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SINGLE CRYSTAL X-RAY STUDY OF RHOMBOHEDRAL COBALT-
FLUORINE (OH) BORACITE

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Abstract $Co_3B_7O_{13}F(OH)$, space group R3c, a_{rh}=12.0738(6) Å,
α_{rh} = 89.59(5)°, Z=6, residual R=0.059 (1970 reflections, 78
parameters). In contrast to cubic boracites the structure
contains strong metal-halogen bonds (d(Co-F)=2.169(3) Å). Some
of the oxygen-boron bonds are considerably weakened.

INTRODUCTION

Due to the frequent occurrence of structural phase transitions only
a few single crystal diffraction studies on non-cubic boracites have
been reported to date[1,2]. A compound which does not transform into a
cubic high-temperature modification up to the decomposition tempera-
ture is $Co_3B_7O_{13}F(OH)$ which was found to be rhombohedral at room
temperature[3] and presumably isostructural to ericaite[2] $((Mg,Fe)_3B_7$
$O_{13}Cl)$. In this paper we report its atomic coordinates and compare
its structure to that of cubic boracites.

EXPERIMENTAL

Dark violet crystals of $Co_3B_7O_{13}F(OH)$, up to 5 mm, were grown by a
high-pressure technique (25Kb, 1000°C) similar to that described by
Bither and Young[3]. The as-grown crystals showed pseudo-cubic {100},
{110} and {111} facets. Each crystal consisted of a single trigonal
domain with an optical indicatrix of negative sign. The OH⁻ concen-

tration was derived from neutron activation and found to be less than 10 at%. A crystal fragment of prismatic shape (0.06x0.2x0.16 mm) was prepared by polishing, and was investigated on a computer-controlled four-circle X-ray diffractometer at room temperature (MoK$_\alpha$ radiation). The intensities of symmetry equivalent reflections and the systematically absent reflections were consistent with the proposed space group R3c. Intensity data for 2358 unique reflections (1624 with I>σ(I)) were recorded and a full-matrix least-squares refinement was performed based on the atomic coordinates of ericaite[2]. Convergence was obtained at R=0.059. (24 positional and 52 anisotropic thermal parameters). Results are listed in table 1.

DISCUSSION

Rhombohedral Co$_3$B$_7$O$_{13}$F(OH) is isostructural to ericaite. Compared to cubic boracites (for a review of the latter see Nelmes[4]), its atomic arrangement differs mainly with respect to the metal and halogen ligand spheres (see below), while the differences in the oxygen and boron atom network (mainly O(1) and B(3)) are less pronounced and appear to be mainly a consequence of the changes in the former.
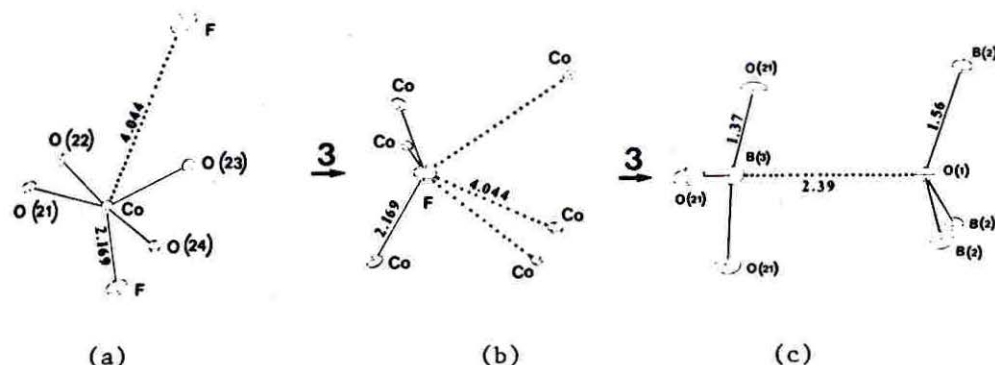

Fig. 1 : Atomic environment around Co (a), F(OH) (b), O(1) and
          B(3) (c), in Co$_3$B$_7$O$_{13}$F(OH). Thermal ellipsoids drawn at
          10% probability scale, distances in Å.

The Co ion has four O and one F(OH) neighbours which form a distorted square-pyramidal configuration (a). The distances to these ligands are short, in particular that to the F(OH) atom at the apex of the pyramid which suggests the formation of a strong metal-halogen (OH) bond. Evidence for the latter comes from the significant displacement of the Co atom out of the oxygen least-squares plane by 0.46 Å towards the halogen ligand (displacement of (Mg,Fe) in ericaite 0.32 Å). The second halogen atom is much further away (see dotted line) and belongs to the ligand sphere of a neighbouring Co atom. Fivefold metal coordinations also occur in orthorhombic $Mg_3B_7O_{13}Cl^2$.

In cubic boracites the metal atoms occupy the centre of nearly square-planar oxygen coordination sphere. They are only weakly bonded to two halogen atoms (both at a distance of about 3 Å).

The halogen (OH) atoms have three nearest Co neighbours which form a trigonal configuration (b). The three other Co atoms (see dotted lines) belong to the ligand sphere of a neighbouring F(OH) atom. In cubic boracites, the halogens are octahedrally surrounded by six metal atoms.

The boron-oxygen network is similar to that in cubic boracites, except for the O(1)-B(3) bonds which are considerably weakened (c). Both O(1) and B(3) have trigonal non-metal coordinations. In cubic boracites they belong to each other's coordination spheres such that they have tetrahedral (or nearly tetrahedral) coordinations.

These structural differences, and in particular the tendency of the metal atoms to increase at low temperature their coordination number from four to five could be of relevance for the understanding of the phase transitions in cubic boracites.

The observed strong displacement of the Co^{2+} and $F^-(OH^-)$ ions from the cubic positions (which come into play in the potential ferroelectric switching) are consistent with the tendency of birefringence[5], Curie point[5] and coercive field[6] of boracites to increase

in the sense $I^- \to Br^- \to Cl^-$ (known)$\to F^-$ (expected). A correlation between these properties and ionic shifts also holds for other displacive ferroelectrics[7].

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TABLE 1

Atomic coordinates and equivalent isotropic temperature factors for $Co_3B_7O_{13}F(OH)$, space group R3c, hexagonal setting (a_h=8.5309(3), c_h=21.12(1) Å). Atom numbering and choice of cell origin as in ericaite[2]. Estimated standard deviations in parentheses.

		x	y	z	Ueq
Co	18f	0.1390(1)	0.27961(9)	0.3270	0.009(2)
F(OH)	18f	0	0	0.2957(5)	0.023(1)
B(1)	18f	0.1645(8)	-0.1656(8)	0.0857(3)	0.006(1)
B(2)	18f	0.1022(8)	-0.1023(8)	-0.0261(3)	0.005(1)
B(3)	6a	0	0	0.1055(5)	0.006(2)
O(1)	6a	0	0	-0.0082(4)	0.007(1)
O(21)	18f	-0.1595(5)	0.0024(5)	0.1087(2)	0.0067(9)
O(22)	18f	0.2925(5)	0.2645(5)	-0.0336(2)	0.0069(9)
O(23)	18f	0.1992(5)	-0.0241(5)	-0.0847(2)	0.007(1)
O(24)	18f	-0.3085(5)	-0.2294(5)	0.0246(2)	0.007(1)

U_{eq}(Å^2): equivalent isotropic temperature factor coeffic

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