KNORR, K., JAHN, I. R. & HEGER, G. (1974). *Solid State Commun.* **15**, 231–238.

PETERSON, E. R. & WILLETT, R. D. (1972). *J. Chem. Phys.* **56**, 1879.

SAX, M. & PLETCHER, J. (1969). *Science*, **166**, 1546.

STEWART, J. M. (1967). The X-RAY 67 system. Tech. Rep. TR-67-58. Computer Science Center, Univ. of Maryland, College Park, Maryland.

The Crystal Structure of α-Ca₃(PO₄)₂*

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α-Ca$_3$(PO$_4$)$_2$ crystallizes in the monoclinic space group $P2_1/a$ with $a = 12.887$ (2), $b = 27.280$ (4), $c = 15.219$ (2) Å, $\beta = 126.20$ (1)°, and $Z = 24$. An approximate subcell with $b' = b/3$ exists. The structure was solved by direct methods of phase determination and refined to $R = 0.051$ and $R_w = 0.049$ with 7002 reflections collected from a single crystal by counter methods. The structure consists of columns of cations, and columns of cations and anions with compensating cation vacancies, and is closely related to the structure of K$_3$Na(SO$_4$)$_2$, the mineral glaserite. The calcium ions in α-Ca$_3$(PO$_4$)$_2$ exhibit a wide range of coordination numbers and geometries.

Introduction

The chemistry of calcium phosphates is generally complex, and the phases with stoichiometry Ca$_3$(PO$_4$)$_2$ provide no exception. A brief general description of these phases has been given in the paper on the crystal structure of pure β-Ca$_3$(PO$_4$)$_2$ (Dickens, Schroeder & Brown, 1974). The phase α-Ca$_3$(PO$_4$)$_2$ is thermodynamically stable between 1120 and 1470°C (Fix, Heymann & Heinke, 1969) in the absence of impurities, but is metastable at room temperature. Here we report the determination of its crystal structure and discuss its place in the calcium phosphate family.

Experimental methods and structure determination

Samples of α-Ca$_3$(PO$_4$)$_2$ were made by heating pressed pellets of stoichiometric amounts of CaHPO$_4$ and

CaCO$_3$, mixed with 1% cornstarch and a few drops of distilled water, to 1400°C for 2 d. Several crystals were ground into approximate spheres and mounted in random orientations on goniometer heads. A crystal with diameter 0.190 (5) mm was mounted on a Picker§ four-circle diffractometer equipped with a highly oriented graphite monochromator and using Mo radiation. The cell dimensions were determined by least-squares refinement of 2θ values observed by automatically centering 30 reflections in the range $48° < 2\theta < 60°$ [λ(Mo Kα_1) $= 0.709260$ Å]. The diffractometer-controlling program was written by Lenhert (1975).

α-Ca$_3$(PO$_4$)$_2$ crystallizes in the monoclinic space group $P2_1/a$, with cell parameters $a = 12.887$ (2), $b = 27.280$ (4), $c = 15.219$ (2) Å and $\beta = 126.20$ (1)° at 25°C. The calculated density for $Z = 24$ of 2.863 g cm^{-3} and the observed density of 2.81 (1) g cm^{-3} (Mackay, 1953) indicate some porosity, as expected for a sample prepared by a solid-state reaction between two different phases.

A prominent subcell exists with $b'' = b/3$, the cell reported by Mackay (1953). The real cell is shown by weak reflections for $k \neq 3n$. The metric symmetry is

§ Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the NBS nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

