

référence: 404, 511 et  $\bar{4}0\bar{4}$  mesurées toutes les heures avec une variation moyenne d'intensité de 0,06. Correction de l'absorption par la méthode analytique de Meulenaer & Tompa (1965). Transmission comprise entre 0,018 et 0,152.

Les sections de Patterson tridimensionnelles montrent que la structure est centrée et donnent les positions du thorium. Les séries-différence de Fourier révèlent peu à peu les autres atomes. Affinements par moindres carrés [*AFINE*, modification du programme Busing, Martin & Levy (1963)] des coordonnées atomiques et des facteurs de température isotrope, puis anisotrope pour Th. Fonction minimisée  $\sum w(\Delta F^2)$  avec  $w = 1/\sigma^2$ .  $R = 0,070$ ,  $wR = 0,101$  pour les 665 réflexions telles que  $I \geq 3\sigma(I)$ .

Au dernier cycle,  $S = 7,37$ ;  $\Delta/\sigma_{\max} = 0,01$ ;  $\Delta\rho_{\max} = 3,6 \text{ e } \text{Å}^{-3}$  situés au voisinage de l'atome de thorium. Facteurs de diffusion extraits de *International Tables for X-ray Crystallography* (1974, Tome IV). Dispersion anormale prise en compte pour Th. Paramètre d'extinction secondaire  $0,183 \times 10^{-5}$ . Ordinateur utilisé: MATRA 570/CX.

**Discussion.** Les paramètres atomiques et les facteurs de température sont reportés dans le Tableau 1.\* Les distances et les angles entourant les cations figurent dans le Tableau 2 ainsi que les distances entre cations inférieures à 4 Å et les distances entre les atomes d'oxygène liés au bore.

Les atomes de thorium sont entourés de 8 atomes d'oxygène – 2[O(1), O(2), O(3), O(4)] – qui se placent aux sommets d'un dodécaèdre légèrement déformé

\* Les listes des facteurs de structure et des paramètres thermiques anisotropes ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 53309: 7 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

(Fig. 1) à une distance Th—O moyenne de 2,42 Å. Si l'on projette la structure selon l'axe *b*, ces dodécaèdres apparaissent sous forme de pentagones en raison de la superposition, dans cette direction, des deux paires d'atomes O(1)—O(2). La Fig. 2 représente une telle projection pour les polyèdres entourant les atomes de thorium aux environs du niveau  $\frac{1}{4}$ . On voit que dans le plan *ac*, les polyèdres sont reliés par les arêtes O(3)—O(3) et O(4)—O(4) en rangées parallèles à [101]. Par le jeu des miroirs *c*, la couche suivante, aux environs de  $y = \frac{3}{4}$ , s'intercale entre ces files par l'intermédiaire des arêtes O(1)—O(2): chaque atome d'oxygène est donc commun à deux polyèdres Th—O.

Les deux atomes indépendants de bore sont au centre de triangles BO<sub>3</sub> qui se groupent par deux en groupements B<sub>2</sub>O<sub>5</sub> par l'intermédiaire de l'atome d'oxygène O(5). L'originalité de ce groupement, par ailleurs fréquent, est que les deux triangles qui le constituent se trouvent dans deux plans perpendiculaires. Chacun d'eux partage une arête avec une file de dodécaèdres différente, ce qui consolide la structure dans la direction  $[\bar{1}01]$ . Les distances moyennes B—O, respectivement de 1,36 et 1,40 Å sont conformes aux normes habituelles.

Signalons enfin que, dans ce borate de thorium, tous les atomes d'oxygène reçoivent une charge de 2 ce qui, ajouté à l'arrangement tridimensionnel des dodécaèdres, contribue à sa stabilité.

#### Références

- BASKIN, Y., HARADA, J. H. & HANDWERK, J. H. (1961). *J. Am. Ceram. Soc.* **44**, 456–460.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, EU.  
 MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.

