Tableau 2. *Distances interatomiques* (Å) *et écarts-type entre parenthèses*

Site 1		
Yb(1)—S(2^{iv})	2,803 (7) × 2	
Yb(1)—S(1^{xiv})	2,824 (8) × 2	⟨Yb(1)—S⟩ 2,870 (9)
Yb(1)—S(4^{iv})	2,867 (8) × 2	
Yb(1)—S(5)	3,106 (13)	
Site 2 (Yb, In)		
M(1)—S(6^{ix})	2,575 (9) × 2	
M(1)—S(2)	2,577 (11)	⟨*M*(1)—S⟩ 2,656 (10)
M(1)—S(6^{vi})	2,590 (13)	
M(1)—S(4^{ix})	2,810 (8) × 2	
Site 3 (Yb, In)		
M(2)—S(5^{iii})	2,585 (7) × 2	
M(2)—S(3^{x})	2,587 (11)	⟨*M*(2)—S⟩ 2,640 (9)
M(2)—S(1^{xi})	2,632 (11)	
M(2)—S(1^{iii})	2,751 (8) × 2	
Site 4 (Yb, In)		
M(3)—S(3^{iv})	2,596 (7) × 2	
M(3)—S(5)	2,624 (11)	⟨*M*(3)—S⟩ 2,665 (9)
M(3)—S(4)	2,624 (12)	
M(3)—S(2^{iv})	2,775 (8) × 2	
Site 5		
In(1)—S(3^{iv})	3,484 (10) × 6	
In(1)—S(5)	3,555 (13) × 3	

Code de symétrie: (nul) x, y, z; (i) $1-y, 1+x-y, z$; (ii) $1+y, 1+y-x, z+\frac{1}{2}$; (iii) $1-x, 1-y, z+\frac{1}{2}$; (iv) $y, y-x, z+\frac{1}{2}$; (v) $1+x-y, x, z+\frac{1}{2}$; (vi) $-y, x-y, z$; (vii) $1+y-x, 1-x, z$; (viii) $y, 1+y-x, z+\frac{1}{2}$; (ix) $x-y, x, z+\frac{1}{2}$; (x) $y-x, 1-x, z$; (xi) $x, 1+y, z$; (xii) $1+x-y, 1+x, z+\frac{1}{2}$; (xiii) $1-y, x-y, z$; (xiv) $1-x, -y, z+\frac{1}{2}$.

octaédriques tant pour l'ytterbium que pour l'indium sont habituels pour ces éléments dans leurs sulfures avec des longueurs de liaisons du même ordre de grandeur: par exemple, on retrouve dans Yb_3S_4 (Chevalier, Laruelle & Flahaut, 1967): Yb^{3+}(VI)—S^{2-} = 2,68 Å ainsi que dans $CdYb_2S_4$ (Tomas, Vovan, Guittard, Flahaut & Guymont, 1986); de même dans KIn_5S_8 (Carré & Pardo, 1983) In^{3+}(VI)—S^{2-} = 2,62 Å.

Le site 5 prismatique de coordinence 9, est occupé par de l'indium monovalent dont la présence est compensée du point de vue de l'équilibre des charges par la présence de lacunes sur le site 2. Les distances correspondantes, comprises entre 3,48 et 3,55 Å, sont cohérentes avec l'ensemble des longueurs de liaisons In^{+}—S^{2-}(2,524 à 4,151 Å) existant dans le composé In_6S_7 (Hogg & Duffin, 1967) qui présente cependant une distribution de distances plus dispersée. La valeur élevée du facteur de température ($B_{éq}$ = 6 $Å^2$) est vraisemblablement liée à des longueurs de liaisons relativement grandes.

Nous remarquons enfin que la répartition atomique que nous obtenons est globalement semblable à celle observée lors de la résolution de la structure de $K_2Tm_{23,33}S_{36}$. Toutefois, dans ce dernier composé les sites cationiques, octaédriques et prismatiques, sont occupés uniquement par du thulium trivalent, le site 5 par du potassium monovalent, le site 1 étant lacunaire.

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Structure of Calcium Fluoroborate, $Ca_5(BO_3)_3F$

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Abstract. M_r = 395·83, monoclinic, Cm, a = 8·129 (3), b = 16·051 (5), c = 3·5390 (4) Å, β = 100·94 (6)°, V = 453·4 $Å^3$, Z = 2, D_x = 2·899, D_m = 2·897 g cm^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 29·4 cm^{-1}, $F(000)$ = 392, T = 296 K, R = 0·038 for 776 unique reflections with $I > 3\sigma(I)$. The structure

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contains Ca^{2+} ions octahedrally coordinated by O and F atoms and $(BO_3)^{3-}$ anions which are principally responsible for the second-harmonic-generation effect.

