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Dehydration Process of $TlB_5O_6(OH)_4 \cdot 2H_2O$ and Crystal Structure of TlB_5O_8

M. Touboul*, [1] 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 Cristallochimie et Physicochimie du Solide, URA452, ENSC Lille, B.P. 108, 59652 Villeneuve d'Ascq Cedex, France

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The dehydration of $TlB_5O_6(OH)_4 \cdot 2H_2O$ leads to a loss of water in one step, forming anhydrous TlB_5O_8, which is amorphous to X-ray diffraction. This can be explained by structural considerations; a decrease in oxygenated coordination of thallium ions occurs during the heating. TlB_5O_8 crystallizes at about 450°C and melts at 660°C. By slow cooling from the melt, single crystals were obtained. TlB_5O_8 is orthorhombic, space group *Pbca*, with unit cell parameters $a = 7.557(3)$ Å, $b = 11.925(6)$ Å, $c = 14.734(19)$ Å; $Z = 8$. The structure was solved from 1113 reflections until $R = 0.023$ and $R_w = 0.026$. The structure consists of two separate interlocking three-dimensional networks of pentaborate groups, which form large empty tunnels. Nine oxygen atoms belonging to four different pentaborate groups surround each thallium ion. Except for the presence of pentaborate groups with almost the same geometry, there is no relation between the structure of TlB_5O_8 and that of its hydrated precursor, $TlB_5O_6(OH)_4 \cdot 2H_2O$; the shorthand notation of polyborate anions in these compounds is $5{:}\infty^3(4\Delta+T)$ and $5{:}4\Delta+T$, respectively. © 1998 Academic Press

INTRODUCTION

Numerous papers have been published recently concerning borates mainly for two reasons: one is the study of the dehydration mechanisms of hydrated borates (1–4), and the other concerns the search for anhydrous borates showing interesting physical properties, such as piezoelectricity for $Li_2B_4O_7$ (5), and especially nonlinear optical behavior, as observed for BBO (β-BaB_2O_4), LBO (LiB_3O_5), CBO (CsB_3O_5) (6), CLBO ($CsLiB_6O_{10}$) (7–9), and GdCOB ($Ca_4GdO(BO_3)_3$) (10). For these reasons we have re-examined thallium borates. A primary report on TlB_3O_5 (TBO), which is a possible candidate for second harmonic generation applications, has been published (11). The present paper deals with hydrated and anhydrous thallium pentaborates.

Previous studies about thallium borates have shown the existence of three TlB_5O_8 hydrates: $TlB_5O_8 \cdot H_2O$ and $TlB_5O_8 \cdot 2H_2O$, which are only characterized by unindexed powder patterns (12), and $TlB_5O_8 \cdot 4H_2O$, which is well characterized by its structure (13, 14) and an indexed powder pattern (PDF 38-1131). As for other anhydrous borates, TlB_5O_8 can be obtained by classical ceramic routes from mixtures of H_3BO_3 (or B_2O_3) and Tl_2CO_3; however, due to the low melting point of B_2O_3 ($\sim$450°C) and the weak thermal stability of Tl_2CO_3, volatilization may occur, which may lead to a change from the mixture's initial composition. To avoid this inconvenience, another way to synthesize TlB_5O_8 is the dehydration of its hydrated precursor. In this paper, this latter route was studied, and the structure of TlB_5O_8 was determined. A previous study (15) had shown that TlB_5O_8 was isotypic of the low-temperature modification of potassium pentaborate, β-KB_5O_8; the structure of this compound had been remarkably established by Krogh-Moë (16, 17) using intensity data obtained from Weissenberg exposures until $R = 11.1\%$. It was necessary to obtain better intensity data for TlB_5O_8 to establish more precisely the borate polyanion geometry existing in this compound and compare it with the structure of its hydrated precursor, $TlB_5O_6(OH)_4 \cdot 2H_2O$ (14).

EXPERIMENTAL

The hydrated thallium pentaborate $TlB_5O_6(OH)_4 \cdot 2H_2O$ was obtained from an aqueous solution of Tl_2CO_3 and H_3BO_3 in stoichiometric proportions; after CO_2 release, its evaporation under constant stirring and heating led to the wanted compound as a white powder. Chemical analyses were performed by means of the usual acid–base titration; after Tl titration by a 0.1 M HCl solution, a glycerol–water mixture (1 : 1 in volume) was added to analyze B using 0.1 M NaOH solution; the B/Tl ratio was equal to 5. The compound was also well characterized by its X-ray powder pattern. Thermogravimetry (TG) and differential thermal

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[1] To whom correspondence should be addressed.