Table 1. *Atomic parameters of* α-Ca$_3$(PO$_4$)$_2$

The positional parameters are multiplied by 10^5 for Ca and P and by 10^4 for O atoms. The form of the thermal factor is $\exp|-2\pi^2(\Sigma_{ij}U_{ij}h_ih_ja_i^*a_j^*)|$. The thermal parameters are $\times 10^4$ for Ca and P; values for O are $\times 10^3$. The figures in parentheses are standard deviations in the last significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca(1)	39138 (13)	2600 (4)	8612 (10)	210 (8)	94 (6)	163 (7)	29 (11)	275 (13)	7 (10)
Ca(2)	14742 (12)	4937 (4)	32729 (9)	66 (7)	173 (7)	73 (6)	−69 (11)	41 (11)	−31 (9)
Ca(3)	8768 (12)	7286 (4)	4976 (9)	114 (7)	106 (6)	79 (6)	47 (11)	85 (11)	−2 (9)
Ca(4)	14267 (12)	8946 (4)	55957 (9)	77 (7)	102 (6)	86 (6)	−9 (10)	86 (11)	−7 (9)
Ca(5)	5783 (13)	8708 (4)	74743 (10)	160 (8)	98 (6)	167 (7)	−43 (11)	201 (13)	−51 (10)
Ca(6)	36805 (13)	13863 (4)	33207 (10)	129 (8)	98 (6)	178 (6)	20 (11)	201 (12)	46 (10)
Ca(7)	12125 (12)	19139 (4)	94434 (10)	77 (7)	170 (7)	145 (6)	−24 (12)	113 (12)	−46 (10)
Ca(8)	37108 (12)	21591 (4)	67698 (9)	72 (7)	147 (6)	114 (6)	68 (11)	53 (11)	22 (10)
Ca(9)	38603 (12)	23433 (4)	93751 (9)	113 (7)	113 (6)	105 (6)	63 (11)	140 (11)	78 (10)
Ca(10)	36956 (12)	25894 (4)	43849 (10)	83 (7)	109 (6)	96 (6)	57 (11)	99 (11)	49 (9)
Ca(11)	41359 (14)	24537 (4)	20819 (10)	209 (8)	117 (7)	169 (7)	−57 (11)	241 (13)	25 (10)
Ca(12)	14746 (12)	30227 (4)	67533 (10)	98 (8)	109 (6)	152 (6)	−40 (11)	149 (12)	−61 (9)
Ca(13)	39021 (12)	35179 (5)	7293 (10)	82 (7)	188 (7)	125 (6)	−49 (12)	100 (12)	37 (10)
Ca(14)	17089 (13)	37277 (4)	32417 (10)	93 (8)	121 (6)	123 (6)	−46 (11)	23 (12)	12 (10)
Ca(15)	10282 (12)	41293 (4)	4926 (9)	60 (7)	113 (6)	69 (6)	26 (10)	38 (11)	−15 (9)
Ca(16)	13909 (12)	42447 (4)	56149 (9)	81 (7)	83 (6)	79 (6)	−20 (10)	71 (11)	−10 (9)
Ca(17)	11815 (12)	41466 (4)	80001 (10)	102 (7)	102 (6)	151 (6)	46 (11)	153 (12)	−7 (9)
Ca(18)	35132 (12)	47366 (4)	30781 (10)	99 (7)	90 (6)	138 (6)	−14 (11)	126 (12)	−25 (9)
P(1)	38800 (15)	13702 (5)	11108 (11)	62 (9)	83 (9)	87 (7)	−23 (13)	61 (14)	−17 (11)
P(2)	37924 (16)	13123 (5)	54396 (12)	60 (9)	94 (8)	99 (7)	−39 (13)	80 (14)	−37 (11)
P(3)	10908 (16)	19220 (5)	70029 (12)	88 (9)	64 (8)	98 (7)	19 (13)	100 (14)	−12 (12)
P(4)	13563 (16)	20844 (5)	15665 (12)	72 (9)	98 (8)	80 (7)	42 (13)	52 (14)	−22 (11)
P(5)	12481 (15)	30784 (5)	89906 (11)	64 (9)	79 (8)	91 (8)	1 (13)	87 (14)	−8 (12)
P(6)	12715 (16)	29631 (5)	45789 (12)	53 (9)	90 (8)	112 (8)	22 (13)	85 (14)	−2 (12)
P(7)	39490 (16)	36306 (5)	29933 (12)	76 (9)	68 (8)	95 (7)	−13 (13)	66 (14)	7 (11)
P(8)	37340 (15)	36794 (5)	84241 (12)	62 (9)	87 (8)	71 (7)	0 (13)	51 (14)	12 (11)
P(9)	38889 (16)	47498 (5)	10213 (12)	83 (9)	72 (8)	92 (8)	−6 (13)	72 (15)	8 (11)
P(10)	36219 (16)	46463 (5)	52427 (12)	65 (9)	90 (8)	93 (7)	3 (13)	80 (14)	3 (12)
P(11)	13742 (16)	52919 (5)	69994 (12)	104 (10)	83 (8)	89 (7)	−7 (14)	91 (15)	−2 (12)
P(12)	12623 (16)	53965 (5)	15574 (12)	65 (9)	113 (8)	80 (7)	7 (14)	64 (14)	−22 (12)
O(11)	2761 (4)	1011 (1)	641 (3)	12 (3)	12 (2)	18 (2)	−14 (4)	16 (4)	−9 (3)
O(12)	3488 (4)	1793 (1)	326 (3)	13 (3)	16 (2)	17 (2)	4 (4)	15 (4)	13 (4)
O(13)	5086 (4)	1095 (1)	1384 (3)	7 (3)	21 (2)	13 (2)	−1 (4)	8 (4)	−6 (3)
O(14)	4290 (4)	1592 (1)	2211 (3)	16 (3)	17 (2)	13 (2)	0 (4)	13 (4)	−1 (3)
O(21)	3132 (4)	1366 (1)	6013 (3)	12 (3)	18 (2)	18 (2)	−7 (4)	20 (4)	−8 (3)
O(22)	2897 (4)	1103 (1)	4287 (3)	14 (3)	14 (2)	15 (2)	−5 (4)	19 (4)	−6 (3)
O(23)	4194 (4)	1833 (1)	5351 (3)	18 (3)	15 (2)	17 (2)	−5 (4)	12 (4)	4 (4)
O(24)	5032 (4)	1002 (1)	6140 (3)	12 (3)	25 (2)	17 (2)	13 (4)	15 (4)	2 (4)
O(31)	35 (4)	2320 (1)	6347 (3)	10 (3)	14 (2)	16 (2)	2 (4)	9 (4)	1 (4)
O(32)	845 (4)	1475 (1)	6307 (3)	19 (3)	19 (2)	19 (2)	−4 (4)	15 (4)	−15 (4)
O(33)	2388 (4)	2181 (1)	7446 (3)	9 (3)	15 (2)	13 (2)	0 (4)	7 (4)	1 (3)
O(34)	1104 (4)	1741 (1)	7957 (3)	28 (3)	19 (2)	20 (2)	−4 (4)	34 (5)	1 (4)
O(41)	70 (4)	2316 (1)	1227 (3)	12 (3)	17 (2)	19 (2)	7 (4)	15 (4)	5 (4)
O(42)	1014 (4)	1557 (1)	1099 (3)	14 (3)	15 (2)	26 (2)	−4 (4)	22 (4)	−8 (4)
O(43)	1856 (4)	2361 (1)	1007 (3)	28 (3)	19 (2)	25 (3)	3 (4)	43 (5)	7 (4)
O(44)	2366 (4)	2081 (1)	2791 (3)	13 (3)	24 (2)	8 (2)	9 (4)	−4 (4)	−2 (3)
O(51)	2461 (4)	2766 (1)	9563 (3)	11 (3)	14 (2)	19 (2)	11 (4)	16 (4)	9 (4)
O(52)	1543 (4)	3530 (1)	9698 (3)	12 (3)	15 (2)	17 (2)	1 (4)	8 (4)	−21 (4)
O(53)	116 (4)	2771 (1)	8759 (3)	9 (2)	16 (2)	11 (2)	−4 (4)	9 (4)	1 (3)
O(54)	852 (4)	3257 (1)	7864 (3)	8 (2)	17 (2)	9 (2)	−3 (4)	7 (4)	1 (3)
O(61)	2139 (4)	2728 (1)	5702 (3)	21 (3)	17 (2)	17 (2)	12 (4)	24 (4)	7 (4)
O(62)	1847 (4)	2938 (1)	3931 (3)	19 (3)	22 (2)	25 (3)	18 (4)	36 (5)	19 (4)
O(63)	1033 (4)	3501 (1)	4688 (3)	18 (3)	16 (2)	24 (2)	10 (4)	5 (5)	−3 (4)
O(64)	−51 (4)	2706 (1)	3896 (3)	11 (3)	26 (2)	21 (2)	−16 (4)	16 (4)	−5 (4)
O(71)	5038 (4)	4012 (1)	3672 (3)	8 (2)	14 (2)	9 (2)	−5 (4)	6 (4)	−1 (3)
O(72)	3707 (4)	3332 (1)	3704 (3)	17 (3)	20 (2)	18 (2)	2 (4)	25 (4)	1 (4)
O(73)	2720 (4)	3944 (1)	2247 (3)	10 (3)	14 (2)	12 (2)	5 (4)	2 (4)	−2 (3)
O(74)	4199 (4)	3301 (1)	2315 (3)	18 (3)	14 (2)	19 (2)	−2 (4)	25 (4)	−6 (3)
O(81)	5017 (4)	3874 (1)	8709 (3)	6 (2)	14 (2)	13 (2)	−2 (4)	9 (4)	−5 (3)
O(82)	3861 (4)	3117 (1)	8594 (3)	11 (3)	8 (2)	20 (2)	5 (4)	16 (4)	3 (3)
O(83)	3476 (4)	3919 (1)	9191 (3)	10 (3)	14 (2)	12 (2)	3 (4)	12 (4)	3 (3)

