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## The Crystal Structure of Cesium Triborate, $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$

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Crystalline cesium triborate,  $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ , has been prepared and the structure determined. The crystals belong to the space group  $P2_12_12_1$ , with unit-cell dimensions

$$a = 6.18, b = 8.48, c = 9.17 \text{ \AA}.$$

A complete set of atomic parameters has been determined from electron-density projections along the two shortest axes. The structure has one out of every three boron atoms four-fold coordinated by oxygen, the other two being three-fold coordinated. The basic unit of the structure is a six-membered ring, interlinked with identical rings to a continuous three-dimensional network. The structure is related to the structure of some other crystalline and vitreous alkali borates. It is shown that the fraction of boron atoms in four-fold coordination in the known alkali borate structures is a simple fraction of the alkali content up to the diborate composition.

### Introduction

Glasses can be prepared in a wide composition range of the binary systems of boron oxide with any one of the alkali metal oxides. Moreover a considerable number of crystalline compounds can be obtained in these systems. A total of between 30 and 40 anhydrous alkali borates are reported in the literature, and more are certain to exist. Very little has previously been known about the crystal structures of the anhydrous alkali borates; only two borates of the metaborate composition have been investigated (Zachariassen, 1937; Fang, 1938). The author has recently determined the crystal structures of potassium pentaborate and rubidium pentaborate (Krogh-Moe, 1959*a*). In the present work the crystal structure of cesium triborate will be reported. These new structure investigations indicate some basic principles in the crystal chemistry of the alkali borates. The results are also of interest in discussing the structure of the alkali borate glasses.

### Experimental

Cesium triborate was prepared by crystallization from a melt (or glass) below 800 °C. The melt was obtained by fusing together the stoichiometric amounts of cesium carbonate and boric acid, raising the temperature to about 1000 °C. for a short time to drive off water and carbon dioxide.

Phase relationships, unit-cell data and the approximate cesium-atom position have previously been reported for this compound (Krogh-Moe, 1958*a, b*). The crystals are orthorhombic, space group  $P2_12_12_1$ , with axial lengths:

$$a = 6.18, b = 8.48, c = 9.17 \text{ \AA}.$$

2 formula units  $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$  in the cell correspond to a calculated density of 3.39 g.cm.<sup>-3</sup>.

Mo  $K\alpha$  radiation and the multiple-film technique were used to take integrated, equatorial Weissenberg  $0kl$  and  $h0l$  photographs. The crystals used for the exposures had quadratic crosssections perpendicular to the axis of rotation, with side lengths about 0.008 cm. No corrections for absorption were made. (The linear absorption coefficient of cesium triborate for Mo  $K\alpha$ -radiation is  $\mu = 81.4 \text{ cm.}^{-1}$ ). The relative intensities were estimated visually by comparison with a standard scale, and the usual corrections for the Lorentz and polarization factors were made.

### Structure analysis

According to an earlier study by the author, the cesium atoms occupy a general four-fold position in the structure (Krogh-Moe, 1959*b*). Three cesium parameters therefore have to be determined. Using the signs calculated from the approximate cesium posi-

tions given previously, electron-density projections were calculated. From these projections improved cesium parameters were derived.

Since the scattering from the heavy cesium atom tends to obscure the contribution from the comparatively light boron and oxygen atoms, the theoretical structure factor for the cesium atom,  $F_{Cs}$ , was subtracted from the observed structure factors,  $F_o$ , in the subsequent calculations of electron-density projections. A majority of the signs were determined by the heavy atom, and a recognizable structure was therefore obtained from the  $F_o - F_{Cs}$  synthesis. The structure was then refined until reliability indexes of  $R(0kl)=10.0\%$  and  $R(h0l)=12.0\%$  were attained (neglecting unobserved reflections).

The electron-density projections were calculated with a Hägg-Laurent Fourier synthesizer and the structure factors were calculated with an Alwac III E electronic computer.

