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## The Crystal Structure of the High-Temperature Modification of Potassium Pentaborate

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The high-temperature modification of potassium pentaborate,  $\alpha$ - $K_2O \cdot 5B_2O_3$ , is orthorhombic with 4 formula units in the unit cell of dimensions  $a = 8.383 \pm 0.001$ ,  $b = 8.418 \pm 0.001$ ,  $c = 21.540 \pm 0.003$  Å. The space group is *Pbca*. The calculated density of the phase,  $1.93 \text{ g.cm}^{-3}$ , is much less than the density of the low-temperature modification,  $2.29 \text{ g.cm}^{-3}$ , for which the structure was reported previously. The structure in this study was determined and refined by least-squares methods to an *R* value of 0.062 with three-dimensional diffractometer data. The weighted *R* value was 0.038. The structure contains the characteristic double-ring pentaborate groups connected in two separate interpenetrating networks. The bond lengths of the boron–oxygen bond in the planar  $BO_3$  triangle are about 1.320 Å if the adjacent bond to the oxygen atom is from a fourfold coordinated boron atom, and 1.385 Å if the adjacent bond to the oxygen atom is from a threefold coordinated boron atom. The standard deviation for the boron–oxygen bond is 0.006 Å. The potassium ion is surrounded by 8 close oxygen neighbours at distances ranging from 2.770 to 3.139 Å.

### Introduction

The crystal structure of the low-temperature modification of potassium pentaborate,  $\beta$ - $K_2O \cdot 5B_2O_3$ , was determined previously by Krogh-Moe (1959*a*, 1965). Unit-cell data for the high-temperature modification were also reported (Krogh-Moe, 1959*b*). Because of the great difference in density of these two phases (the ratio of the densities is  $\rho_\beta/\rho_\alpha = 1.19$ ), it was assumed that there might be interesting structural differences between the two phases; therefore, a complete structure determination of the high-temperature modification was undertaken.

### Experimental

Crystalline  $\alpha$ - $K_2O \cdot 5B_2O_3$  was prepared by fusing potassium carbonate with boric acid in the stoichiometric ratio in a platinum crucible and crystallizing the mixture at 760°C. A single crystal in the shape of a prism bounded by the (100), (010), and (001) faces was used for collecting data. Dimensions of the crystal were  $0.0090 \times 0.0095 \times 0.0080$  cm along the *a*, *b*, and *c* axes respectively; the *a* axis was aligned with the goniometer head axis. Data were collected with an on-line

Picker single-crystal automatic diffractometer. Unit-cell dimensions and standard errors  $a = 8.383 \pm 0.001$ ,  $b = 8.418 \pm 0.001$ ,  $c = 21.540 \pm 0.003$  Å were obtained by the method of least-squares from angle data recorded at 22°C for 12 high-angle reflections (based on the wavelength 1.5405 Å for  $Cu K\alpha_1$ ). For four formula units of  $K_2O \cdot 5B_2O_3$  in the cell, the calculated density is  $1.93 \text{ g.cm}^{-3}$ . Krogh-Moe (1959*b*) obtained an experimental value of  $1.95 \text{ g.cm}^{-3}$  for this phase.

### Structure determination

The systematic extinction corresponds to that of space group *Pbca*. The experimental intensities were converted in the usual manner to observed structure factors. No correction for absorption was made. With a linear absorption coefficient of  $62.9 \text{ cm}^{-1}$ , the absorption error in the relative structure factors from a crystal of the above mentioned size and shape will not be large. (A sphere of about the same size would require a maximum relative correction of 2% in the intensities between the high-angle and low-angle limit of the observations.) Preliminary signs for the largest structure factors were determined by the symbolic-

Table 1. Final observed and calculated structure factors

The columns are I, 10F<sub>o</sub>, and 10F<sub>c</sub> respectively. Five reflexions marked by an asterisk are affected by extinction and were omitted from the least-squares refinement.