Table 1 (cont.)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(84)	2571 (4)	3781 (1)	7261 (3)	8 (3)	17 (2)	10 (2)	−8 (4)	−1 (4)	4 (3)
O(91)	2479 (4)	4592 (2)	362 (3)	9 (3)	41 (3)	27 (3)	2 (5)	15 (5)	−23 (4)
O(92)	4076 (5)	5066 (2)	330 (4)	98 (5)	40 (3)	25 (3)	−69 (7)	60 (7)	−14 (5)
O(93)	4774 (4)	4299 (1)	1399 (3)	18 (3)	23 (2)	15 (2)	19 (4)	8 (4)	−2 (4)
O(94)	4314 (4)	5011 (1)	2099 (3)	12 (3)	18 (2)	12 (2)	−2 (4)	8 (4)	−5 (3)
O(101)	3400 (4)	4363 (1)	5990 (3)	14 (3)	19 (2)	20 (2)	4 (4)	23 (4)	14 (4)
O(102)	2842 (4)	4424 (1)	4084 (3)	18 (3)	15 (2)	15 (2)	−6 (4)	18 (4)	−11 (3)
C(103)	3292 (4)	5193 (1)	5186 (3)	14 (3)	11 (2)	18 (2)	3 (4)	18 (4)	−3 (3)
O(104)	5078 (4)	4605 (1)	5782 (3)	6 (2)	18 (2)	20 (2)	−2 (4)	14 (4)	−1 (4)
O(111)	163 (4)	5607 (1)	6247 (3)	9 (3)	17 (2)	13 (2)	6 (4)	2 (4)	8 (4)
O(112)	1716 (4)	4979 (1)	6369 (3)	25 (3)	19 (2)	19 (2)	−2 (4)	30 (5)	−7 (4)
O(113)	2515 (4)	5665 (1)	7643 (3)	11 (2)	11 (2)	12 (2)	−2 (4)	11 (4)	0 (3)
O(114)	1269 (4)	4986 (1)	7785 (3)	17 (3)	17 (2)	14 (2)	−3 (4)	20 (4)	−1 (3)
O(121)	45 (4)	5568 (1)	1439 (3)	8 (3)	16 (2)	18 (2)	5 (4)	16 (4)	0 (3)
O(122)	1229 (4)	4831 (1)	1540 (3)	8 (3)	11 (2)	20 (2)	1 (4)	9 (4)	−1 (3)
O(123)	1189 (4)	5592 (1)	578 (3)	15 (3)	19 (2)	12 (2)	4 (4)	16 (4)	3 (4)
O(124)	2542 (4)	5551 (1)	2620 (3)	10 (2)	12 (2)	12 (2)	1 (4)	4 (4)	−1 (3)

higher than the crystal symmetry. Moreover, a pseudo-orthorhombic cell with $a' = 15\cdot22$, $b' = 20\cdot71$, $c' = 9\cdot11$ Å has been reported on ASTM card 9-348 and can be derived from the monoclinic cell by taking $a' \simeq c$, $b' \simeq 2a\cos(\beta - 90°)$ and $c' \simeq b/3$. Nevertheless, precession photographs and the intensity data show that the Laue symmetry is $2/m$.

X-ray intensity data for the structural determination were measured and processed as described by Dickens & Bowen (1971). 13 950 reflections were measured by θ–2θ scans up to a maximum $\sin\theta/\lambda$ of $0\cdot705$. These were merged into a unique set of 12 610, of which 11 109 had intensity $I > 2\sigma(I)$ and were considered observed. An absorption correction for a sphere was applied with the equations of Rouse, Cooper, York & Chakera (1970). For α-$Ca_3(PO_4)_2$, $\mu(Mo) = 28\cdot03$ cm^{-1}, the maximum and minimum transmission factors for the approximate spherical sample employed were $0\cdot6852$ and $0\cdot6733$ respectively. Equivalent reflections (1340 pairs) agreed within 4% on average, calculated on F. The X-RAY system of crystallographic computer programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used to calculate quasi-normalized structure factors, E.