*Acta Cryst.* (1991). **C47**, 12–14

## Pentacalcium Triborate Fluoride and its Relationship to Fluorapatite

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**Abstract.** Ca<sub>5</sub>(BO<sub>3</sub>)<sub>3</sub>F,  $M_r = 395.83$ , monoclinic, *Cm*,  $a = 8.125$  (3),  $b = 16.051$  (5),  $c = 3.538$  (2) Å,  $\beta =$

100.90 (4)°,  $Z = 2$ ,  $D_x = 2.900 \text{ Mg m}^{-3}$ ,  $V = 453.1$  (3) Å<sup>3</sup>, room temperature, Mo *K*α,  $\lambda = 0.71069$  Å,  $\mu = 2.941 \text{ mm}^{-1}$ ,  $F(000) = 392$ . Single crystals have been prepared and characterized by

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Table 1. Atomic parameters for  $\text{Ca}_5(\text{BO}_3)_3\text{F}$  with *e.s.d.'s in parentheses*

Fractional coordinates are  $\times 10^4$ .

	No. of atoms and Wyckoff notation	Fractional coordinates			$B_{\text{eq}}^*(\text{\AA}^2 \times 10^2)$
		x	y	z	
Ca(2)	4(b)	617 (2)	6784 (1)	96 (4)	71
Ca(3)	4(b)	6838 (2)	6174 (1)	3477 (4)	48
O(2)	4(b)	8538 (6)	5743 (3)	9162 (14)	103
O(3)	4(b)	320 (6)	8238 (3)	7901 (13)	92
O(4)	4(b)	8626 (6)	7289 (3)	4024 (13)	97
O(5)	4(b)	7389 (6)	8552 (3)	5837 (13)	79
B(2)	4(b)	8753 (8)	8042 (4)	5912 (19)	52 (8)
B(1)	2(a)	9408 (10)	$\frac{1}{2}$	9677 (25)	33 (11)
O(1)	2(a)	1133 (8)	$\frac{1}{2}$	538 (20)	118
Ca(1)	2(a)	7961 (2)	0	6443 (5)	51
F(1)	2(a)	0†	0	$\frac{1}{2}$ †	76

\*  $B_{\text{eq}} = \frac{1}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + \text{accos}\beta B_{11})$  for anisotropic thermal vibration correction of the form  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{12}hk + B_{13}hl)]$ . For B atoms the isotropic vibration parameter is given.

† Invariant in order to define the origin.

X-ray crystal structure analysis;  $R = 0.042$  for 662 unique reflections. The structure exhibits many similarities to that of fluorapatite.

**Introduction.** The apatite structure is not uncommon in mineralogical and biological systems and for this reason substitutions in this structure have been extensively investigated. Fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , is the prototype of the apatite family (Elliott, 1965). Many substitutions are possible for both anions and cations. The replacement of calcium and fluorine has received a great deal of attention, as has the substitution of phosphate by other tetrahedral ions. However, substitution of the tetrahedral phosphate by planar ions has in comparison received little attention. The compound described here is an example of this type of planar-tetrahedral substitution; the planar ion is  $\text{BO}_3^{3-}$ . The borate-phosphate substitution is homovalent so no added complication of charge balance in other sites arises.

**Experimental.** Crystals were grown by heating  $\text{Ca}_3(\text{BO}_3)_2$  in the presence of excess  $\text{CaF}_2$  at 1373 K for 24 h in an open crucible in air. Crystals were extracted from the cooled, crushed preparation under the petrographic microscope. X-ray diffraction data were obtained from a suitable small crystal ( $ca$   $0.22 \times 0.18 \times 0.08$  mm) on a Nicolet P3 four-circle diffractometer with Mo  $K\alpha$  radiation and graphite monochromator. Cell dimensions were determined using 14 reflections at  $22-26^\circ$  in  $2\theta$ . Data were collected using the  $\omega/2\theta$  method for  $2\theta$  in the range  $0-60^\circ$  for unique reflections with  $h$  0-11,  $k$  0-21,  $l$  -4-4.

Pre-scan intensities ( $I_p$ ) were used to select  $2\theta$  scan rates in the range  $5.33$  to  $58.6^\circ \text{ min}^{-1}$ , the limiting values corresponding to  $I_p < 150$  and  $I_p > 2500$ , respectively. The  $2\theta$  scan width varied from  $2.4-2.8^\circ$

depending on  $2\theta$  for the reflection. The resulting data contained 679 unique reflections of which 17 were classed as unobserved [ $I < 3\sigma(I)$ ]. These were converted to structure amplitudes in the usual way. The intensities of the 162 and  $15\bar{3}$  reflections monitored at intervals of 50 measurements showed no significant variation and no absorption correction was applied.