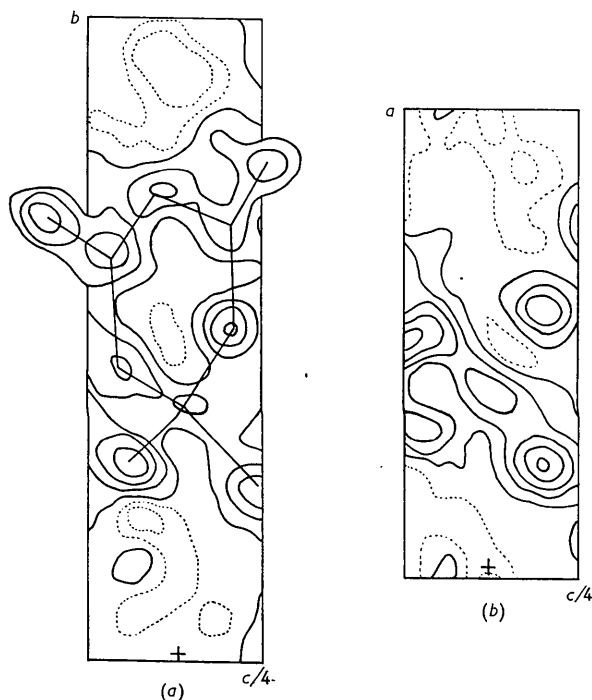


Fig. 1. (a) Electron-density projection of the asymmetric unit along the  $a$ -axis. The boron-oxygen bonds are indicated. (b) Electron-density projection of the asymmetric unit along the  $b$ -axis.

Fig. 1 shows the difference synthesis ( $F_o - F_{Cs}$ ) for projections of the asymmetric unit along the  $a$  and  $b$  axis. Boron-oxygen bonds are indicated in Fig. 1(a). The position of the subtracted cesium atom is marked with a cross in the figure. It should be noted that the two projections do not have the same origin on the  $c$  axis. (Whereas the space group  $P2_12_12_1$  has no center of symmetry, the projections belong to the centrosymmetrical plane group  $pgg$ . The origin in each projection is conveniently chosen at the centers

Table 1. Observed and calculated structure factors

Values are 2.5 times absolute scale

$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$
002	37	-25	058	0	-42	204	342	-385
4	303	-325	060	319	289	5	0	-4
6	63	-8	1	81	-91	6	67	-59
8	208	221	2	0	-26	7	21	28
011	171	177	3	46	-63	8	200	199
2	0	-19	4	227	-213	9	0	1
3	326	-335	5	130	138	301	274	258
4	36	-15	6	45	42	2	100	-105
5	239	-253	7	66	72	3	232	-210
6	0	5	8	108	135	4	67	-43
7	263	272	071	192	180	5	206	-220
8	0	-34	2	126	-124	6	184	189
020	389	422	3	183	-162	7	138	163
1	0	-34	4	95	-59	8	0	0
2	31	-20	5	165	-138	9	131	169
3	0	-1	6	0	72	400	318	307
4	346	-356	7	108	132	1	136	-103
5	46	57	8	0	-46	2	0	26
6	80	113	080	206	187	3	101	-121
7	0	19	1	113	-118	4	194	-185
8	223	219	2	0	-27	5	39	37
031	372	342	3	0	-18	6	58	-58
2	171	-136	4	169	-175	7	36	41
3	280	-282	5	67	88	8	119	152
4	0	-25	6	0	34	9	45	47
5	217	-215	7	0	58	501	153	153
6	84	90	8	127	145	2	142	-128
7	211	205	091	104	102	3	206	-213
8	0	-14	2	95	-100	4	0	12
040	427	454	3	105	-103	5	146	-145
1	98	-88	4	0	16	6	127	124
2	87	-71	5	71	-70	7	72	66
3	0	-15	101	142	-167	8	47	62
4	304	-277	2	165	-131	600	144	128
5	0	36	3	277	-263	1	122	-139
6	56	0	4	72	50	2	80	60
7	55	45	5	328	-330	3	114	-112
8	216	199	6	18	20	4	128	-134
051	189	173	7	127	137	5	65	61
2	106	-100	8	0	23	6	0	-20
3	241	-212	9	147	202	701	87	96
4	0	6	200	397	440	2	124	-100
5	157	-159	1	72	-78	3	74	-69
6	0	55	2	120	90	4	32	-14
7	211	237	3	26	-32	5	94	-90

of symmetry, which, however, do not coincide when projected on any axis.)

Observed structure factors and final values of the calculated structure factors are given in Table 1. The calculated values include a common temperature factor  $\exp(-B \sin^2 \theta / \lambda^2)$  with the coefficient  $B=1.2$ . Signs of the calculated structure factors are valid only

Table 2. Positional parameters

Atom	$x/a$	$y/b$	$z/c$
Cs	0.981	0.261	0.130
O <sub>I</sub>	0.421	0.565	0.056
O <sub>II</sub>	0.688	0.529	0.242
O <sub>III</sub>	0.767	0.705	0.043
O <sub>IV</sub>	0.468	0.769	0.213
O <sub>V</sub>	0.615	0.972	0.093
B <sub>I</sub>	0.769	0.871	0.033
B <sub>II</sub>	0.461	0.927	0.203
B <sub>III</sub>	0.589	0.646	0.138

for the particular choice of origin in the projection. (Signs of the  $F(00l)$  structure factors correspond to the projection along the  $a$  axis.)