Although the structure was solved by direct methods with the program MULTAN (Germain, Main & Woolfson, 1971), the presence of the supercell and the pseudosymmetry caused some difficulties in the initial stages. For example the highest E value with $k \neq 3n$ (i.e. providing details of the real structure rather than of the structure as averaged in the subcell) was No. 311 in a list of E values ordered in decreasing magnitude. The data were divided into two sets, one with $k = 3n$ and the other with $k \neq 3n$, and E values were calculated separately for each set. The resultant E values were then reordered into a single set, which had less than 25% of the reflections with odd h values; difficulties then arose in choosing effective origin-defining reflec-

tions. To make up a more appropriate set, the 270 highest E values were selected from the merged set and the 60 reflections with odd h indices and highest E values were included from the remaining list. With this set of reflections, the MULTAN program proceeded smoothly. An E map calculated from the 'best' combination indicated the positions of most of the Ca and P atoms. The remaining atoms were located in subsequent Fourier syntheses.

The refinement was carried out with a block-diagonal least-squares procedure (4 × 4 for isotropic; 3 × 3 and 6 × 6 for anisotropic thermal parameters). Because of the large amount of data, a randomly selected subset of only 8500 reflections, of which 7002 were observed, was used in the refinements. The quantity minimized in the least-squares calculations was $\Sigma w(F_o - F_c)^2$, where $w = [\sigma(F_o)]^{-2}$ and $\sigma(F_o)$ is based on counting statistics. Only observed reflections were included in all the calculations. The structure was refined to a final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of $0\cdot051$ and $R_w = \Sigma w[(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ of $0\cdot049$. The scattering factors used were those for the neutral atoms taken from International Tables for X-ray Crystallography (1974).

The final atomic parameters along with their estimated standard deviations are listed in Table 1.*

Description of the structure

The structure consists of calcium and phosphate ions arranged in columns along [001]. Both the pseudocell translation and the 2_1 axis are along **b**, giving a pseudo-

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* The observed and calculated structure factors, P—O distances and angles, and O···Ca contacts have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32219 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
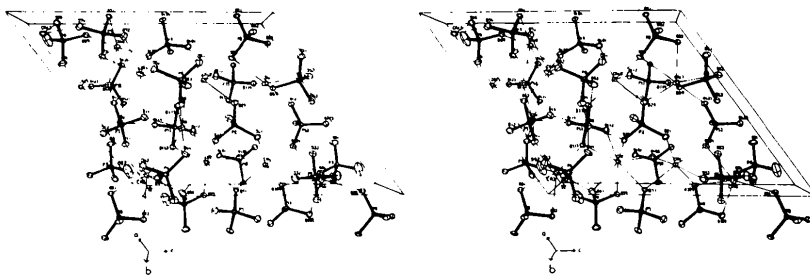
Fig. 1. A stereoscopic illustration viewed along the b axis of the first sixth of the α-Ca₃(PO₄)₂ structure. The origin of the coordinate system is marked by an asterisk.
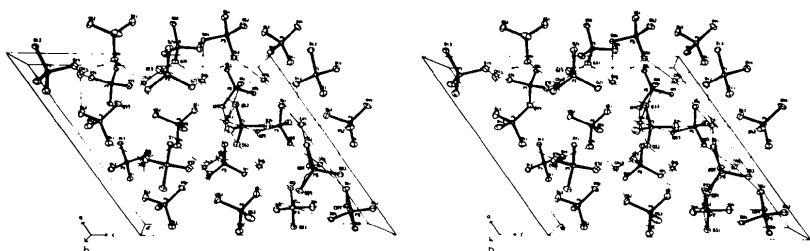

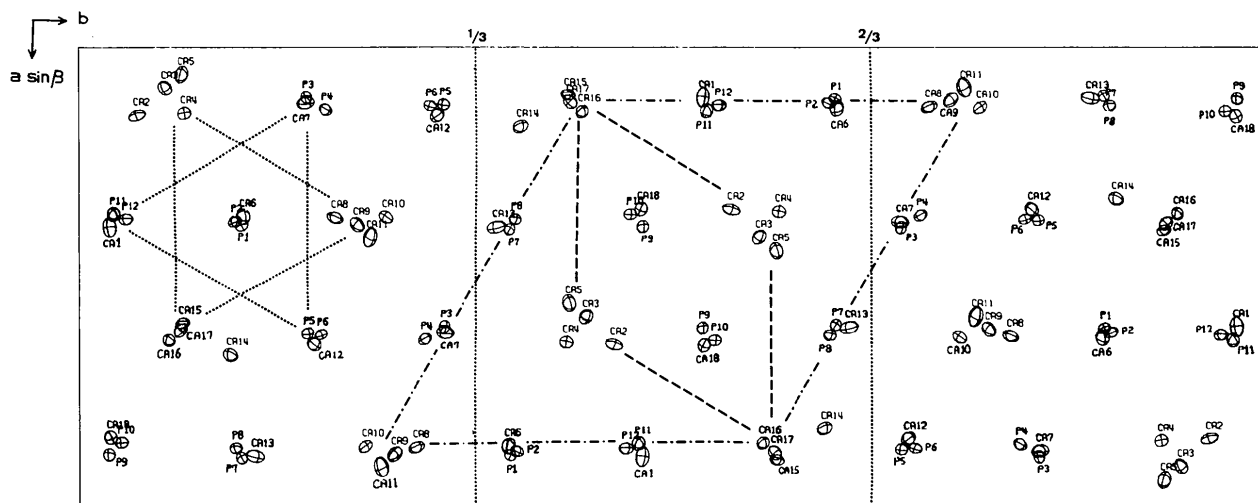Fig. 2. A stereoscopic illustration viewed along the b axis of the second sixth of the α-Ca₃(PO₄)₂ structure.

Fig. 3. A projection of the α-Ca₃(PO₄)₂ structure on the (001) plane. O atoms of the phosphate groups have been omitted for clarity. The dashed lines outline a cell corresponding to that of glaserite, K₃Na(SO₄)₂, while the dashed-dotted lines outline a cell corresponding to that of hydroxyapatite, Ca₅(PO₄)₃OH.

unique slice of b/6 for α-Ca₃(PO₄)₂. The crystal packing is illustrated in Figs. 1 and 2 in sections of ½ along the b axis. These two sections make up the subcell given by ⅓ of the unit-cell translation along the b axis. This pseudorepetition may also be seen in Fig. 3, for example, in the close correspondence of the motifs comprising Ca(3), Ca(2), Ca(4), Ca(5) and Ca(15), Ca(14), Ca(16), Ca(17) at the top of the figure.