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analysis (DTA) were simultaneously performed with a Setaram TG DTA 92 apparatus. All experiments were carried out in air; samples of about 25 mg were heated at 10°C/min in platinum crucibles, and Al_2O_3 was used as the reference material. Temperature-resolved X-ray powder diffraction (TRXRPD) was performed using a Guinier-Lenné camera between 20 and 600°C with a heating rate of 6°C/h.

Dehydration of $TlB_5O_6(OH)_4 \cdot 2H_2O$

The $TlB_5O_6(OH)_4{\cdot}2H_2O$ (14) crystal structure consists of thallium ions, which are disposed between isolated $B_5O_6(OH)_4^-$ polyanions and isolated water molecules. From this description, the following theoretical scheme of dehydration could be imagined:

$$TlB_5O_6(OH)_4{\cdot}2H_2O \xrightarrow{-2H_2O} TlB_5O_6(OH)_4 \xrightarrow{-2H_2O} TlB_5O_8.$$

Figure 1 shows the thermal analyses (TG and DTA) performed on $TlB_5O_6(OH)_4{\cdot}2H_2O$. There is only one loss in weight, which corresponds to the loss of four water molecules, but a change in slope occurs at about 205°C on the TG curve. From this result, the following scheme can be proposed:

$$TlB_5O_6(OH)_4{\cdot}2H_2O \xrightarrow[-3H_2O]{\sim 120-205^\circ C} TlB_5O_7(OH)_2$$

$$\xrightarrow[-1H_2O]{\sim 205-350^\circ C} TlB_5O_8.$$

This scheme is confirmed by the interpretation of the peaks appearing on the DTA curve. Two very close endothermic peaks correspond to the loss of three water molecules; the loss of the last water molecule is slow, and no thermal phenomenon appears. Only a small endothermic peak appears on the DTA curve at about 310°C, nearly at the end of total water removal. Two other peaks appear at about 450 and 660°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 TlB_5O_8 in the previous study of the Tl_2O–B_2O_3 phase diagram (12).

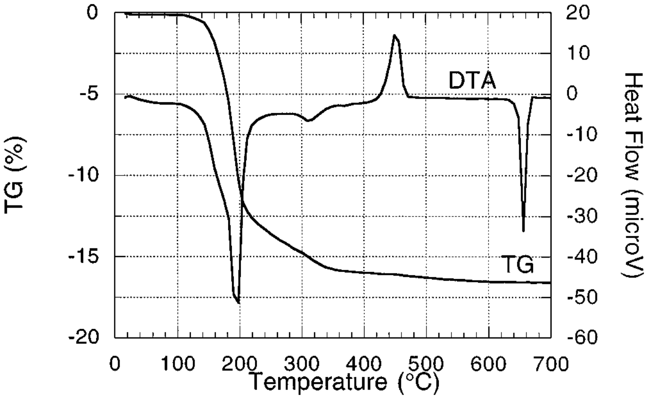

FIG. 1. TG and DTA of $TlB_5O_6(OH)_4{\cdot}2H_2O$ with a heating rate of 10°C/min.

This dehydration process can be explained by examining the oxygenated environment of thallium ions and its change when the product is heated. It consists of two isolated water molecules (at 2.835 and 2.91 Å), two oxygens (at 2.972 and 2.976 Å), and two hydroxyl groups (at 3.011 and 3.024 Å) (14). The last four oxygen atoms belong to two isolated pentaborate groups. By heating, the water molecules first escape, leading to an unstable oxygenated coordination of thallium ions, which cannot permit the stabilization of an intermediate hydrate, $TlB_5O_6(OH)_4$. So the dehydration immediately continues with the loss of two other water molecules, which correspond to the four hydroxyl groups. After that, the oxygenated coordination of thallium ions becomes two, which is even more unstable and leads to the structure collapse giving an amorphous anhydrous borate, which subsequently recrystallizes at about 450°C. This scheme is confirmed by the result of TRXRPD experiment where only the powder pattern of the starting material, $TlB_5O_6(OH)_4{\cdot}2H_2O$, is present until 130°C; no other powder pattern appears until 600°C.