Introduction. Most crystals of anhydrous borates have a wide transparency range, chemical stability and high damage threshold. These properties led us to search for new nonlinear optical (NLO) crystals among the anhydrous borates. The crystals of β-BaB_2O_4 and LiB_3O_5 are two excellent NLO materials possessing many useful characteristics as found in our institute in recent years (Chen, Wu, Jiang & You, 1984; Chen, Wu, Jiang, Wu, You, Li & Lin, 1989). Unfortunately, most crystals of such compounds reported so far contain either centers of symmetry or arrangements of their anionic groups unfavorable for producing large macroscopic second-harmonic-generation (SHG) coefficients, thereby limiting their application as NLO materials. We therefore decided to study the reactions between borates and other salts, such as fluorides and phosphates, in order to obtain new compounds with NLO properties. This work has produced a new type of NLO crystal, $Ca_5(BO_3)_3F$, in the pseudobinary system $Ca_3(BO_3)_2$–CaF_2 in a ratio 3:1, which has large SHG coefficients ($d_{\rm eff} = 2$–3 relative to $d_{\rm eff}$ for powdered $NH_4H_2PO_4$) and a wide transparency range (190–3600 nm), as well as good chemical stability. The nonlinear optical properties and transparency *etc.* will be discussed elsewhere. In this paper the structure of this new compound is described.

Experimental. The crystals of the title compound were obtained by the flux method. The starting materials, $CaCO_3$, H_3BO_3 and CaF_2 (analytically pure), were mixed thoroughly in the appropriate ratio and then heated in a platinum crucible until they were completely melted. The melt was then cooled slowly at a rate of $5\,{\rm K\,d^{-1}}$ until crystal growth stopped. D_m was measured by flotation in a mixture of CH_3I and CH_2I_2. A colorless single crystal with dimensions 0·68 × 0·40 × 0·25 mm was used for X-ray determination. A total of 780 independent reflections were collected at 296 K on an Enraf–Nonius CAD-4 diffractometer; ω–2θ scan technique in the range $1 < \theta < 30°$ $(-11 < h < 11,\ -22 < k < 0,\ 0 < l < 4)$, scan speed from 2 to $7°\,{\rm min^{-1}}$, scan width $(0{\cdot}5 + 0{\cdot}35\ \tan\theta)°$. Cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $14{\cdot}5 < \theta < 16{\cdot}5°$. Three standard reflections were measured during data collection, and only random deviations were observed. The data were corrected for Lorentz–polarization effects and empirically for absorption; max. and min. absorption corrections were 1·0407 and 0·8799 respectively. 776 reflections with $I > 3\sigma(I)$ were considered observed and used in the structure analysis.

Table 1. *Atom coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	$B_{\rm eq}$(Å^2)
Ca3	0·6691	0·11750 (8)	0·7352	0·48 (2)
Ca1	1·0473 (2)	0·1782 (1)	0·3973 (5)	0·72 (2)
Ca2	1·2816 (3)	0	0·0310 (7)	0·52 (3)
F	1·4864 (8)	0	−0·357 (2)	0·8 (1)
O1	0·8376 (7)	0·0737 (3)	0·309 (2)	0·99 (9)
O2	1·0186 (6)	0·3278 (4)	0·188 (2)	0·96 (9)
O3	1·099 (1)	0	0·450 (2)	1·3 (1)
O4	0·8457 (7)	0·2293 (3)	0·796 (2)	0·98 (9)
O5	1·2250 (6)	0·1439 (3)	−0·024 (2)	0·77 (8)
B1	0·8616 (9)	0·3043 (5)	−0·016 (2)	0·5 (1)
B2	0·926 (1)	0	0·357 (3)	0·4 (2)

Table 2. *Bond distances* (Å) *and angles* (°) *for selected atoms with e.s.d.'s in parentheses*