The atomic labeling is such that the first one-third of each type of atom is related to the rest by the subcell translations. For example: Ca(1) is related to Ca(7) and Ca(13); P(1) is related to P(5) and P(9). O atoms are numbered so that the digits other than the unit digit refer to the PO₄ group as given by the P atom number, e.g. O(123) refers to O atom No. 3 of PO₄ group No. 12.

There are three independent cation columns in the asymmetric unit (related by the subcell translations) with the repeat units Ca(3)–Ca(2)–Ca(4)–Ca(5), Ca(9)–Ca(8)–Ca(10)–Ca(11) and Ca(15)–Ca(14)–Ca(16)–Ca(17). There are also cation–anion columns, the six independent cation–anion columns being P(12), Ca(1), P(11); P(1), Ca(6), P(2); P(3), Ca(7), P(4); P(6), Ca(12), P(5); P(8), Ca(13), P(7) and P(9), Ca(18), P(10). Each cation–anion column contains a vacant 'site' between anions, e.g. P(1), Ca(6), P(2), □, P(1') where □ denotes the site occupied by a cation in K₃Na(SO₄)₂, the mineral glaserite (Gossner, 1928); this

'site' is hereinafter referred to as a 'vacancy'. The columns are arranged in a pseudohexagonal pattern (Fig. 3). This feature and its relation to glaserite and other calcium phosphates will be discussed later.

Calcium ion environments

Individual Ca $\cdots$ O distances are given in Table 2. Most cation sites show a relatively continuous variation in Ca $\cdots$ O distances; the increments are of the order of 0·1 Å until a large increment (average value is

Table 2. *Calcium–oxygen distances (up to 3·2 Å) in* α-Ca₃(PO₄)₂

Figures in parentheses are standard deviations in the last significant digit.

Ca	O	Symmetry operation	Distance (Å)	Ca	O	Symmetry operation	Distance (Å)	Ca	O	Symmetry operation	Distance (Å)
Ca(1)	O(123)	D(0Ī0)	2·301 (4)	Ca(7)	O(34)	A(000)	2·233 (5)	Ca(13)	O(74)	A(000)	2·287 (4)
	O(114)	D(0Ī1)	2·331 (5)		O(43)	A(001)	2·346 (4)		O(83)	A(00Ī)	2·336 (4)
	O(11)	A(000)	2·435 (5)		O(12)	A(001)	2·420 (6)		O(93)	A(000)	2·342 (4)
	O(91)	D(0Ī0)	2·463 (5)		O(81)	C(Ī00)	2·493 (4)		O(42)	C(000)	2·441 (6)
	O(122)	C(000)	2·528 (6)		O(82)	C(Ī00)	2·497 (6)		O(52)	A(00Ī)	2·464 (6)
	O(121)	C(000)	2·548 (4)		O(53)	A(000)	2·609 (4)		O(41)	C(000)	2·583 (4)
	O(13)	A(000)	2·585 (4)		O(51)	A(000)	2·772 (5)		O(51)	A(00Ī)	2·628 (4)
Ca(2)	O(22)	A(000)	2·273 (4)		O(42)	A(001)	2·850 (5)	Ca(14)	O(102)	A(000)	2·275 (4)
	O(103)	D(0Ī1)	2·330 (4)		O(11)	A(001)	3·013 (4)		O(62)	A(000)	2·357 (4)
	O(93)	C(Ī00)	2·424 (4)	Ca(8)	O(61)	A(000)	2·295 (5)		O(13)	C(Ī00)	2·370 (4)
	O(113)	D(0Ī1)	2·450 (5)		O(21)	A(000)	2·355 (4)		O(72)	A(000)	2·481 (6)
	O(112)	D(0Ī1)	2·491 (6)		O(53)	C(000)	2·450 (4)		O(73)	A(000)	2·581 (6)
	O(71)	C(Ī00)	2·634 (5)		O(33)	A(000)	2·458 (6)		O(14)	C(Ī00)	2·677 (5)
	O(94)	C(Ī00)	2·639 (5)		O(54)	C(000)	2·500 (5)		O(63)	A(000)	2·873 (5)
Ca(3)	O(92)	D(0Ī0)	2·225 (5)		O(31)	C(000)	2·577 (5)	Ca(15)	O(73)	A(000)	2·294 (4)
	O(113)	D(0Ī1)	2·325 (4)		O(23)	A(000)	2·727 (5)		O(52)	A(00Ī)	2·350 (5)
	O(42)	A(000)	2·405 (4)	Ca(9)	O(51)	A(000)	2·297 (6)		O(91)	A(000)	2·359 (6)
	O(11)	A(000)	2·431 (6)		O(53)	C(000)	2·321 (6)		O(13)	C(Ī00)	2·373 (6)
	O(93)	C(Ī00)	2·491 (6)		O(12)	A(001)	2·324 (5)		O(122)	A(000)	2·405 (4)
	O(81)	C(Ī0Ī)	2·500 (4)		O(33)	A(000)	2·416 (4)		O(123)	B(010)	2·429 (5)
	O(83)	C(Ī0Ī)	2·680 (5)		O(82)	A(000)	2·423 (4)		O(121)	B(010)	2·536 (4)
	O(92)	C(Ī00)	3·073 (7)		O(41)	C(001)	2·459 (4)	Ca(16)	O(112)	A(000)	2·222 (4)
Ca(4)	O(32)	A(000)	2·279 (5)	Ca(10)	O(62)	A(000)	2·261 (6)		O(101)	A(000)	2·321 (6)
	O(21)	A(000)	2·289 (4)		O(72)	A(000)	2·279 (4)		O(111)	B(011)	2·345 (4)
	O(104)	C(Ī00)	2·354 (5)		O(64)	C(000)	2·288 (6)		O(63)	A(000)	2·355 (4)
	O(71)	C(Ī00)	2·377 (4)		O(23)	A(000)	2·392 (4)		O(84)	A(000)	2·386 (4)
	O(103)	D(0Ī1)	2·393 (4)		O(44)	A(000)	2·416 (4)		O(24)	C(Ī00)	2·410 (6)
	O(124)	D(0Ī1)	2·399 (4)		O(31)	C(000)	2·422 (4)	Ca(17)	O(114)	A(000)	2·325 (4)
Ca(5)	O(94)	D(0Ī1)	2·415 (4)	Ca(11)	O(41)	C(000)	2·322 (5)		O(24)	C(Ī00)	2·328 (4)
	O(101)	C(Ī00)	2·429 (5)		O(74)	A(000)	2·333 (4)		O(121)	B(011)	2·330 (6)
	O(34)	A(000)	2·458 (4)		O(64)	C(000)	2·344 (4)		O(54)	A(000)	2·450 (4)
	O(81)	C(Ī00)	2·478 (5)		O(14)	A(000)	2·356 (4)		O(83)	A(000)	2·466 (5)
	O(32)	A(000)	2·591 (5)		O(43)	A(000)	2·387 (6)		O(84)	A(000)	2·800 (5)
	O(104)	C(Ī00)	2·602 (4)		O(12)	A(000)	2·907 (4)		O(52)	A(000)	2·882 (4)
	O(124)	D(0Ī1)	2·656 (6)		O(62)	C(000)	3·107 (5)		O(91)	A(001)	3·177 (4)
Ca(6)	O(14)	A(000)	2·314 (5)	Ca(12)	O(54)	A(000)	2·348 (5)	Ca(18)	O(102)	A(000)	2·320 (5)
	O(44)	A(000)	2·344 (5)		O(61)	A(000)	2·357 (5)		O(94)	A(000)	2·380 (5)
	O(22)	A(000)	2·352 (5)		O(84)	A(000)	2·363 (4)		O(73)	A(000)	2·407 (4)
	O(113)	D(0Ī1)	2·393 (4)		O(23)	C(Ī00)	2·437 (5)		O(104)	B(111)	2·410 (4)
	O(111)	D(0Ī1)	2·452 (4)		O(31)	A(000)	2·478 (5)		O(124)	A(000)	2·441 (4)
	O(63)	C(000)	2·483 (5)		O(33)	A(000)	2·510 (4)		O(122)	A(000)	2·464 (5)
	O(64)	C(000)	2·806 (5)		O(82)	A(000)	2·682 (5)		O(71)	A(000)	2·546 (5)
	O(23)	A(000)	3·008 (4)		O(24)	C(Ī00)	3·060 (5)				
	O(42)	A(000)	3·120 (5)		O(63)	A(000)	3·129 (5)				