Single-Crystal X-Ray Diffraction Study of TlB_5O_8

Single crystals were easily obtained by slow cooling from the melt. Data collection was made at 20°C from a small crystal of about 1.20×10^{-3} mm^3 using an Enraf-Nonius CAD-4 diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) isolated with a graphite monochromator. The crystal system is orthorhombic, and the unit cell parameters near to those previously published (13), refined from 25 reflections, are $a = 7.557(3)$ Å, $b = 11.925(6)$ Å, $c = 14.734(19)$ Å; $V = 1328(2)$ Å^3; $M = 386{,}417$ g mol^{-1}; $D_m = 3.6$ g cm^{-3}; $D_x = 3.865$ g cm$^{-\ 3}$; $Z = 8$; $F(000) = 1360$. Systematic extinctions of $l = 2n + 1$ reflections for $(0kl)$ and $(h0l)$ and $h = 2n + 1$ for $(hk0)$ have confirmed the $Pbca$ space group previously proposed (13) by anology with isotypic β-KB_5O_8 (16, 17).

Intensity data were collected using the 2θ–ω scanning method between $2\theta = 4°$ and $2\theta = 60°$, with $h = \pm 10$, $k = \pm 16$, and $l = 0$ to 20. Standard reflections 200, $10\bar{2}$ and $\bar{2}\bar{3}3$ were monitored every 200 reflections, and no significant intensity deviation was detected. Out of 7900 measured reflections, 4019 had an intensity greater than three times their standard deviation, and after averaging, 1113 independent reflections were kept ($R_{int} = 0.238$). The Patterson function led to the coordinates of the thallium atom; successive refinements and Fourier difference syntheses gave the positions of other atoms. Absorption corrections were performed according to the method of De Meulenaer and Tompa (18) after indexing the crystal faces ($\mu = 245.68\ \mathrm{cm}^{-1}$): 010, $0\bar{1}0$; 105, $\bar{1}0\bar{5}$; $\bar{1}00$, 201. The transmission factor varied from 0.336 to 0.0343 and the R_{int} became 0.044 for 1113 reflections. Refinement made use of the program SHELX-76 (19). The final R values with anisotropic thermal vibrations for all the atoms are $R = \sum|F_{\mathrm{obs}} - F_{\mathrm{cal}}|/\sum|F_{\mathrm{obs}}| = 0.023$, and $R_w = (\sum_w(F_{\mathrm{obs}} - F_{\mathrm{cal}})^2/\sum_w F_{\mathrm{obs}}^2)^{1/2} = 0.026$ for 128 refined parameters. The scattering factors used are those for neutral atoms taken from the "International Tables for X-ray Crystallography" (20). A correction for anomalous dispersion was applied. The weighing scheme used is taken from the counting statistics $\sigma(I) = (I + L + R + 0.04(I - L - R)^2)^{1/2}$ where I, L, and R are the total intensity, left background, and right background, respectively. The atomic coordinates and the thermal motion parameters are reported in Table 1; significant bond lengths and angles are listed in Table 2.

DESCRIPTION OF THE STRUCTURE

Figures 2 and 3 give two representations of the TlB_5O_8 structure. It consists of two separate interlocking three-dimensional networks built from the pentaborate group B_5O_8. This one is well known; it is formed by one tetrahedrally coordinated boron and four triangularly coordinated boron. The BO_3 triangles and the BO_4 tetrahedron are almost regular (Table 2). Considering the shorter Tl–B distances, each thallium ion is coordinated to nine oxygens. Note that these thallium ions are not situated in the large tunnels, which are empty (Fig. 2). Following the crystal chemical classification of borate structures proposed by Christ and Clark (21) and Heller (22), the shorthand notation of borate polyanion existing in TlB_5O_8 is $5:\infty^3(4\Delta + \mathrm{T})$.

DISCUSSION

The structure of TlB_5O_8 is very close to that of β-KB_5O_8 (16, 17); indeed the average B–O bond lengths are 1.46 and 1.471(10) Å, for the tetrahedrally coordinated boron, respectively, and 1.37 and 1.364(10) Å for the triangularly coordinated borons for the potassium and the thallium pentaborate, respectively. The oxygenated environment of the potassium ion (nine oxygen atoms between 2.90 and 3.20 Å) is almost the same as that of the thallium ion, probably due to K^+ and Tl^+ radii being of almost the same size. The structure of high-temperature modification of potassium pentaborate, α-KB_5O_8, was reported by Krogh-Moë (23): $a = 8.383$ Å, $b = 8.418$ Å, $c = 21.540$ Å, $Z = 8$, space group *Pbca*. The structure of α-KB_5O_8 differs from both the β-modification and TlB_5O_8 in the mutual arrangement of the pentaborate groups: a twofold screw axis runs close to one end of the pentaborate group in the c direction. As described by Krogh-Moë (23), these groups are attached to each other by a common oxygen atom, located in the neighborhood of the twofold screw axis, and extend from this atom in opposite directions in α-KB_5O_8 (trans configuration). In the β-modification and TlB_5O_8, however, a twofold screw axis runs near the center of the pentaborate groups, and these groups run back in nearly the same direction, b, around this screw axis (cis configuration). Obviously, this is related to the considerable difference in packing of the two modifications of potassium pentaborate, which leads to $d = 2.29\ \mathrm{g\,cm^{-3}}$ for β-KB_5O_8 and $1.93\ \mathrm{g\,cm^{-3}}$ for α-KB_5O_8 (23). Such dimorphism has not been found for TlB_5O_8 in the study of Tl_2O–B_2O_3 system (12).

