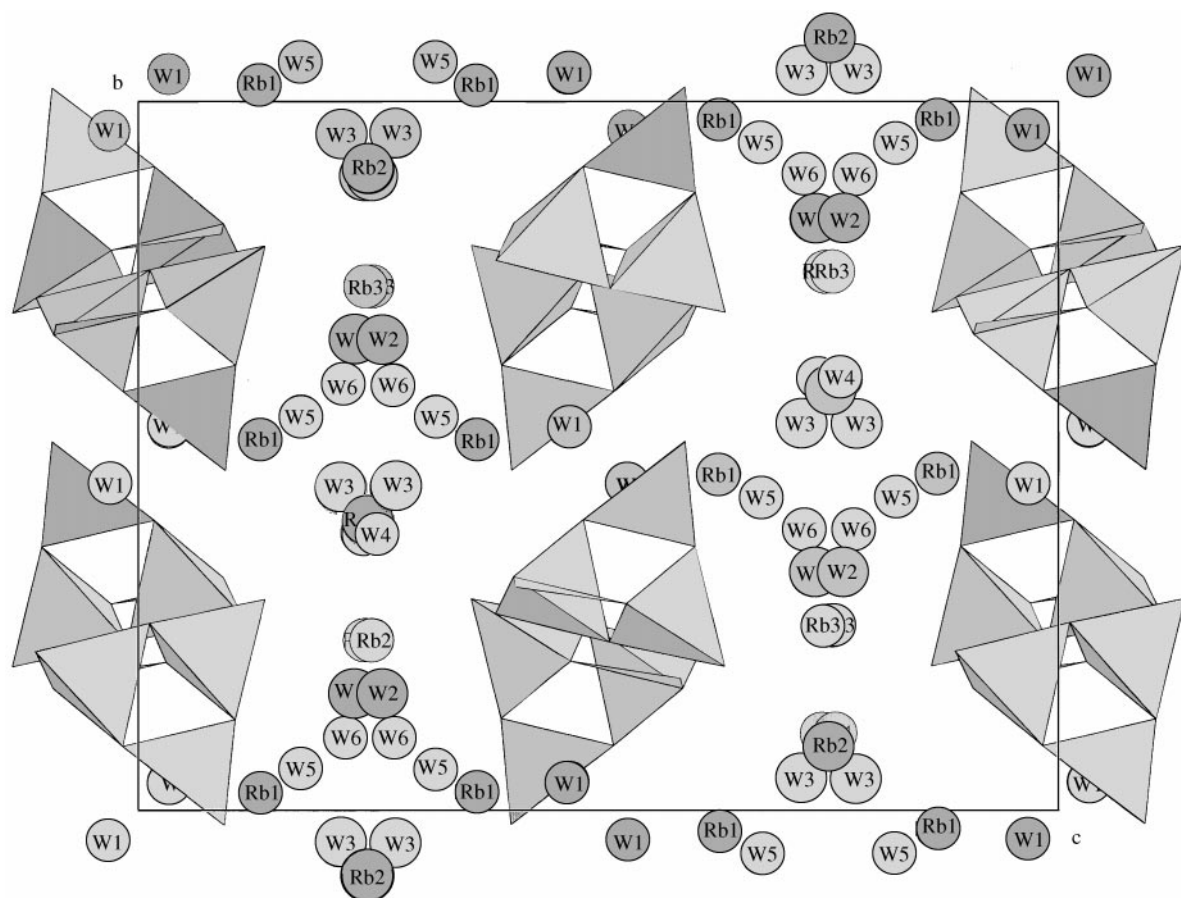


FIG. 1. Projection of the structure of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ in the (100) plane; W represents an oxygen atom of a water molecule.

potassium compound $\text{K}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ is orthorhombic. Indeed although these three borates contain the same $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ anions, they do not have the same number of isolated water molecules, 2 for the potassium compound, 3 for the cesium compound, and 3.6 for the studied rubidium compound.