Symmetry code: (*A*) *x,y,z*; (*B*) −*x*,−*y*,−*z*; (*C*) ½ + *x*,½ − *y*,*z*; (*D*) ½ − *x*,½ + *y*,−*z*. Quantities in parentheses are unit-cell translations added to positions generated by application of *A*, *B*, etc. to atomic positions given in Table 1.

Table 3. *Summary of Ca ion environments in* α-Ca₃(PO₄)₂

For a given range of Ca · · · O distances the numbers of PO₄ edges and corners making up the
coordination are given in the last two columns.

	Coordination number, geometry		Range of Ca · · · O distances (Å)	Number of PO₄ edges	Number of PO₄ corners
Ca(1)	7	a*	2·301–2·585	2	3
Ca(2)	7	c	2·273–2·639	2	3
Ca(3)	7	a	2·225–2·680	1	5
Ca(4)	6	d	2·279–2·399	–	6
Ca(5)	7	d	2·415–2·656	2	3
Ca(6)	8	a	2·314–3·008	3	2
Ca(7)	9	b	2·233–3·013	4	1
Ca(8)	7	c	2·295–2·727	2	3
Ca(9)	6	d	2·297–2·459	–	6
Ca(10)	6	d	2·261–2·422	–	6
Ca(11)	5	e	2·322–2·387	–	5
Ca(12)	7	a	2·348–2·682	2	3
Ca(13)	7	a	2·287–2·628	2	3
Ca(14)	7	c	2·275–2·873	3	1
Ca(15)	7	a	2·294–2·536	1	5
Ca(16)	6	d	2·222–2·410	–	6
Ca(17)	5	e	2·325–2·466	–	5
Ca(18)	7	a	2·320–2·546	2	3

* a Pentagonal bipyramid, b hexagonal bipyramid, c irregular polyhedron, d distorted octa-
hedron, e trigonal bipyramid.

~0·6 Å) occurs usually at a Ca · · · O distance of 2·7–2·8 Å. Table 2 gives the longer distances only for those cases in which the large increment is 0·5 Å or less. We interpret this gap, usually occurring after seven contacts, as indicating the completion of the primary coordination of Ca. Thus, coordination numbers and geometries can be assigned to all cations, and Table 3 summarizes the primary coordination of the Ca ions.

The structure is unusual in that the Ca ions exhibit a wide range of coordination numbers and geometries. All the Ca ions in the cation–anion columns have at least seven O contacts and the most frequently observed geometry corresponds to pentagonal bipyramids with the equatorial plane approximately perpendicular to the column. Ca ions Nos. 1, 6, 7, 12, 13, and 18 are in the cation–anion columns and, as Table 3 shows, all geometries involve coordination of a PO₄ edge. In all cases these PO₄ edges lie in the equatorial plane. Ca(7) is perhaps the most unusual in that the apparent coordination is a hexagonal bipyramid with three shared PO₄ edges in the equatorial plane.

The Ca ions in the cation–cation columns have coordination numbers of 5 to 7, the most frequently observed configuration is seven O atoms arranged in an irregular polyhedron. We note that the coordination around Ca(3) and Ca(15) can be represented by nearly ideal pentagonal bipyramids with one shared PO₄ edge in the equatorial plane. The five Ca · · · O bonds of Ca(11) and Ca(17) are all from different PO₄ corners and correspond to nearly ideal trigonal bipyramidal configuration.

