

Table 2. Short interatomic distances (Å)

E.s.d.'s of distances involving O are 0.01 Å.					
As(1)—O(2)	1.62	K(2)—O(8)	2.71	K(4)—O5	2.68
As(1)—O(1)	1.65	K(2)—O(10)	2.80	K(4)—O(1)	2.70
As(1)—O(4)	1.75	K(2)—O(3)	2.85	K(4)—O(3)	2.82
As(1)—O(7)	1.76	K(2)—O(1)	2.93	K(4)—O(10)	2.82
As(2)—O(10)	1.64	K(2)—O(1)	2.94	K(4)—O(1)	2.92
As(2)—O(8)	1.64	K(2)—O(3)	2.96	K(4)—O(7)	2.92
As(2)—O(9)	1.66	K(2)—O(6)	3.28	K(5)—O(5)	2.68
As(2)—O(7)	1.81	K(2)—O(4)	3.28	K(5)—O(2)	2.69
As(3)—O(6)	1.63	K(3)—O(6)	2.67	K(5)—O(9)	2.81
As(3)—O(5)	1.66	K(3)—O(2)	2.71	K(5)—O(7)	3.13
As(3)—O(3)	1.68	K(3)—O(4)	2.78	K(5)—O(4)	3.15
As(3)—O(4)	1.79	K(3)—O(9)	2.86	K(5)—O(6)	3.16
K(1)—O(6)	2.64	K(3)—O(8)	2.88	K(5)—O(2)	3.18
K(1)—O(5)	2.71	K(3)—O(9)	2.92	K(5)—O(9)	3.20
K(1)—O(10)	2.74	K(3)—O(10)	3.25	K(5)—O(10)	3.31
K(1)—O(3)	2.79	K(3)—O(2)	3.27	As(1)—As(2)	3.25
K(1)—O(9)	2.80			As(1)—As(3)	3.27
K(1)—O(8)	2.83				

The As atoms are surrounded by four O atoms in almost regular tetrahedra, forming chains of three by sharing corners (see Fig. 1). The angles As(1)—O(7)—As(2) and As(1)—O(4)—As(3) have normal values of 131.4 and 134.9° respectively. For the non-bridging O atoms a mean As—O distance of 1.65 Å is found, and for the bridging O atoms 1.78 Å, in agreement with other arsenates. The strong bending of the chain is shown by the angle As(2)—As(1)—As(3),

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Structure of Hydroxellestadite

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Abstract. $Ca_{10}(SiO_4)_3(SO_4)_3(OH,Cl,F)_2$, monoclinic, $P2_1/m$, with $a = 9.476$ (2), $b = 9.508$ (2), $c = 6.919$ (1) Å, and $\gamma = 119.53$ (2)° (c is taken as the unique axis because of the relation to the hexagonal apatite structure). In hydroxellestadite, a main constituent of normal apatite, PO_4 , is completely replaced by SiO_4 and SO_4 groups without compensating substitutions elsewhere in the structure. The structure resembles that of apatite. Least-squares refinement with 3040 independent diffractometer-measured X-ray intensities showed three different sizes for tetrahedral groups (average Si,S to O distances 1.52, 1.54 and 1.57 Å), indicating a preferential substitution of SO_4 and SiO_4 for different PO_4 groups but not a complete substitution by one atom at any particular site.

Introduction. The ellestadite series, the sulfate silicate apatites showing substitutions for phosphorus, have only been subjected to limited structural analysis.

which is only 105.0°, compared with a corresponding angle of 173° in the chains of $Na_5P_3O_{10}$ (Corbridge, 1960).