DEHYDRATION

As shown before, the $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ crystal structure consists of isolated $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ polyanions which are separated by Rb^+ cations and isolated water molecules. From this description, the following theoretical scheme of dehydration can be imagined since, by heating, the isolated water molecules are in principle removed first, followed by the hydroxyl groups:

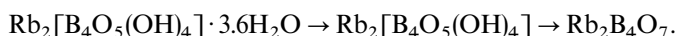


Figure 3 shows the thermal analyses (TG and DTA) performed on $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$. An identical be-

havior has been obtained when the heating rate was changed from 0.5, 1, 5, to $10^\circ\text{C}/\text{mn}$. On the TG curve only one weight loss appears; it corresponds to the loss of 5.6 water molecules with only a slight change in slope at about 140°C . This result is coherent with the occupancy factors attributed to the water molecules in the refinement of the structure. The true water rate of this compound, 5.6, is therefore included between the values proposed before, 6 (6) and 5 (7, 9). On the DTA curve, the first endothermic peak involves the loss of water molecules. Two other peaks appear at about 475 and 717°C ; the first is exothermic and corresponds to a crystallization, while the second is due to fusion. This melting point corresponds to that found for $\text{Rb}_2\text{B}_4\text{O}_7$ in the previous study of the $\text{Rb}_2\text{O}-\text{B}_2\text{O}_3$ phase diagram (10), where $\text{Rb}_2\text{B}_4\text{O}_7$ melts congruently around 720°C . All these results are confirmed by examination of the Guinier-Lenné photograph (Fig. 4); the powder pattern of the starting material, $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$, is visible until 85°C ; then an amorphous phase appears until 450°C , and above this temperature the powder patterns of two anhydrous $\text{Rb}_2\text{B}_4\text{O}_7$ phases successively appear. A