The PO₄ groups and their environments

The P–O distances vary from 1·516 to 1·568 Å [with one exception, P(9)–O(92) = 1·486(6) Å, see *Discussion*] with a mean value of 1·538(13) Å. (The standard deviation was estimated from the spread of the individual values.) This is in excellent agreement with the value of 1·539 Å obtained by Baur & Khan (1970) by averaging a large number of PO₄ groups in various forms.

It is difficult to draw any definite conclusion regarding the correlation of P–O bond lengths with the number of O · · · Ca contacts,* although a trend exists. One possible reason is that the coordination numbers of the O atoms are not widely different (mostly only two or three).

O(92) has the most unusual geometry in that it has only one normal O · · · Ca contact [O(92) · · · Ca(3) = 2·225 Å, the angle P(9)–O(92)–Ca(3) is 160°] approximately in the same direction as the P(9)–O(92) bond. All other O(92) · · · Ca distances are greater than 3·0 Å. O(92) has one apparent r.m.s. amplitude of vibration (0·33 Å) that is nearly perpendicular to the plane of Ca(3)–O(92)–P(9) (see the left-hand side of Fig. 1). The magnitude of this apparent amplitude is approximately twice the size of the other two r.m.s. amplitudes of O(92) and the observation that no other Ca · · · O(92) contacts shorter than 3·0 Å exist suggests that O(92) may be disordered over positions separated

* See previous footnote, p. 1327.

by 0·1 Å or less. This could result from a slight disorder of the PO_4 group about axes perpendicular to the P(9)—O(92) bond that are located closer to the P and remaining O atoms than to O(92). Hence, O(92) would be most affected. The P(9)—O(92) distance of 1·486 (6) Å is the shortest P—O bond in the compound but is to some extent an artifact resulting from an incomplete description of the behavior of O(92) by the atomic parameters obtained from the refinement process.

The O—P—O angles vary from 104·1 to 115·2°. As is usual, O—P—O angles less than the ideal tetrahedral angle of 109·5° are all associated with PO_4 edge coordination to Ca.

Considering all the Ca · · · O distances less than 3·0 Å, we obtain PO_4 coordinations ranging from 8 to 12. All O atoms except one, O(92), are bonded to at least two Ca ions. The maximum number of edge coordinations is only 4 as in the case of other phosphates. In α-$Ca_3(PO_4)_2$ there is no example of PO_4 face coordination as in the β-$Ca_3(PO_4)_2$ phase (Dickens et al., 1974) or SO_4 face coordination as in $K_3Na(SO_4)_2$ (Gossner, 1928), even though α-$Ca_3(PO_4)_2$ is nominally an analog of the latter.

Most of the O · · · O distances between different phosphate groups are 2·7 Å or more although two are shorter: O(104)· · ·O(124) and O(23)· · ·O(31), 2·586 and 2·622 Å respectively. The coordination of O(104) and O(124) is somewhat unusual in that both atoms are bound to the same three cations, Ca(4), Ca(5), Ca(18), all Ca · · · O distances being less than 2·66 Å. O(23) and O(31) are involved in a similar situation, the maximum Ca · · · O distance being 2·727 Å. The presence of six Ca · · · O interactions has evidently balanced the increased repulsive energy resulting from the shorter O · · · O separations.

Discussion

Columnar structures

The Ca and phosphate ions are packed in two kinds of columns along [001], one containing only cations and the other both cations and anions. Each cation column is surrounded by six cation–anion columns and

each cation–anion column by alternate cation–cation and cation–anion columns. The arrangement of these columns in a pseudohexagonal form is quite similar to that of glaserite and hence α-$Ca_3(PO_4)_2$ was correctly classified under the glaserite-type phosphates (Dickens & Brown, 1972). The dashed line in Fig. 3 outlines a cell corresponding to that of glaserite.

The cation–cation columns are quite distorted from linearity (Fig. 4). Cation displacements are generally in the direction of the cation 'vacancy' in the surrounding cation–anion columns. The detailed environments of the Ca ions in the cation columns are quite different from those of the cations in glaserite (Gossner, 1928), as expected from the different sizes of the ions in the two structures and the 'vacancies' in α-$Ca_3(PO_4)_2$. Nonetheless, there are close similarities in the cation–anion columns in both compounds. In glaserite, the K ions in the cation–anion column have ten O neighbors comprising one face, three shared edges and an apex of SO_4 ions. This coordination may be described as hexagonal bipyramidal with the three shared edges in the equatorial plane and the face occupying one of the axial positions. The Ca ions in the cation–anion columns in α-$Ca_3(PO_4)_2$ have pentagonal or hexagonal bipyramidal configurations with two or three shared PO_4 edges, respectively, in the equatorial (ac) plane. The maximum coordination of nine O atoms may still be depicted as hexagonal bipyramidal with a PO_4 edge at one of the axial positions replacing a face in glaserite.

Fig. 3 shows that a given cation–anion column is surrounded by three cation–cation and three cation–anion columns (denoted by triangles). The dashed-dotted lines outline a cell related to that of hydroxyapatite, in which the OH columns would 'replace' the cation–cation columns at the cell corners. By analogy, the Ca—PO_4 positions in hydroxyapatite may be considered as very distorted cation–anion 'columns' and each 'column' is surrounded by three cation–anion 'columns' as in α-$Ca_3(PO_4)_2$ and by two cation–cation and one OH column.