Table with multiple columns of numerical data representing structure factors. The data is organized in a grid-like format with various labels (e.g., 0,0,L, 1,0,L, 2,0,L) interspersed among the numbers. The table is very dense and covers the entire page.

addition method, using a program written by Hjortås (1969). An electron-density map showed the potassium position clearly, and it was found that the potassium atom alone was heavy enough to dominate most signs.

With additional signs derived from potassium coordinates, the structure was clearly revealed by electron-density calculations. The structure was refined by the method of least-squares, using a version of the full-

Table 2. *Final atomic parameters*

Positional parameters are in fractions of the cell edge  $\times 10^4$ , and temperature factors are of the form:  
 $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
K	1055.6	4058.0	3764.6	88	85	7.9	-6	4	-2
O(1)	1716	3498	1024	66	110	7.2	-17	2	-15
O(2)	221	1966	1760	105	57	5.6	5	-2	-2
O(3)	4141	2358	4254	67	90	5.2	-9	-2	6
O(4)	4301	4568	3560	74	62	6.7	13	4	4
O(5)	3824	3415	321	47	122	8.3	-15	3	-15
O(6)	1275	2440	20	57	151	6.7	-4	0	-12
O(7)	357	4171	2453	147	42	7.7	3	-11	13
O(8)	718	1671	2858	146	47	7.6	-14	-11	5
B(1)	101	3093	1238	72	79	9.2	-4	5	-5
B(2)	2257	3119	468	84	58	8.7	12	-4	-1
B(3)	4696	2141	4822	63	66	10.3	9	2	0
B(4)	410	2537	2327	76	67	10.3	-8	-6	0
B(5)	342	119	2996	84	74	7.2	8	2	-2

Standard deviations:

K	1.3	1.2	0.4	2	2	0.2	2	0.5	0.5
O	4	3	1	5	5	0.6	5	2	2
B	7	6	2	9	9	1.2	8	3	3

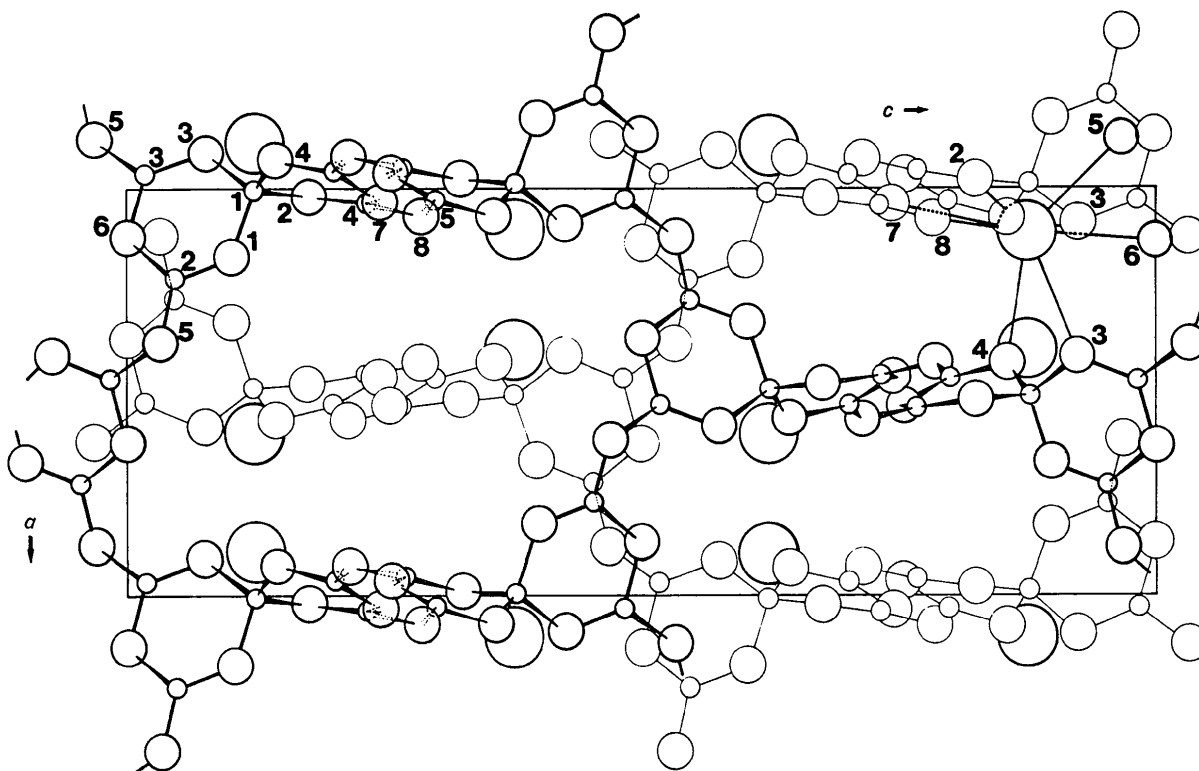


Fig. 1. Projection of the structure of  $\alpha$ - $K_2O \cdot 5B_2O_3$  along the *b* axis. The small circles represent boron, intermediate circles represent oxygen, and large circles represent potassium. The numbering of atoms is consistent with Table 2. The structure has two identical interlocking boron-oxygen networks, of which one is drawn with thin lines. The networks connect through O(8) to unit cells directly above and below. The oxygen atoms surrounding one potassium ion are indicated in the upper right corner. Unit-cell dimensions are indicated by the rectangle.

matrix program *ORFLS* (Busing, Martin & Levy, 1962), revised by Borgen & Mestvedt (1966). Structure factors corresponding to the five strongest experimental intensities were clearly affected by extinction and were omitted from the refinement, as were the unobserved reflexions. This left a total of 1087 observed structure factors (Table 1) in the refinement. Atomic scattering factors used for O, B, and  $K^+$  were taken from *International Tables for X-ray Crystallography* (1962). The refinement was carried out with a weighting scheme based on a combination of statistical counting errors with other errors assumed to be 1% of the

observed intensity. With anisotropic temperature factors the structure refined to an *R* value of 0.062 (or 0.038 for weighted *R*.) Final atomic coordinates with standard deviations, and the parameters of the anisotropic temperature factors, are given in Table 2.

### Discussion of the structure

A projection of the structure along the *b* axis is shown in Fig. 1. The structure consists, as in the case of the  $\beta$ -modification (Krogh-Moe, 1965), of two three-dimensional interpenetrating networks, built up from the double-ring pentaborate group. Fig. 2 shows a schematic picture of this group.

The present structure differs from the  $\beta$ -modification in the mutual arrangement of the pentaborate groups: a twofold screw axis runs close to one end of the pentaborate group. Groups attached to each other by a common oxygen atom, located in the neighbourhood of the twofold screw axis, extend from this atom in opposite directions (*trans* configuration). In the denser  $\beta$ -modification, however, a twofold screw axis runs near the centre of the pentaborate groups. The groups turn back in nearly the same direction around this screw (*cis* configuration). Obviously, this relates to the considerable difference in packing of these modifications.

The boron-oxygen bond lengths of the pentaborate group are listed in Table 3. They show some interesting systematic variations, apart from the well-known difference between boron coordinated by four oxygen atoms (average bond length 1.473 Å) and boron coordinated by three oxygen atoms (average bond length 1.365 Å). As seen in Fig. 2, the boron-oxygen bond length from a threefold coordinated boron (trigonal bond) depends on the second bond associated with the same oxygen atom. If this is a long tetrahedral bond, the trigonal bond becomes appreciably shortened, from  $\sim 1.385$  Å to  $\sim 1.320$  Å. This effect seems to be present also in the previously studied  $\beta$ -modification, where the average for the shorter trigonal bonds is 1.35 Å and for the longer trigonal bonds 1.38 Å. The accuracy of the structure determination of the  $\beta$ -modification, however, does not permit a detailed discussion of bond lengths in that phase.