F—Ca3$^{\rm vi}$	2·385 (3)	Ca1—O4	2·495 (4)
F—Ca2$^{\rm ii}$	2·467 (5)	Ca1—O5	2·330 (4)
F—Ca2	2·351 (6)	Ca1—O5$^{\rm i}$	2·338 (4)
Ca3—O1	2·331 (5)	Ca2—O3$^{\rm ii}$	2·299 (6)
Ca3—O1$^{\rm i}$	2·331 (4)	Ca2—O3	2·290 (6)
Ca3—O2$^{\rm iii}$	2·263 (4)	Ca2—O5	2·355 (5)
Ca3—O2$^{\rm iv}$	2·361 (5)	B1—O2	1·394 (6)
Ca3—O4	2·282 (4)	B1—O4$^{\rm ii}$	1·372 (7)
Ca1—O1	2·369 (4)	B1—O5$^{\rm iii}$	1·383 (6)
Ca1—O2	2·512 (4)	B2—O1	1·379 (6)
Ca1—O4$^{\rm ii}$	2·562 (4)	B2—O3	1·377 (9)
Ca3$^{\rm vi}$—F—Ca3$^{\rm vii}$	104·5 (2)	O2—Ca1—O4	79·6 (1)
Ca3$^{\rm vi}$—F—Ca2$^{\rm ii}$	114·9 (1)	O2—Ca1—O5	94·1 (1)
Ca3$^{\rm vi}$—F—Ca2	114·3 (2)	O2—Ca1—O5$^{\rm i}$	119·5 (1)
Ca2$^{\rm ii}$—F—Ca2	94·6 (2)	O4$^{\rm ii}$—Ca1—O4	88·8 (1)
F$^{\rm v}$—Ca3—O1	95·7 (2)	O4$^{\rm ii}$—Ca1—O5	85·5 (1)
F$^{\rm v}$—Ca3—O1$^{\rm i}$	97·4 (2)	O4$^{\rm ii}$—Ca1—O5$^{\rm i}$	174·3 (1)
F$^{\rm v}$—Ca3—O2$^{\rm iii}$	88·1 (2)	O4—Ca1—O5	173·2 (2)
F$^{\rm v}$—Ca3—O2$^{\rm iv}$	89·9 (2)	O4—Ca1—O5$^{\rm i}$	86·8 (2)
F$^{\rm v}$—Ca3—O4	177·4 (3)	O5—Ca1—O5$^{\rm i}$	98·7 (2)
O1—Ca3—O1$^{\rm i}$	98·8 (2)	F—Ca2—F$^{\rm i}$	94·6 (2)
O1—Ca3—O2$^{\rm iii}$	81·4 (2)	F—Ca2—O3$^{\rm ii}$	83·5 (3)
O1—Ca3—O2$^{\rm iv}$	174·3 (2)	F—Ca2—O3	175·6 (3)
O1—Ca3—O4	82·0 (2)	F—Ca2—O5	95·9 (1)
O1$^{\rm i}$—Ca3—O2$^{\rm iii}$	174·4 (2)	F$^{\rm i}$—Ca2—O3$^{\rm ii}$	178·0 (3)
O1$^{\rm i}$—Ca3—O2$^{\rm iv}$	79·5 (1)	F$^{\rm i}$—Ca2—O3	81·2 (2)
O1$^{\rm i}$—Ca3—O4	84·3 (2)	F$^{\rm i}$—Ca2—O5	99·3 (2)
O2$^{\rm iii}$—Ca3—O2$^{\rm iv}$	99·9 (2)	O3$^{\rm ii}$—Ca2—O3	100·9 (2)
O2$^{\rm iii}$—Ca3—O4	90·3 (2)	O3$^{\rm ii}$—Ca2—O5	81·0 (2)
O2$^{\rm iv}$—Ca3—O4	92·5 (2)	O3—Ca2—O5	85·0 (1)
O1—Ca1—O2	127·9 (1)	O5—Ca2—O5$^{\rm viii}$	157·3 (2)
O1—Ca1—O4$^{\rm ii}$	77·6 (1)	O2—B1—O4$^{\rm ii}$	118·8 (5)
O1—Ca1—O4	76·9 (1)	O2—B1—O5$^{\rm iii}$	120·0 (5)
O1—Ca1—O5	105·4 (1)	O4$^{\rm ii}$—B1—O5$^{\rm iii}$	121·2 (5)
O1—Ca1—O5$^{\rm i}$	105·0 (1)	O1—B2—O1$^{\rm viii}$	118·2 (6)
O2—Ca1—O4$^{\rm ii}$	55·9 (1)	O1—B2—O3	121·0 (3)

Symmetry code: (i) $x, y, z+1$; (ii) $x, y, z-1$; (iii) $-0{\cdot}5+x, 0{\cdot}5-y, z$; (iv) $-0{\cdot}5+x, 0{\cdot}5-y, z+1$; (v) $x-1, y, z+1$; (vi) $x+1, y, z-1$; (vii) $x+1, -y, z-1$; (viii) $x, -y, z$.