Three other pentaborate groups, different from those existing in TlB_5O_8, are reported in anhydrous borates. Discrete $B_5O_{10}^{5-}$ anions form the structure of $CaNa_3B_5O_{10}$

TABLE 1
Final Atomic Coordinates, Equivalent Isotropic Thermal Vibration Parameters (Å^2), and Anisotropic Thermal Vibration Parameters (×10^4) (Esd's in Parentheses)

Atom	x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl	0.06591(4)	0.20798(3)	0.12226(2)	1.909(7)	102.0(5)	29.4(2)	20.1(1)	−16.9(3)	−4.0(3)	−3.2(2)
O(1)	0.4203(6)	0.2944(4)	0.0736(3)	1.2(1)	82(8)	11(3)	12(2)	1(6)	−10(4)	−1(3)
O(2)	0.6768(6)	0.1792(4)	0.0640(4)	1.2(1)	71(9)	11(4)	18(3)	0(4)	14(4)	−3(2)
O(3)	0.9036(6)	0.4904(4)	0.0921(4)	1.2(1)	75(9)	8(3)	17(3)	−3(4)	−13(4)	3(2)
O(4)	0.4874(6)	0.4637(4)	0.1508(3)	1.0(1)	55(8)	12(3)	11(3)	−0(4)	−8(3)	−0(2)
O(5)	0.4453(6)	0.1350(4)	0.1724(3)	1.2(1)	69(8)	12(4)	15(3)	−3(5)	18(4)	−5(2)
O(6)	0.6313(6)	0.2937(5)	0.1966(3)	0.9(1)	59(7)	8(3)	12(2)	3(5)	−3(3)	−3(3)
O(7)	0.3002(6)	0.4689(4)	0.0235(3)	0.9(1)	59(8)	11(3)	10(2)	−2(4)	−6(3)	−1(2)
O(8)	0.1119(6)	0.4433(4)	0.2031(4)	1.1(1)	59(9)	17(4)	11(3)	7(4)	2(3)	7(2)
B(1)	0.5797(10)	0.3995(6)	0.2129(6)	0.8(2)	39(11)	8(5)	14(4)	−2(7)	3(6)	0(3)
B(2)	0.5472(10)	0.2261(5)	0.1265(7)	0.9(2)	78(12)	10(5)	5(3)	−4(6)	−2(7)	−2(5)
B(3)	0.6917(10)	0.0704(7)	0.0445(6)	1.0(2)	52(12)	12(5)	13(4)	3(7)	−0(6)	1(4)
B(4)	0.4033(10)	0.4060(7)	0.0813(6)	1.0(2)	50(14)	19(6)	10(4)	5(7)	9(5)	1(4)
B(5)	0.4775(10)	0.0259(7)	0.1565(6)	0.9(2)	45(13)	14(5)	10(4)	0(6)	−8(5)	6(3)