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Wilkeite, a mineral from Southern California containing approximately 12% SO_3 , 9% SiO_2 and 21% P_2O_5 , has been assigned to the apatite group by Eakle & Rogers (1914) on the basis of its crystallographic, physical and optical properties. Ellestadite and other sulfate silicate apatites containing halogens and minor amounts of CO_3 and PO_4 were first described by McConnel (1937, 1938). It is one of the skarn minerals from Crestmore, Riverside County, California. Hydroxellestadite and fluorellestadite have been synthesized by Dihn & Clement (1942) and Takemoto & Kato (1968). Harada, Nagashima, Nakao & Kato (1971) reported the existence of the mineral hydroxellestadite in the Chichibu Mine, Saitama Prefecture, Japan. From a chemical analysis they have proposed the formula $(Ca_{9.656}Na_{0.109}Sr_{0.027}Fe_{0.026}K_{0.615}Mn_{0.001})(SiO_4)_{2.860}(SO_4)_{2.675}(CO_3OH)_{0.370}(PO_4)_{0.002}(OH)_{1.877}Cl_{0.255}F_{0.146}$. The importance of this mineral is that it is the only mineral reported in which PO_4 , a main constituent of © 1980 International Union of Crystallography

normal apatite, is completely replaced by SO_4 and SiO_4 groups without compensating substitutions elsewhere in the structure. Isomorphous charge-compensated substitutions of PO_4^{3-} by SiO_4^{4-} and SO_4^{2-} have been suggested by McConnell (1937, 1938) for the minerals wilkeite and ellestadite, apparently the only silicate apatites which can crystallize without any rare-earth elements.

Si and S are present as trace elements in human hard dental tissues (Hardwick & Martin, 1967; Curzon, Losee & Magalister, 1971; Losee, Cutress & Brown, 1973). Losee *et al.* analyzed 56 samples of enamel by spark-source spectrometry and found that Si is present to 100–450 p.p.m. and S to 100–560 p.p.m. Dental silicate cements have been in use for more than a century. With silicate restorations there is less caries on proximal contacts of the adjacent teeth than with silver or copper amalgam restoration (Swartz & Philips, 1958). Therefore, crystal structure studies of apatite in which SiO_4 and SO_4 have replaced PO_4 groups take on relevance in dental research.

A spherical single-crystal specimen of radius 0.13 mm, prepared from hydroxyellestadite from Chichibu Mine, Japan, was used to collect 3040 independent X-ray intensities with a computer-controlled four-circle diffractometer. The lattice parameters were determined from least-squares refinements with crystal setting data for 12 reflections (within the angular range $70^\circ < 2\theta < 105^\circ$) measured on the diffractometer with $\text{Mo } K\alpha$ radiation ($\lambda = 0.70926 \text{ \AA}$). Harada *et al.* (1971) (from powder data and from Buerger precession photographs) report the crystal to be hexagonal with $a = 9.491 (1)$ and $c = 6.921 (1) \text{ \AA}$ but from the measured lattice parameters and Laue symmetry we found the crystal not to be hexagonal. The systematic absences showed that the space group is either $P2_1/m$ or $P2_1$.

A balanced-filter (Zr + Y) ω -scan technique with $\text{Mo } K$ radiation was used for measurement of the intensities of lower-angle reflections for which the absorption edge of Zr fell within the scanning range for peak plus background and the θ - 2θ scan method with Zr-filtered radiation was employed for other reflections. Simultaneous diffraction effects were assessed by remeasurement of each reflection intensity after the specimen was rotated about the diffraction vector by 1° . Those measured reflection intensities which for the two settings of the crystal differed by more than three times the expected standard deviation (on the basis of counting statistics) were not used in the refinements. Each reflection was scanned repeatedly, as required, up to a maximum of 16 times to yield 1% statistical precision (counting statistics) in the net intensities. Absorption corrections were made based on the tabular data in *International Tables for X-ray Crystallography* (1968) for a spherical specimen ($\mu R = 0.04$).