Table 2 shows the final atomic parameters  $x/a$ ,  $y/b$  and  $z/c$ . The parameters used in the projection along the  $a$  axis are  $y/b - \frac{1}{4}$ ,  $z/c$  and along the  $b$  axis:  $1 - x/a$ ,  $\frac{1}{4} - z/c$ .

### Discussion of the structure

The basic structural unit of the borate network is shown in Fig. 2. It consists of a six-membered ring, where two of the boron atoms are three-fold coordinated and the third boron atom in the ring is four-fold coordinated by oxygen. The closest interatomic distances in the unit are given in Table 3. The average boron-oxygen distance for the tetrahedron, 1.48 Å, seems to be significantly larger than the average value of 1.38 Å found for the triangles. This agrees with the results from several other studies of borate structures, where average values of about 1.47 Å and 1.37 Å have been found for borate tetrahedra and triangles respectively (Clark, 1959).

Table 3. *Interatomic distances*

B <sub>I</sub> -O <sub>V</sub>	1.39 Å	O <sub>I</sub> -O <sub>II</sub>	2.40 Å
B <sub>I</sub> -O <sub>III</sub>	1.41	O <sub>I</sub> -O <sub>III</sub>	2.45
B <sub>I</sub> -O <sub>I</sub>	1.35	O <sub>I</sub> -O <sub>IV</sub>	2.27
B <sub>II</sub> -O <sub>V</sub>	1.44	O <sub>II</sub> -O <sub>III</sub>	2.41
B <sub>II</sub> -O <sub>IV</sub>	1.34	O <sub>II</sub> -O <sub>IV</sub>	2.46
B <sub>II</sub> -O <sub>II</sub>	1.37	O <sub>III</sub> -O <sub>IV</sub>	2.48
B <sub>III</sub> -O <sub>I</sub>	1.46	O <sub>II</sub> -O <sub>I</sub>	2.35
B <sub>III</sub> -O <sub>II</sub>	1.50	O <sub>V</sub> -O <sub>I</sub>	2.35
B <sub>III</sub> -O <sub>III</sub>	1.49	O <sub>III</sub> -O <sub>V</sub>	2.49
B <sub>III</sub> -O <sub>IV</sub>	1.45	O <sub>IV</sub> -O <sub>V</sub>	2.24
		O <sub>IV</sub> -O <sub>II</sub>	2.45
		O <sub>V</sub> -O <sub>II</sub>	2.46

The unit shown in Fig. 2 forms part of a continuous three-dimensional network by sharing its four corners with four identical units. (By the 'corners' are understood the four oxygens in Fig. 2 which are bonded to only one boron.) The structure may be described as a system of parallel helix chains, each chain being tied to four other chains at regular intervals along the chain. The helix itself consists of two units in each winding, both identical to the one shown in Fig. 2.

The general arrangement is shown in Fig. 3 as a projection along the  $a$  axis. The helix axis, perpendicular to the projection plane, is indicated in this figure with the symbol for a screw axis.

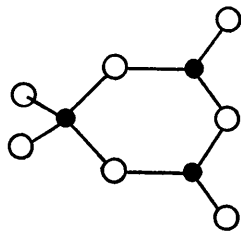


Fig. 2. The basic unit of cesium triborate. The boron atoms are indicated by filled circles, the oxygens by open circles.

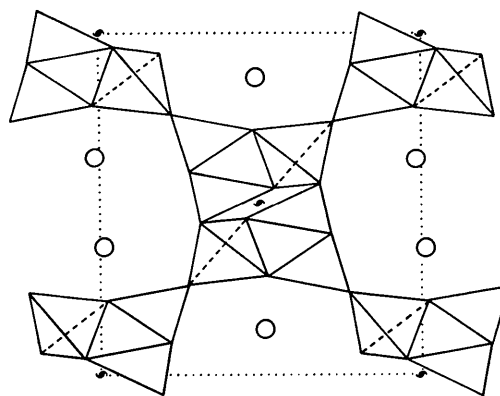


Fig. 3. Projection along the  $a$ -axis, showing the structure as a network of borate triangles and tetrahedra. Dotted lines represent repetition unit in the projection. Open circles indicate cesium atoms.