The structure was solved using Patterson and Fourier techniques and refined by block-diagonal least squares minimizing  $\sum w(\Delta F)^2$  with  $w = 1/\{1 + [(|F_o| - 35)/18]^2\}$  and with all atoms except boron vibrating anisotropically giving, finally,  $R = 0.042$ ,  $wR = 0.044$  and  $S = 1.26$  for 662 reflections and 79 refined parameters;  $\max. \Delta/\sigma = 0.007$ .

A difference map then showed no feature in excess of  $\pm 1.0 e \text{ \AA}^{-3}$ . Atomic parameters are given in Table 1.\* Calculations were carried out on the Bull DPS8 computer (CP6 operating system) of the Computer Centre of the University of Aberdeen using the NRC programs of Ahmed, Hall, Pippy & Huber (1966) and, for the preparation of Fig. 1(b), STRU-PL082 (Fischer, 1982). Scattering factors for neutral B, O and F and  $\text{Ca}^{2+}$  were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No allowance was made for anomalous dispersion.

**Discussion.** The results are in excellent agreement with those obtained independently by Lei, Huang, Zheng, Jiang & Chen (1989). The structure consists of  $\text{Ca}^{2+}$ ,  $\text{F}^-$  and  $\text{BO}_3^{3-}$  ions, shown in (001) projection (Fig. 1a). The borate anions are clearly non-polymeric. B(1) and B(2) are both trigonally coordinated, B(1) by O(1) and  $2 \times \text{O}(2)$  and B(2) by O(3), O(4) and O(5). The planar borate units lie approximately parallel to (001). Ca(1) and Ca(3) are in more or less regular octahedral sites (Fig. 1a). Ca(2) has six nearest neighbour O atoms [Ca(2)—O 2.32–2.56 Å] forming a very distorted octahedral coordination. This atom also has a somewhat longer contact with O(1) at 2.894 (2) Å (dashed line in Fig. 1a). Conversely, O(2–5) are all surrounded by an approximately tetrahedral arrangement of  $1 \times \text{B}$  and  $3 \times \text{Ca}$ . The primary coordination of O(1) is trigonal planar involving  $1 \times \text{B}(1)$  and  $2 \times \text{Ca}(1)$ . With the inclusion of the long Ca(2)—O(1) contact mentioned above the coordination of O(1) becomes distorted trigonal bipyramidal. Fluoride has a distorted tetrahedral coordination made up by  $2 \times \text{Ca}(1)$  and  $2 \times \text{Ca}(3)$ , shown schematically in Fig. 2(a).

\* Lists of bond lengths, angles, anisotropic thermal vibration parameters, structure factors and powder diffraction intensity data calculated for the final parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53278 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

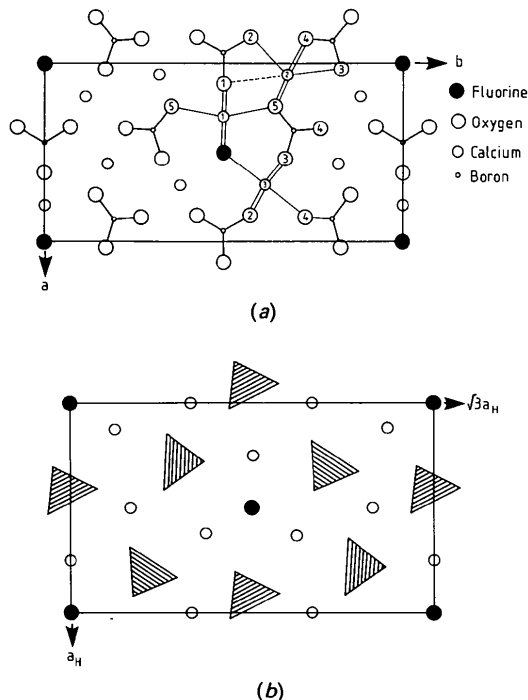


Fig. 1. (a)  $\text{Ca}_5(\text{BO}_3)_3\text{F}$ , (001) projection. Representative Ca and O are numbered as in Table 1. B—O and Ca—X (X=O, F) contacts are indicated. Double lines represent contacts to pairs of atoms related by a  $c$  translation. (b) Projection on (001) of the fluorapatite orthohexagonal cell.  $\text{PO}_4$  tetrahedra are shown as shaded triangles.