TABLE 2
Interatomic Distances (Å) and Angles (°) with E.s.d.'s in Parentheses

		B Triangles			
B(1)–O(4)	1.382(9)	O(4)–O(6)	2.397(7)	O(4)–B(1)–O(6)	123(1)
–O(6)	1.342(9)	O(4)–O(8)	2.362(7)	O(4)–B(1)–O(8)	119(1)
–O(8)	1.365(10)	O(6)–O(8)	2.321(8)	O(6)–B(1)–O(8)	118(1)
Mean value	1.363(9)	Mean value	2.360(7)	Mean value	120(1)
B(3)–O(2)	1.334(10)	O(2)–O(3^{i})	2.368(7)	O(2)–B(3)–O(3^{i})	121(1)
–O(3^{i})	1.386(10)	O(2)–O(7^{ii})	2.377(7)	O(2)–B(3)–O(7^{ii})	123(1)
–O(7^{ii})	1.377(9)	O(3^{i})–O(7^{ii})	2.347(7)	O(3^{i})–B(3)–O(7^{ii})	116(1)
Mean value	1.366(10)	Mean value	2.364(7)	Mean value	120(1)
B(4)–O(1)	1.342(10)	O(1)–O(4)	2.372(7)	O(1)–B(4)–O(4)	121(1)
–O(4)	1.388(10)	O(1)–O(7)	2.387(7)	O(1)–B(4)–O(7)	123(1)
–O(7)	1.377(9)	O(4)–O(7)	2.350(8)	O(4)–B(4)–O(7)	116(1)
Mean value	1.369(10)	Mean value	2.370(7)	Mean value	120(1)
B(5)–O(3^{i})	1.374(10)	O(3^{i})–O(5)	2.383(7)	O(3^{i})–B(5)–O(5)	122(1)
–O(5)	1.344(10)	O(3^{i})–O(8^{iii})	2.338(7)	O(3^{i})–B(5)–O(8^{iii})	116(1)
–O(8^{iii})	1.377(10)	O(5)–O(8^{iii})	2.370(7)	O(5)–B(5)–O(8^{iii})	121(1)
Mean value	1.365(10)	Mean value	2.364(7)	Mean value	120(1)
		B Tetrahedron			
B(2)–O(1)	1.480(9)	O(1)–O(2)	2.280(7)	O(1)–B(2)–O(2)	108.3(9)
–O(2)	1.456(10)	O(1)–O(5)	2.402(7)	O(1)–B(2)–O(5)	107.7(8)
–O(5)	1.493(9)	O(1)–O(6)	2.414(6)	O(1)–B(2)–O(6)	110.6(9)
–O(6)	1.456(10)	O(2)–O(5)	2.427(7)	O(2)–B(2)–O(5)	110.7(9)
		O(2)–O(6)	2.408(7)	O(2)–B(2)–O(6)	112(1)
		O(5)–O(6)	2.384(7)	O(5)–B(2)–O(6)	107.9(9)
Mean value	1.471(10)	Mean value	2.403(7)	Mean value	109.5(9)
		B–B Distances in the Pentaborate Group			
B(2)–B(1)	2.441(11)	B(2)–B(5)	2.484(10)		
B(2)–B(3)	2.470(11)	B(1)–B(4)	2.354(12)		
B(2)–B(4)	2.496(11)	B(3)–B(5)	2.372(12)		
		B–B Distances between the Pentaborate Groups			
B(1)–B(5^{iv})	2.482(12)	B(3)–B(4)	2.464(12)		
		Tl–O Distances <3.5 Å			
Tl–O(6^{viii})	2.900(5)	Tl–O(5)	3.086(5)		
–O(1)	2.958(5)	–O(1^{vi})	3.088(4)		
–O(4^{iii})	2.971(5)	–O(2^{vi})	3.169(6)		
–O(8)	3.068(5)	–O(5^{viii})	3.2777(4)		
–O(2^{ix})	3.082(5)	–O(7^{iii})	3.357(5)		
		Other distances			
Shorter	Tl–B	distance	3.335(8)		
Shorter	Tl–Tl	distance	5.316(2)		

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

(24); its shorthand notation is $5{:}4\Delta + T$. Several $M\mathrm{Ln}(BO_2)_5$ compounds (22) (where M is a bivalent ion) have a bidimensional borate anion with the shorthand notation $5{:}\infty^2(2\Delta + 3T)$. Finally, a third type of $B_5O_{10}^{5-}$ ion, unidimensional, with the shorthand notation $3{:}\infty^1(2\Delta + T)$, was found more recently in $Ba_2LiB_5O_{10}$ (25) and $CuTbB_5O_{10}$ (26).

A comparison between the structure of TlB_5O_8 and its hydrated precursor $TlB_5O_6(OH)_4 \cdot 2H_2O$ may be made. The geometry of the pentaborate groups, which occurs in these compounds is very close: the average three-coordinate B–O bonds are 1.36 and 1.364(10) Å, and 1.48 and 1.471(10) Å for tetrahedral borons in hydrated and anhydrous thallium pentaborate, respectively. However, there is no correlation between these structures because, as seen before, the structure of the precursor collapses when the water molecules escape; after that, an amorphous anhydrous phase occurs and the structure of the crystallized compound must be rebuilt to give the three-dimensional networks of pentaborate groups.