The lattice dimensions and the formula are compar-

able to those of apatites. Moreover, the structure of apatite permits a wide range of ionic substitutions. As such, the structure was assumed to be similar to that of apatite. Least-squares refinement of the structural parameters was carried out, starting from the parameters derived for the monoclinic space group from the published parameters for hexagonal hydroxyapatite (Sudarsanan & Young, 1969), with the program *ORXFLS3* (Busing, Johnson, Ellison, Thiessen & Levy, 1973). The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ where $w^{-1} = \sigma^2(|F_o|^2) + 0.04|F_o|^2$; $\sigma^2(|F_o|^2)$ is the standard deviation estimated from counting statistics. All the measured reflections, including the unobserved reflections, were included in the least-squares refinement. To remove the strong correlation between pseudo hexagonal parameters in the initial stages of refinement the parameters of the sets of atoms related by hexagonal symmetry were only alternately refined. After a few cycles the parameters of all the atoms were refined simultaneously. The correlation between pseudo hexagonal parameters was less than 0.5. The initial refinements indicated three different sizes for tetrahedral groups ($X\text{-O} = 1.52, 1.54$ and 1.57 \AA , where X is Si or S). The site giving the smallest size was attributed to S, the largest to Si and the intermediate to S/Si in $\frac{1}{2}/\frac{1}{2}$ occupancy. Refinements were attempted in space groups $P2_1/m$ and $P2_1$. Owing to the strong correlation between site-occupancy factors and the temperature parameters of the atoms related by the center of symmetry, meaningful refinements cannot be carried out in space group $P2_1$. Hence, refinements were continued in space group $P2_1/m$. The atomic scattering factors for Ca^{2+} , S^0 , Si^0 , O^{1-} , Cl^- and F^- were taken from *International Tables for X-ray Crystallography* (1967). Anomalous-dispersion corrections were made with values of f' and f'' calculated by Cromer (1965). The observed structure factors were corrected for isotropic secondary extinction. The final values of the reliability factors are $R_1 = 6.6\%$, $R_2 = 6.0\%$ and $wR_2 = 8.4\%$, where $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|$; $R_2 = \sum (|F_o|^2 - |F_c|^2) / \sum |F_o|^2$; and $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w |F_o|^4]^{1/2}$.

Discussion. The structure resembles that of apatites. The positional parameters are listed in Table 1.* The atom-numbering scheme used in published hexagonal apatite structures has been retained to facilitate comparisons. Atoms designated A , B and C are the equivalent positions in the hexagonal apatite structure. Least-squares refinement indicated that there are indeed two distinct positions for the Ca(2) atoms about

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35187 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) with standard deviations in parentheses

	Site-occupancy factor	x	y	z	B (\AA^2)*
Ca(1)	1.0588 (39)	3365 (1)	6727 (1)	20 (1)	2.16 (3)
Ca(2A)	0.9231 (107)	38 (1)	2471 (3)	$\frac{1}{4}$	1.52 (3)
Ca(2A')	0.0879 (93)	131 (14)	2943 (27)	$\frac{1}{4}$	1.52 (3)
Ca(2B)	0.9065 (126)	-2537 (3)	-2421 (3)	$\frac{1}{4}$	1.44 (3)
Ca(2B')	0.0980 (107)	-2948 (23)	-2785 (22)	$\frac{1}{4}$	1.44 (3)
Ca(2C)	0.9475 (169)	2465 (3)	-62 (1)	$\frac{1}{4}$	1.47 (3)
Ca(2C')	0.0723 (145)	2797 (34)	-1631 (21)	$\frac{1}{4}$	1.47 (3)
Si	0.9955 (50)	-3694 (1)	299 (1)	$\frac{1}{4}$	0.67 (2)
S	0.9417 (46)	-303 (1)	-4003 (1)	$\frac{1}{4}$	0.87 (2)
(Si,S)	0.9717 (50)	3985 (1)	3720 (1)	$\frac{1}{4}$	0.81 (2)
O(1A)	1.011 (139)	3270 (4)	4851 (3)	$\frac{1}{4}$	1.85 (8)
O(1B)	1.0104 (116)	-4840 (3)	-1584 (3)	$\frac{1}{4}$	1.49 (6)
O(1C)	1.0029 (124)	1536 (3)	-3293 (3)	$\frac{1}{4}$	1.64 (7)
O(2A)	1.0268 (146)	5861 (3)	4666 (3)	$\frac{1}{4}$	1.80 (8)
O(2B)	0.9991 (122)	-4664 (3)	1243 (3)	$\frac{1}{4}$	1.52 (7)
O(2C)	1.0246 (129)	-1207 (3)	-5862 (3)	$\frac{1}{4}$	1.87 (7)
O(3A)	1.0144 (110)	3462 (3)	2624 (3)	705 (3)	1.92 (10)
O(3B)	0.9788 (98)	-2567 (2)	895 (2)	671 (3)	1.76 (9)
O(3C)	0.9997 (103)	-878 (2)	-3485 (3)	716 (3)	3.17 (12)
OH	0.8068 (91)	-12 (5)	-12 (5)	2023 (5)	1.36 (11)
Cl	0.151 (67)	-20 (5)	-28 (1)	3644 (5)	1.79 (22)
F	0.0924 (54)	41 (5)	-27 (6)	$\frac{1}{4}$	1.46 (29)

