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Structure Refinement of Trigonal Iron–Chlorine Boracite

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Abstract. $Fe_3B_7O_{13}Cl$, $M_r = 486{\cdot}66$, $R3c$, $a_{hex} = 8{\cdot}6231\ (5)$, $c_{hex} = 21{\cdot}0503\ (5)$ Å, $V_{hex} = 1355{\cdot}6\ (1)$ Å^3, $Z = 6$, $a_{rh} = 8{\cdot}6035\ (7)$ Å, $\alpha_{rh} = 60{\cdot}15\ (1)^\circ$, $D_x = 3{\cdot}576$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 5·145 mm^{-1}, $F(000) = 1404$, $T = 298$ K, $R = 0{\cdot}038$ ($wR = 0{\cdot}054$) for 1544 unique reflections. Bond lengths and bond angles do not differ significantly from, but are more accurate than, those reported for isostructural $Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$ [Dowty & Clark (1973). *Z. Kristallogr.* **138**, 64–99].

Introduction. Fe–Cl boracite, $Fe_3B_7O_{13}Cl$, belongs to a class of ferroelectric compounds with interesting dielectric, optic, magnetoelectric and elastic properties (Schmid, 1965, 1970, 1973; Quezel & Schmid, 1968; Nelmes, 1974; Toledano, Schmid, Clin & Rivera, 1985). Its structure transforms from a cubic high-temperature modification into a series of low-temperature modifications with various symmetries:

$$\bar{4}3m \xleftrightarrow{609\ \mathrm{K}} mm2 \xleftrightarrow{543\ \mathrm{K}} m \xleftrightarrow{528\ \mathrm{K}} 3m.$$

The rhombohedral lattice of the room-temperature modification is characterized by an elongation along the polar direction relative to the cubic lattice, whereas a compression along that direction is found for Zn–Cl boracite [$\alpha_{rh} = 60°09'$ for Fe–Cl and $\alpha_{rh} = 59°52'$ for Zn–Cl (Schmid, 1970)].

In order to gain a better understanding of the factors which govern this technologically important parameter (Schmid, 1978), accurate atomic coordinates are desirable. Trigonal boracites for which structure refinements have been performed are the Fe-rich analogue $Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$ [$\alpha_{rh} = 59{\cdot}90\ (1)^\circ$ (Dowty & Clark, 1972); later corrected to $\alpha_{rh} = 60{\cdot}06\ (3)^\circ$ (Dowty & Clark 1973)], and $Co_3B_7O_{13}F(OH)$ [$\alpha_{rh} = 59{\cdot}53\ (1)^\circ$ (Berset, Yvon, Depmeier, Boutellier & Schmid, 1984)].

Experimental. Sample preparation: crystals up to 2 mm in size were grown by a chemical-vapour-transport technique (Schmid, 1965): mixtures of Fe and Fe_2O_3 (Merck, pro analysis, purity >>99%), $FeCl_2$ (Merck, pro analysis, purity >>99%), H_3BO_3 (Merck, pro analysis, purity >>99%) and B_2O_3 (Johnson Matthey Co. Ltd, puratronic) were heated in quartz tubes to temperatures of up to 1100 K (temperature gradient ~8 K/10 cm) for 2 d. A single domain of triangular shape (0·036 × 0·034 × 0·044 mm; thickness 0·075 mm) was cut from a (111) platelet under a polarizing microscope using a sapphire knife and mounted in a glass capillary. X-ray diffraction: four-circle diffractometer, monochromated Mo $K\alpha$ radiation; $T = 298$ K; lattice parameters determined by least-squares analysis of 28 measured Bragg angles with $24° \le \theta \le 45°$; integrated intensities collected for 3254 reflections with $0 < h < 18$, $-16 \le k \le 0$, $0 \le l \le 38$; $(\sin\theta/\lambda)_{max} = 1{\cdot}08$ Å^{-1}; θ–2θ scan mode; after averaging symmetry-equivalent reflections a unique set of 1544 observed intensities was obtained, 161 of which with $I < 3\sigma(I)$; reflection conditions $hkil$: $-h+k+l = 3n$; $h\bar{h}0l$: $l = 2n$ were consistent with space group $R3c$. Structure refinement: initial atomic coordinates from Fe-rich analogue (Dowty & Clark, 1973); function minimized by full-matrix least-squares method $\sum w(|F_o| - |F_c|)^2$; unit weights; no absorption correction; scattering factors for neutral atoms (*International Tables for X-ray Crystallography,* 1974); 74 variables {scale factor, isotropic extinction parameter [$g = 0{\cdot}44\ (1)^\circ$], enantiomorph-polarity parameter (Flack,

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Table 1. *Atomic parameters*