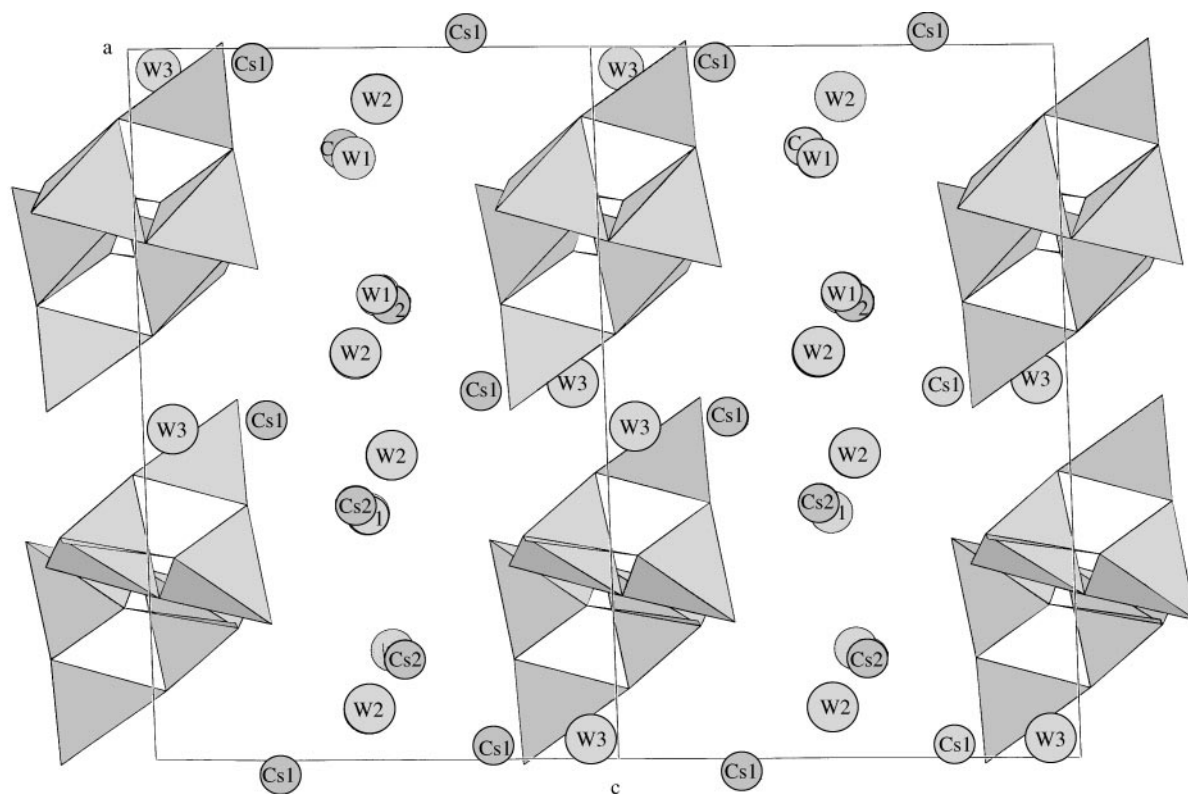


FIG. 2. Projection of two unit cells of $\text{Cs}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ in the (010) plane; W represents an oxygen atom of a water molecule.

$\text{Rb}_2\text{B}_4\text{O}_7$ form crystallizes at about 450°C ; indexation of the powder pattern allows us to show that this phase corresponds to the triclinic form, the structure of which has been solved recently (16). A phase transformation appears at about 600°C ; it is reversible and not visible on the DTA curve (Fig. 3); a complementary study will help determine the nature of this new form.

As shown in other borates (1, 3, 4), there is no analogy between the borate polyanions existing in the hydrated

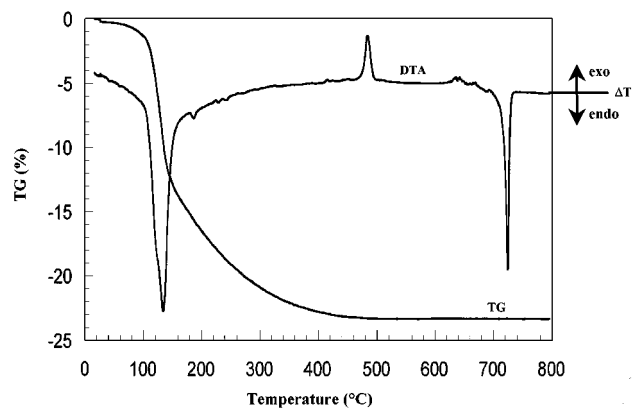


FIG. 3. TG and DTA of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ with a heating rate of $10^\circ\text{C}/\text{mn}$.

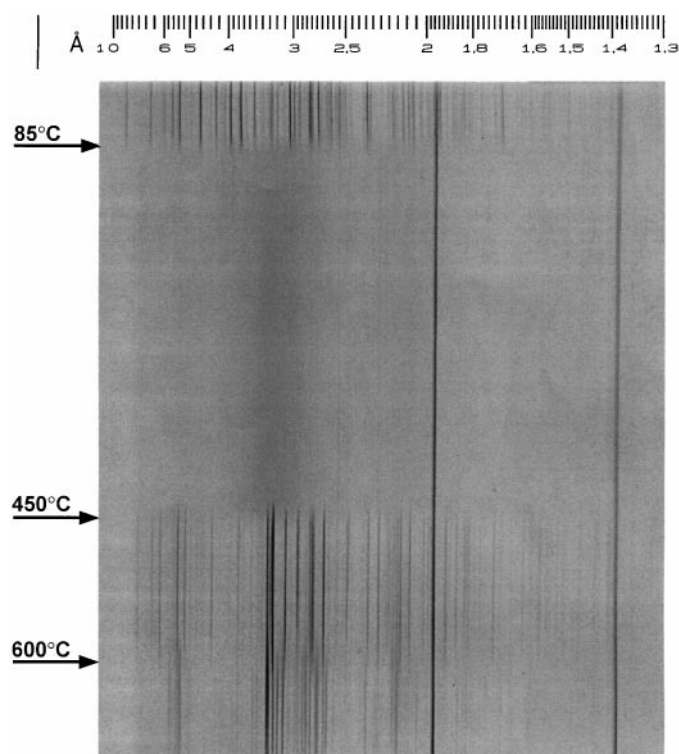


FIG. 4. Guinier-Lenné photograph of $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ with a heating rate of $0.1^\circ\text{C}/\text{mn}$.