* These are 'equivalent' isotropic values calculated after the fact from the actually refined anisotropic thermal parameters, which have been deposited.

Table 2. Bond distances (\AA)

Si—O(1B)	1.562 (4)	(S,Si)—O(1A)	1.533 (5)
Si—O(2B)	1.573 (5)	(S,Si)—O(2A)	1.540 (4)
Si—O(3B)	1.568 (3)*	(S,Si)—O(3C)	1.537 (3)*
S—O(1C)	1.522 (4)		
S—O(2C)	1.529 (4)		
S—O(3C)	1.528 (3)*		

* Distance repeated for symmetry-related site of the second atom.

0.2 \AA apart. The occurrence of two sites for Ca(2) atoms indicates two types of Ca(2) triangles around the *c* axis, one associated with F or OH at or near the center of the Ca(2) triangles resulting in a smaller triangle size and the other associated with Cl which is away from the center of the Ca(2) triangles by more than 1 \AA . The position of Cl in ClAp is (0,0,0.444). However, in this case it is found to be at (0,0,0.364). Previous studies (Sudarsanan & Young, 1978) on apatite specimens containing differing X-ion (*X* = Cl, OH or F) contents have shown that the *z* positional parameter of Cl depends roughly linearly on the fractional amount of Cl present. As the relative Cl content decreases the Cl⁻ ions move closer to the planes of associated Ca triangles. The position of the Cl found correlated well with the Cl content as described by Sudarsanan & Young (1978).

Although a preferential substitution for P by S and Si in different sites is evidenced by the three different sizes of the tetrahedra, the observed interatomic distances do

not indicate a complete substitution by any one atom at any particular site as proposed in the model for refinement. The interatomic distances X—O [where *X* = S, Si or (S,Si)] in the three tetrahedra are given in Table 2. As reported in *International Tables* (1968), S—O distances in SO₄²⁻ range from 1.44 to 1.53 (± 0.04) \AA with an average value of 1.49 \AA , and Si—O distances in silicates range from 1.59 to 1.63 (± 0.04) \AA with an average value of 1.61 \AA . The average observed values for the present specimen are S—O 1.52, Si—O 1.57 and (S,Si)—O 1.54 \AA .

Owing to the presence of various trace elements (see formula in *Introduction*) which could not be correctly accommodated in the model used for refinements a correlation between the observed site-occupancy factors and chemical-analysis results cannot be given.