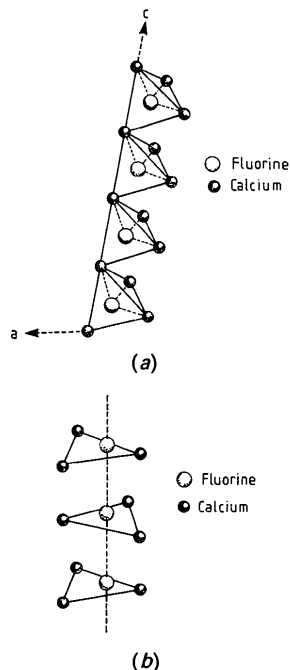


Fig. 2. (a) Schematic representation of the fluoride coordination in  $\text{Ca}_5(\text{BO}_3)_3\text{F}$ . (b) Schematic representation of the fluoride coordination in fluorapatite.

The structural similarity of  $\text{Ca}_5(\text{BO}_3)_3\text{F}$  and fluorapatite is represented well by comparison of the (001) projections (Fig. 1a,b). The basal orthogonal axes of the borate-fluoride correspond to the  $ab$  plane of the fluorapatite with the axes chosen in such a way as to give the C-centred orthohexagonal cell with  $a_o = a_H$ ,  $b_o = \sqrt{3}a_H$  and  $a_H = 9.3684 \text{ \AA}$  (Wyckoff, 1960). However the orthohexagonal projection of the fluorapatite only shows one half of the unit cell ( $z/c$  from 0 to  $\frac{1}{2}$ ); the reason for this is that the  $6_3$  screw axis in fluorapatite produces a crystal with an  $ABAB$  type stacking as represented in Fig. 2(b). This type of stacking is not present in the borate-fluoride structure, where instead an  $AAA$  type arrangement results (Fig. 2a). This feature explains the difference in the  $c$ -axis dimensions, that of the borate-fluoride being approximately half that of fluorapatite ( $3.538$  vs  $6.8841 \text{ \AA}$ ). This stacking arrangement also results in the fluoride being four coordinate instead of three as in fluorapatite. In the absence of a screw axis the 'Ca<sub>3</sub>F' units would be eclipsed; however, the monoclinic angle  $\beta$  causes a translation of the 'Ca<sub>3</sub>F' units so that each planar unit is capped by a calcium from an adjacent layer.

The reported presence of carbonate in well crystallized hydroxyapatite has received a great deal of attention (Posner, 1969), and it has been suggested that the apparent absence of structures in which  $\text{XO}_3^{n-}$  replaces  $\text{XO}_4^{3-}$  implies that replacement does not occur on these sites: instead, carbonate substitutes for hydroxide, as proposed by Elliott (1965). The present structure determination does not shed light directly on this controversy, but does disclose that examples occur amongst apatite-structured phases in which trigonal planar ions can substitute for  $\text{XO}_4^{3-}$ .

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#### References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *NRC Crystallographic Programs for the IBM360 System. World List of Crystallographic Computer Programs*, p.52. Utrecht: Oosthoek.
- ELLIOTT, J. C. (1965). *Tooth Enamel*, edited by M. V. STACK & R. W. FEARNHEAD, pp. 20–22. Bristol: Wright.
- FISCHER, R. X. (1982). *STRUPLO82. A Fortran Program for the Graphical Display of Crystal Structures*. Univ. of Mainz, Germany.
- LEI, S., HUANG, Q., ZHENG, Y., JIANG, A. & CHEN, C. (1989). *Acta Cryst. C45*, 1861–1863.
- POSNER, A. S. (1969). *Physiol. Rev.* **49**, 760–792.
- WYCKOFF, R. W. G. (1960). *Crystal Structures*, Vol. III. New York: Interscience.