Hyman, Perloff, Mauer & Block (1967) determined the structure of sodium tetraborate with the same level of accuracy as in the present work. This structure also has a pentaborate group in the network (together with a triborate group). The bond lengths of this pentaborate group are shown in Fig. 2 for comparison and reveal excellent agreement with the present results with respect to shortening of the trigonal bonds in identical surroundings (*i.e.* the left sides of the pentaborate groups in Fig. 2). However, when two trigonal bonds from the same boron atom are adjacent to tetrahedral bonds, the shortening for each bond is less, (the bonds are shortened from 1.38 to 1.36 Å instead of to about 1.33 Å).

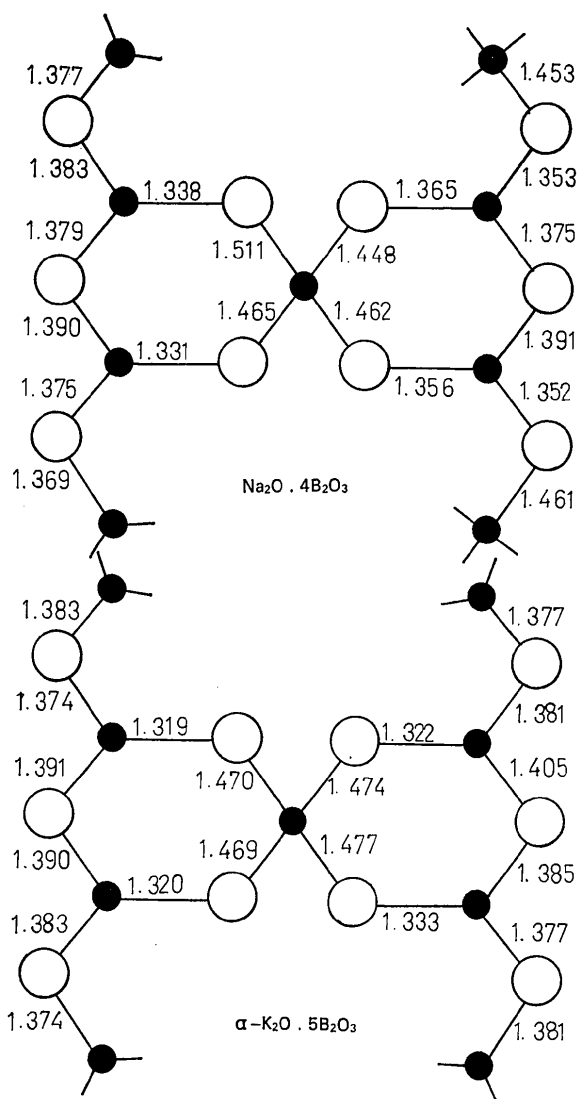


Fig. 2. Schematic drawing of the pentaborate group, including outside boron atoms joined to the group. The planes through the two ring units of the group are approximately perpendicular to each other. Bond distances in this group obtained from sodium tetraborate and from the present work are shown for comparison. For the sodium compound, the two outer boron atoms connected to the right-hand side ring are fourfold-coordinated.

Table 3. *Interatomic distances and bond angles*

Boron–oxygen bond lengths (standard deviation 0.006 Å). Oxygen–boron–oxygen bond angles (standard deviation 0.3°). Potassium–oxygen distances (standard deviation 0.003 Å) shorter than 3.80 Å, and potassium–potassium distances (standard deviation 0.002 Å).