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Structure of Erbium Pentaphosphate

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Abstract. $\text{ErP}_5\text{O}_{14}$, monoclinic, $C2/c$, $a = 12.837$ (8), $b = 12.723$ (7), $c = 12.381$ (7) Å, $\beta = 91.25$ (5)°, $M_r = 546.1$, $V = 2021.6$ Å³, $Z = 8$, $D_x = 3.59$, $D_m = 3.55$ Mg m⁻³, $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 9.49$ mm⁻¹. The final R factor with 2238 independent reflexions was 0.060. The structure is isomorphous with that of the monoclinic form of the holmium salt. Each crystallographically different Er^{3+} ion lies on a twofold axis and has eight O neighbours.

Introduction. It has been shown (Durif, 1971) that the crystal structure of a rare-earth pentaphosphate depends on the ionic radius of the rare-earth ion, but in all cases the individual rare-earth ions are well shielded, with no ions sharing the same oxygen, and the resulting minimum distance between rare-earth ions is not less than 5 Å. Mazurak, Ryba-Romanowski & Jeżowska-Trzebiatowska (1978) have reported the spectroscopic properties of $\text{ErP}_5\text{O}_{14}$ single crystals. The present paper presents the crystal structure of $\text{ErP}_5\text{O}_{14}$, a possible highly concentrated laser material containing Er^{3+} ions.

The title compound was obtained as described by Mazurak *et al.* (1978). Weissenberg photographs showed that the crystals are monoclinic, space group $C2/c$ or Cc . A roughly cubic crystal, with edges of 0.15 mm, was selected for the data collection. A Syntex $P2_1$ diffractometer and $\text{Mo } K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the 2θ - ω scan technique. After each group of 15

reflexions the intensity of a standard reflexion was measured; no significant change in intensity was observed. The data were corrected for Lorentz and polarization effects. Of the 2650 accessible reflexions in the range $10 \leq \theta \leq 30^\circ$, 2238 with $I > 3\sigma(I)$ were used for the structure determination. All calculations were performed on a NOVA minicomputer with programs supplied by Syntex. Neutral-atom scattering factors

Table 1. Final positional parameters of $\text{ErP}_5\text{O}_{14}$

	x	y	z	B_{eq} (Å ²)
Er(1)	$\frac{1}{2}$	0.0317 (1)	$\frac{1}{4}$	0.12
Er(2)	0	-0.0204 (1)	$\frac{3}{4}$	0.13
P(1)	0.3224 (3)	0.2508 (3)	0.2405 (3)	0.38
P(2)	0.1496 (3)	0.1682 (3)	0.1030 (3)	0.13
P(3)	0.0253 (3)	0.3488 (3)	0.0324 (3)	0.18
P(4)	-0.1820 (3)	0.3628 (3)	0.1089 (3)	0.10
P(5)	-0.3535 (3)	0.4659 (3)	-0.0016 (3)	0.29
O(1)	0.3694 (9)	0.1500 (8)	0.2690 (8)	0.93
O(2)	0.5598 (8)	-0.0968 (8)	0.1330 (7)	0.55
O(3)	0.4747 (8)	0.1018 (8)	0.0745 (8)	0.84
O(4)	0.3469 (8)	-0.0490 (8)	0.1771 (8)	0.63
O(5)	-0.1163 (9)	-0.1567 (8)	0.2162 (8)	1.06
O(6)	0.0893 (8)	0.1296 (7)	0.1927 (7)	0.48
O(7)	-0.1143 (9)	0.0374 (8)	0.1149 (8)	0.86
O(8)	0.0763 (8)	-0.0654 (8)	0.0858 (8)	0.75
O(12)	0.2442 (8)	0.2360 (8)	0.1353 (8)	0.82
O(14)	0.2416 (8)	0.2729 (7)	0.3339 (8)	0.77
O(23)	0.0857 (8)	0.2392 (7)	0.0217 (7)	0.69
O(25)	0.1940 (7)	0.0818 (7)	0.0263 (7)	0.35
O(34)	-0.0910 (7)	0.3019 (7)	0.0550 (7)	0.30
O(45)	-0.2499 (9)	0.3963 (7)	0.0098 (7)	0.61