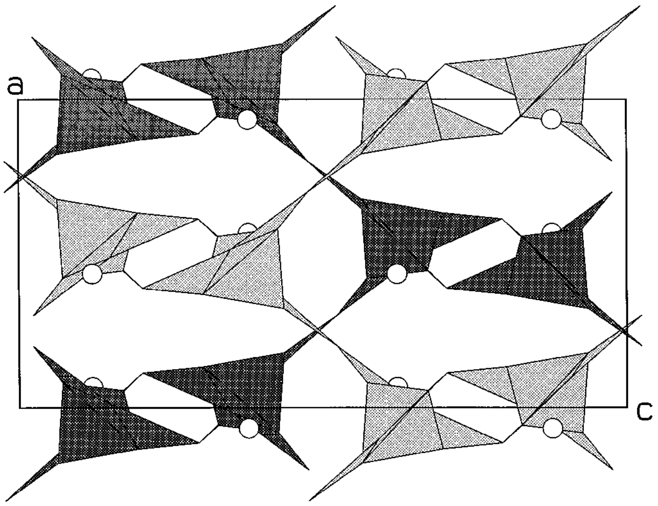

FIG. 2. Polyhedral representation of the structure of TlB_5O_8 on the (010) plane showing large empty tunnels and thallium ions as spheres.

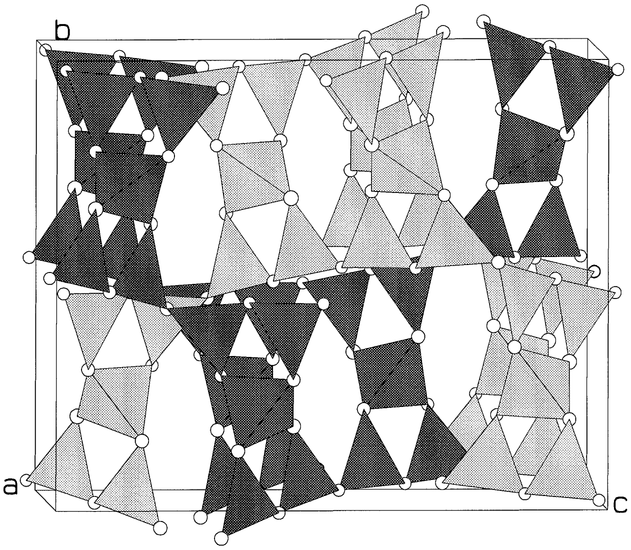

FIG. 3. Polyhedral representation of the structure of TlB_5O_8 showing the manner in which the pentaborate groups are interlinked in two three-dimensional networks; the spheres represent oxygen atoms.

It is interesting to compare TlB_3O_5 and TlB_5O_8 with their isostructural compounds CsB_3O_5 and β-KB_5O_8. In these two series, the borate polyanions were identical as indicated from their shorthand notation: $3:\infty^3(2\Delta + T)$ for the triborates and $5:\infty^3(4\Delta + T)$ for the pentaborates. However, the oxygenated environment of the cations, which is the same in the pentaborates for Tl^+ and K^+ (nine), is different for Tl^+ and Cs^+ (four and seven, respectively) (11). That may be explained by the lower B/Tl ratio (3 instead of 5), which leads to a possible stereochemical activity of the $6s^2$ lone pair of Tl^+ ions in TlB_3O_5. Another reason probably comes from the size of these cations; it is well known that Tl^+ and K^+ ions have almost the same size in numerous complex oxides while Cs^+ ion is always larger than Tl^+ ion in the same materials.

CONCLUSION

This work has allowed us to determine the $TlB_5O_6(OH)_4 \cdot 2H_2O$ dehydration process. Note that the mixture of both this compound and $Tl_2B_4O_6(OH)_2 \cdot 2H_2O$, which is also easy to synthesize, constitutes a convenient precursor of TlB_3O_5(TBO), which is a promising candidate for nonlinear optical applications. Complete dehydration of the hydrated pentaborate leads to an amorphous anhydrous phase which, by heating, crystallizes to give TlB_5O_8. The crystal structure of this compound has been accurately determined. In these two pentaborates, the well-known pentaborate group exists isolated or forming three-dimensional networks in the hydrated and anhydrous compounds, respectively; the shorthand notations of polyborate anions in these pentaborates are $5:4\Delta + T$ and $5:\infty^3(4\Delta + T)$, respectively.

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