B(1)–O(1)	1.470 Å	O(1)–B(1)–O(2)	108.7°
B(1)–O(2)	1.474	O(1)–B(1)–O(3)	112.0
B(1)–O(3')	1.469	O(1)–B(1)–O(4)	108.4
B(1)–O(4')	1.477	O(2)–B(1)–O(3)	108.4
		O(2)–B(1)–O(4)	110.3
		O(3)–B(1)–O(4)	108.4
B(2)–O(1)	1.319	O(1)–B(2)–O(5)	119.6
B(2)–O(5)	1.374	O(1)–B(2)–O(6)	121.8
B(2)–O(6)	1.391	O(5)–B(2)–O(6)	118.7
B(3)–O(3)	1.320	O(3)–B(3)–O(5)	125.5
B(3)–O(5)	1.383	O(3)–B(3)–O(6)	122.6
B(3)–O(6')	1.390	O(5)–B(3)–O(6)	111.9
B(4)–O(2)	1.322	O(2)–B(4)–O(7)	122.0
B(4)–O(7)	1.405	O(2)–B(4)–O(8)	126.5
B(4)–O(8)	1.381	O(7)–B(4)–O(8)	111.1
B(5)–O(4)	1.333	O(4)–B(5)–O(7)	122.1
B(5)–O(7')	1.385	O(4)–B(5)–O(8)	118.4
B(5)–O(8)	1.377	O(7)–B(5)–O(8)	119.4
K–O(5'')	2.770	K–K'	4.856 Å
K–O(4)	2.789	K–K'	5.831
K–O(8)	2.816	K–K'	6.873
K–O(7)	2.886	K–K'	7.107
K–O(2')	2.901	K–K'	7.265
K–O(3'')	2.977		
K–O(6')	2.990		
K–O(3)	3.139		

Table 3 shows that the O–B–O bond angles involving the tetrahedrally coordinated boron atom B(1) are slightly larger ( $\sim 111^\circ$ ) within the rings than adjacent to the rings ( $\sim 108.5^\circ$ ). The average value,  $109.4^\circ$ , however, agrees with the ideal tetrahedral angle. The average B–O–B angle for all the triangularly coordinated boron atoms is  $120.0^\circ$ , also equal to the ideal value; however, bond angles involving B(3) and B(4) show interesting variations from  $120^\circ$ . The large ( $125.5^\circ$ ) bond angle O(5)–B(3)–O(3) and the adjacent small ( $111.9^\circ$ ) bond angle O(5)–B(3)–O(6) (as well as the analogous pair O(8)–B(4)–O(2) and O(8)–B(4)–O(7) in the other subunit of the pentaborate group) arise, perhaps, from the repulsion between pentaborate groups. The structure has two comparatively short oxygen–oxygen distances [O(2)–O(7), 2.940 Å and O(3)–O(6), 2.920 Å], where the oxygen atoms belong to different pentaborate groups. The larger angle in each pair of distorted bond angles is positioned in the

indirect O–B–O–B–O links between the two short 'intergroup' oxygen distances, so as to avoid the even shorter oxygen–oxygen distance following from the normal  $120^\circ$  bond angle. The B–O–B bond angle in the center of the indirect link is the oxygen bond angle between the pentaborate groups. This bond angle is  $128.9^\circ$  and  $129.6^\circ$  for B(2)–O(5)–B(3) and B(4)–O(8)–B(5), respectively, and is larger than the B–O–B bond angles in the rings (average  $119.2^\circ$ ).

The  $\beta$ -modification has an even shorter 'intergroup' oxygen–oxygen distance of 2.73 Å, positioned analogous to the oxygen–oxygen distance discussed above for the  $\alpha$ -modification. Also for this structure, comparatively large ( $\sim 124^\circ$ ) O–B–O bond angles were observed in the O–B–O–B–O indirect linkage connecting the two closely spaced oxygen atoms. (The B–O–B angles for the oxygen atoms connecting the pentaborate groups were, in this case,  $125.3^\circ$  and  $125.6^\circ$ .)

The eight shortest potassium–oxygen distances are given in Table 3. The near surroundings of the potassium ions are indicated for one potassium atom in Fig. 1. Oxygen atoms are seen to surround potassium in an irregular eightfold coordination. The bond distances range from 2.770 to 3.139 Å, the next (9th) neighbour being at 3.817 Å. In the  $\beta$ -modification, the bond distances start at 2.91 Å and go to 3.20 Å for the nine closest neighbours. Apparently, as a rule, regular coordination polyhedra for the cations do not form in the polyborate network structures.

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