The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982); three Ca atoms were located in the *E* map. The remaining atoms were located in the succeeding difference Fourier synthesis. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all atoms (87 variables). Final $R = 0{\cdot}038$, $wR = 0{\cdot}053$ and $S = 2{\cdot}156$, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma_o^2(F_o^2) + (0{\cdot}05F_o^2)^2$, $(\Delta/\sigma)_{\max} = 0{\cdot}1$. Minimum and maximum heights in final difference synthesis were $-0{\cdot}93$ and $+1{\cdot}13$ e Å^{-3} [in the neighborhood of the Ca(3) atom], respectively. Correction for secondary extinction was required [$F_{\rm corr} = F_c/(1 + X{\cdot}{\rm FSQ})$ where X was refined to a final value of $8{\cdot}6 \times 10^{-6}$ and FSQ was F_c^2 multiplied by the Lp factor]. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a VAX 785 computer using *SDP/VAX* program packages (Frenz, 1978).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1;* main bond lengths and angles are given in Table 2. An *ORTEP* (Johnson, 1976) drawing of the molecule is shown in Fig. 1 together with the numbering scheme. Fig. 2 shows the molecular packing. Two types of building units can be recognized; one is a BO_3 group and the other a CaO_4X_2 octahedron (X = O or F). The environment of Ca(2) consists of two F and four O atoms; that of Ca(3) consists of one F and five O atoms; Ca(1) is surrounded by six O atoms only. Each Ca atom has a somewhat distorted octahedral configuration. All octahedra are linked by corner-sharing BO_3 groups to form a three-dimensional network. The Ca(2), O(3), F and B(2) atoms are all located on the crystallographic mirror at $y = 0$. The F atom fits into a slightly distorted tetrahedron formed by two Ca(2) and two Ca(3) atoms (Ca—F distances vary from 2·351 to 2·467 Å).

Calculations of the microscopic SHG coefficients using the 'anionic group theory' and the CNDO approximation method (Chen, 1979) indicate that the major contribution to the SHG effect in the crystal studied comes from the BO_3 groups. The contributions from the Ca octahedra which involve ionic Ca—O or Ca—F bonds are nearly zero. If Ca atoms are replaced by transition-metal atoms, *e.g.* Ti, Ta, *etc.*, to increase the covalency of the *M*—O and *M*—F bonds, the SHG coefficients should be much larger, as has been found for $KTiOPO_4$ (Zumsteg, Bierlein & Gier, 1976) and $BaTiO_3$ (Pressley, 1971).

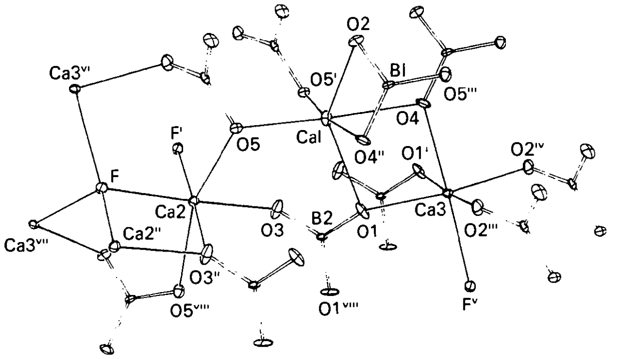

Fig. 1. Atom-numbering scheme.

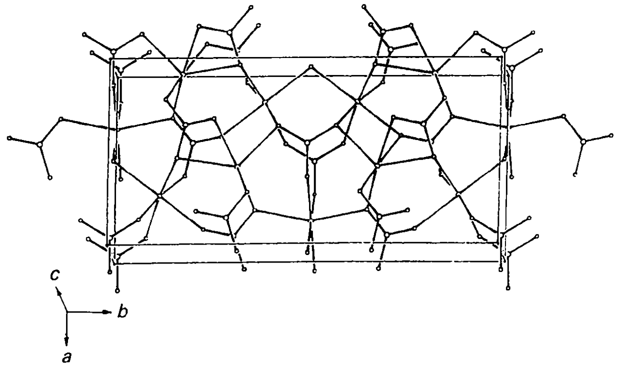

Fig. 2. A view of the packing.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52094 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.