borate $\text{Rb}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3.6\text{H}_2\text{O}$ and those existing in the known form of anhydrous $\text{Rb}_2\text{B}_4\text{O}_7$. In this last compound, the structure is very complex; it consists of a three-dimensional skeleton formed by three kinds of anions, BO_3 triangles (Δ), B_3O_8 rings consisting of a triangle and two tetrahedra ($\Delta + 2\text{T}$), and B_4O_9 double rings formed by two triangles and two tetrahedra ($2\Delta + 2\text{T}$). Using the classification of Heller (22), the notation for $[\text{B}_8\text{O}_{14}]^{4-}$ ions is $8: \infty^3(4 - 1: 2\Delta + 2\text{T}, 3: \Delta + 2\text{T}, +1\Delta)$.

REFERENCES

1. M. Touboul and E. Bétourné, *Solid State Ionics* **63–65**, 340 (1993).
2. E. Bétourné and M. Touboul, *J. Alloys Compounds* **255**, 91 (1997).
3. M. Touboul, E. Bétourné, and G. Nowogrocki, *J. Solid State Chem.* **131**, 370 (1997).
4. M. Touboul and G. Nowogrocki, *J. Solid State Chem.* **136**, 216 (1998).
5. M. Touboul, N. Penin, and G. Nowogrocki, *J. Solid State Chem.* **143**, 260 (1999).
6. Reissig, *Liebig's Ann.* **127**, 37 (1863).
7. A. P. Rollet and L. Andrès, *Bull. Soc. Chim. Fr.* **49**, 847 (1931).
8. H. A. Lehmann and W. Gaube, *Z. Anorg. Allg. Chem.* **335**, 50 (1965).
9. P. Tolédano, *Rev. Chim. Miner.* **1**, 353 (1964).
10. J. Kocher, *Rev. Chim. Miner.* **3**, 209 (1966).
11. J. B. Dmitriev, M. R. Marinov, and D. A. Savrakieva, *Dokl. Bolg. Akad. Nauk* **19**, 1055 (1966).
12. D. W. Schneider and G. B. Carpenter, *Acta Crystallogr.* **B26**, 1189 (1970).
13. I. I. Zviedre and A. F. Ievins, *Latvijas PSR Zinatnu Akad. Vestis Kim. Ser.* 395 (1974).
14. J. Krogh-Moë, *Arkiv Kemi* **14**, 439 (1979).
15. H. Behm, *Acta Crystallogr.* **C40**, 217 (1984).
16. M. G. Krzhiszhanskaya, R. S. Bubnova, I. I. Bannova, and S. K. Filatov, *Crystallogr. Rep.* **42**, 264 (1997).
17. R. S. Bubnova, M. G. Krzhiszhanskaya, I. G. Polyakova, V. B. Trofimov, and S. K. Filatov, *Inorg. Mater.* **34**, 1119 (1998).
18. M. G. Krzhiszhanskaya, R. S. Bubnova, V. S. Fundamenskii, I. I. Bannova, I. G. Polyakova, and S. K. Filatov, *Crystallogr. Rep.* **43**, 21 (1998).
19. "International Tables for X-Ray Crystallography," Vol. IV. Kynoch Press, Birmingham, UK, 1974. [Present distributor, Kluwer Academic, Dordrecht].
20. J. de Meulenaer and H. Tompa, *Acta Crystallogr.* **19**, 1014 (1965).
21. G. M. Sheldrick, "SHELX-76: A Program for Crystal Structure Determination." University of Cambridge, UK, 1976.
22. G. Heller, *Topics Curr. Chem.* **131**, 39 (1986).
23. C. L. Christ and J. R. Clark, *Phys. Chem. Miner.* **2**, 59 (1977).
24. M. Marezio, H. A. Plettinger, and W. H. Zachariasen, *Acta Crystallogr.* **16**, 975 (1963).