### Comparison with other borates

The structure of cesium triborate is related to the structure of potassium pentaborate (Krogh-Moe, 1959a). In the pentaborate the basic unit is a double ring. This double ring can be derived from the unit in the triborate by simply attaching another two  $\text{BO}_3$  triangles to the  $\text{BO}_4$  tetrahedron. Also the manner in which the double rings in the pentaborate are combined to a continuous three-dimensional network is very reminiscent of the triborate structure. The pentaborate structure differs, however, by having two interpenetrating networks.

Another interesting feature of these structures is that all oxygen atoms are shared between two boron atoms. For this to be accomplished, the following rule is obeyed: *Each 'molecule' of alkali oxide added to boron oxide must convert two boron atoms from three-fold to four-fold coordination by oxygen* (starting with a hypothetical boron oxide where all boron atoms are three-fold coordinated.) Fig. 4 shows the fraction of boron atoms in four-fold coordination,  $N_{\text{BO}_4}$ , as a function of the molar alkali content according to this rule. (Solid line.)

The formation of  $\text{BO}_4$  tetrahedra proceeds until at least the triborate composition has been reached, but may possibly continue to even higher alkali contents. Thus in borax,  $\text{Na}_2\text{O} \cdot 2 \text{B}_2\text{O}_3 \cdot 10 \text{H}_2\text{O}$ , half of the boron atoms are four-fold coordinated (Morimoto, 1956). This is what would be expected from the above rule if the water of crystallization can be disregarded. With this reservation, borax is included in the diagram in Fig. 4. (In support of this it has been shown that the boron atoms are three-fold coordinated, with the coordination independent of composition, in the system boron oxide-water (Krogh-Moe, 1959c).)

Even the comparatively basic mineral colemanite,  $2 \text{CaO} \cdot 3 \text{B}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , where two of every three boron atoms are four-fold coordinated (Christ, Clark &

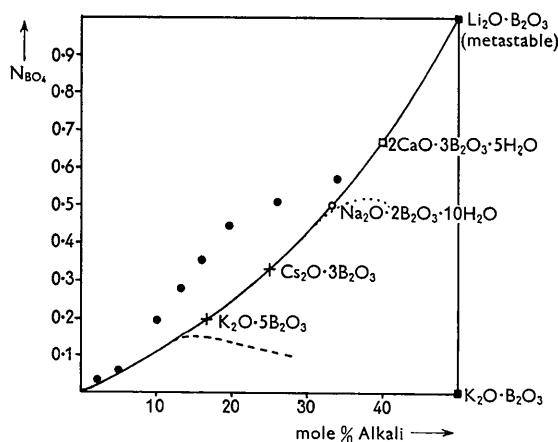


Fig. 4. The fraction of boron atoms in four-fold coordination as a function of the molar alkali content in the system  $\text{Me}_2\text{O}-\text{B}_2\text{O}_3$ . The solid line represents the theoretical curve if as many boron atoms as possible are converted to four-fold coordination. The dashed line represents a theory by Warren; the dotted line is assumed to be more probable in this work. Filled circles show some nuclear magnetic-resonance results for sodium-borate glasses. The position of various crystalline compounds in this diagram is also indicated.

Evans, 1958), can be fitted in with the rule. (See Fig. 4.) Again the presence of water is disregarded.

At the metaborate composition the rule breaks down. For instance in potassium metaborate all the boron atoms are three-fold coordinated (Zachariasen, 1937). A metastable modification of lithium metaborate, however, has recently been reported to have all the boron atoms in four-fold coordination (Lehmann & Tiess, 1959). This again is in agreement with the rule.

For the alkali borate glasses, Warren assumed that the formation of four-fold coordinated borons reached a maximum when about 15 mole per cent alkali oxide had been added (Warren, 1941). The theory of Warren, which is now widely accepted, is shown as a broken

line in Fig. 4. The present author has pointed out that no acceptable evidence for this theory seems to exist (Krogh-Moe, 1959c). A nuclear magnetic-resonance study of sodium-borate glasses indicates that the coordination change proceeds to higher alkali contents than assumed by Warren (Silver & Bray, 1958). The data of Silver & Bray are shown as filled circles in Fig. 4. The crystallographic data reviewed in Fig. 4 strongly indicate that the coordination change continues to higher alkali contents in the glass. Here it should be kept in mind that the infrared spectra of vitreous and crystalline borates of the same chemical composition resemble each other markedly (Krogh-Moe, 1958b). A possible curve for the boron coordination is shown as a dotted line in Fig. 4.

Finally attention will be drawn to the prevalence of six-membered rings in the borate structures quoted above. This ring system, apparently, is energetically favoured in the borates.

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