The temperature factor has the form exp $(-T)$ where $T = 2\pi^2\sum[h(i)h(j)U(i,j)a^*(i)a^*(j)]$ for anisotropic atoms; $a^*(j)$ are reciprocal axial lengths and $h(i)$ are Miller indices. Estimated standard deviations are given in parentheses. U_{eq} is the mean of the eigenvalues of **U**. Space group *R3c*, hexagonal setting; all atoms are at equipoint 18(*b*), except for Cl, B(3) and O(1) which are at 6(*a*). Atom numbering and choice of cell origin are as in $Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$ (Dowty & Clark, 1973).

	x	*y*	*z*	U_{eq}(Å^2)
Fe	0·14727 (8)	0·29642 (7)	0·3270	0·00692 (13)
Cl	0	0	0·26630 (12)	0·01217 (23)
B(1)	0·1636 (5)	−0·1655 (5)	0·08261 (21)	0·0048 (9)
B(2)	0·1002 (5)	−0·1027 (5)	−0·02895 (19)	0·0045 (8)
B(3)	0	0	0·1018 (4)	0·0061 (7)
O(1)	0	0	−0·01215 (23)	0·0039 (5)
O(21)	−0·1593 (3)	−0·0008 (3)	0·10509 (17)	0·0050 (5)
O(22)	0·2888 (3)	0·2591 (3)	−0·03720 (16)	0·0046 (5)
O(23)	0·2003 (3)	−0·0231 (3)	−0·08789 (16)	0·0043 (5)
O(24)	−0·3045 (3)	−0·2246 (3)	0·02118 (16)	0·0046 (5)

1983), 23 positional and 45 anisotropic thermal parameters for 10 independent atoms}; max. $\Delta/\sigma = 0{\cdot}08$; final $R = 0{\cdot}038$ ($R_{int} = 0{\cdot}038$, $wR = 0{\cdot}054$) for 1544 observed reflections;* a final electron density difference map showed residual peaks not higher than 1·6 e Å^{-3} close to the Fe, Cl and O(1) positions; all calculations performed with the *XRAY76* system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a Univac 1100 computer.

Discussion. Atomic coordinates and equivalent isotropic temperature factor coefficients are summarized in Table 1. Fe–Cl boracite has all the structural characteristics of the trigonal boracites (Dowty & Clark 1973; Berset, Yvon, Depmeier, Boutellier & Schmid, 1984): the Fe^{2+} ion surrounded by four basal non-planar O atoms and one apical Cl atom; atom O(1) coordinated to three B(2) atoms; atom B(3) in a triangular coordination; atoms B(1) and B(2) in an almost regular tetrahedral coordination. Bond lengths and a selected group of bond angles are listed in Table 2. They differ by up to 10 e.s.d.'s from the corresponding values of the Fe-rich analogue $Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$, reported by Dowty & Clark (1973). However, in view of the significantly lower accuracy of the latter values, some of these differences may not be significant. Thus a detailed analysis of the influence of metal-atom substitution on the rhombohedral lattice shear in trigonal boracites has to await further structure refinements.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* $Fe_3B_7O_{13}Cl$ *compared to those of* $Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$

	$Fe_3B_7O_{13}Cl$	$Fe_{2.4}Mg_{0.6}B_7O_{13}Cl$*
Fe(Mg)–Cl	2·556 (1)	2·568 (3)
–O(22)	2·122 (3)	2·092 (9)
–O(24)	2·128 (3)	2·113 (10)
–O(23)	2·026 (3)	2·049 (8)
–O(21)	2·078 (3)	2·066 (9)
B(1)–O(21)	1·511 (6)	1·510 (30)
–O(24)	1·451 (5)	1·482 (15)
–O(22)	1·449 (5)	1·495 (18)
–O(23)	1·473 (5)	1·441 (27)
B(2)–O(1)	1·556 (5)	1·559 (21)
–O(23)	1·471 (5)	1·465 (12)
–O(24)	1·446 (5)	1·440 (16)
–O(22)	1·437 (4)	1·412 (15)
B(3)–O(21)	1·372 (3)	1·376 (10)
O(21)–Fe(Mg)–O(22)	87·34 (1)	88·4 (3)
O(21)–Fe(Mg)–O(23)	145·6 (1)	146·0 (3)
O(21)–Fe(Mg)–O(24)	87·4 (1)	87·1 (4)
O(22)–Fe(Mg)–O(23)	89·0 (1)	88·6 (3)
O(22)–Fe(Mg)–O(24)	174·6 (1)	175·3 (2)
O(23)–Fe(Mg)–O(24)	94·6 (1)	94·3 (3)
O(21)–Fe(Mg)–Cl	112·3 (1)	112·0 (2)
O(22)–Fe(Mg)–Cl	92·71 (8)	92·8 (2)

* Values are calculated from data reported by Dowty & Clark (1973).

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* Lists of structure factors and anisotropic thermal parameters arranged in a standard crystallographic data file (Brown, 1983) and interatomic distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42387 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.