The spacing of the PO_4 groups along the columns varies as expected. The P—P distance for the configuration PO_4· · ·Ca· · ·PO_4 is 6·7 Å while that for the configuration PO_4· · ·□· · ·PO_4 is 8·5 Å. Variable spacing of the PO_4 groups along the cation–anion
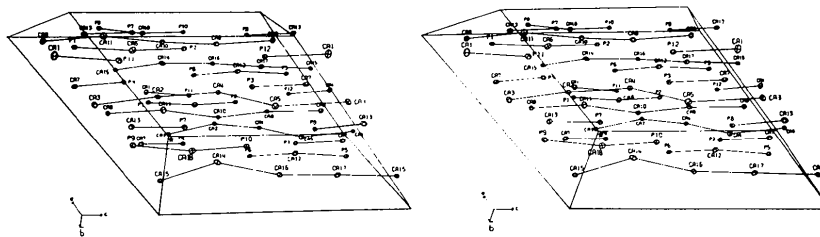

Fig. 4. A stereoscopic view of one-half $(0 \leq y \leq \frac{1}{2})$ of the α-$Ca_3(PO_4)_2$ structure showing the cation–cation and cation–anion columns parallel to [001]. O atoms are omitted for clarity.

columns is also observed in $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ (Dickens & Brown, 1971a). In view of the close relation of $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ to glaserite and α-Ca$_3$(PO$_4$)$_2$ it is not clear why Ca ions do not occupy cation sites in the cation–anion columns in Ca_7Mg_9-$(Ca,Mg)_2(PO_4)_{12}$.

Relation of α-Ca$_3$(PO$_4$)$_2$ to other phases

For pure $Ca_3(PO_4)_2$, the α form is the phase stable in the range 1120–1470°C. Below 1120°C, the β form is the stable phase and the α form is only metastable. Above 1470°C the $\bar{\alpha}$ form (Nurse, Welch & Gutt, 1959) is stable. An examination of the differences in the crystal structures of the α and β forms provides some insight into their relative stabilities. The structure of the $\bar{\alpha}$ form is not known. A major difference between α-Ca$_3$(PO$_4$)$_2$ and β-Ca$_3$(PO$_4$)$_2$ is that there are no cation–cation columns in the β form. Both structures contain 'vacancies', but the vacancies differ in type. Since α-Ca$_3$(PO$_4$)$_2$ does not have a 2:1 cation–anion ratio its emulation of the glaserite structure requires cation 'vacancies'. Vacancies occur in the β form because it has the wrong cation–anion radius ratio to crystallize in the $Ba_3(VO_4)_2$ or $Ba_3(PO_4)_2$ arrangement without considerable distortion (Dickens et al., 1974).

α-Ca$_3$(PO$_4$)$_2$ has a 'looser' structure than the β form, the volumes per formula unit being 180 and 168 Å respectively. Thus, the α form has a higher internal energy (arising from less overall bonding because the structure is 'looser'). Its being a high-temperature phase is consistent, therefore, with thermodynamic considerations. Although the configurational entropy of the α form appears to be lower than that for the β form, because the former is a crystallographically ordered structure [i.e. all ions have full occupancy while β-Ca$_3$(PO$_4$)$_2$ contains cation sites with half occupancy], its effect is not large enough to make the α form more stable than the β form at lower temperatures.

The phase diagram of the $Mg_3(PO_4)_2$–$Ca_3(PO_4)_2$ system as given by Ando (1957) implies the possibility of incorporating Mg ions into the α phase. A comparison of the crystal structures of α-Ca$_3$(PO$_4$)$_2$ and $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ reveals that any Mg taken up by α-Ca$_3$(PO$_4$)$_2$ would substitute at the cation sites in the cation–anion columns. Mg substitution into the cation–anion columns of β-Ca$_3$(PO$_4$)$_2$ has been shown to occur (Dickens & Schroeder, 1976). However, addition of Mg tends to stabilize the β-Ca$_3$(PO$_4$)$_2$ structure well into the α-Ca$_3$(PO$_4$)$_2$ stability range. This indicates that the glaserite-type structure is not stabilized by Mg until sufficient is present for cooperative effects to occur. The phase diagram of the $Mg_3(PO_4)_2$–$Ca_3(PO_4)_2$ system shows that at that point the formation of $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ is favored.

The system Ca_2SiO_4–$Ca_3(PO_4)_2$ forms a continuous series of solid solutions at higher temperatures, with the end members designated as α-Ca$_2$SiO$_4$ and $\bar{\alpha}$-Ca$_3$-(PO$_4$)$_2$ (Nurse et al., 1959). The structures of α-Ca$_2$SiO$_4$ (Trömel & Moller, 1951; Van Valkenburg & McMurdie, 1947) and one intermediate phase, silicocarnotite, $Ca_5(SiO_4)(PO_4)_2$ (Dickens & Brown, 1971b), are known to be related to that of glaserite. The relation of $\bar{\alpha}$-Ca$_3$(PO$_4$)$_2$ to the $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ structure and the latter in turn to the glaserite structure has been discussed by Dickens & Brown (1971a). The present study of α-Ca$_3$(PO$_4$)$_2$ confirms that it is indeed closely related to $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ and glaserite, and thus supports the idea that the structures of $\bar{\alpha}$-Ca$_3$(PO$_4$)$_2$ and α-Ca$_3$(PO$_4$)$_2$ must be quite similar. This, in turn, lends additional support to the view that the Ca_2SiO_4–$Ca_3(PO_4)_2$ solid solution existing at high temperatures has itself a glaserite-type structure.

References

ANDO, J. (1957). Bull. Chem. Soc. Japan, 31, 196–201.
BAUR, W. H. & KHAN, A. A. (1970). Acta Cryst. 17, 1195–1207.
DICKENS, B. & BOWEN, J. S. (1971). Acta Cryst. B27, 2247–2255.
DICKENS, B. & BROWN, W. E. (1971a). Miner. Petrogr. Mitt. 16, 79–104.
DICKENS, B. & BROWN, W. E. (1971b). Miner. Petrogr. Mitt. 16, 1–27.
DICKENS, B. & BROWN, W. E. (1972). Acta Cryst. B28, 3056–3065.
DICKENS, B. & SCHROEDER, L. W. (1976). Unpublished results.
DICKENS, B., SCHROEDER, L. W. & BROWN, W. E. (1974). J. Solid State Chem. 10, 232–248.
FIX, W., HEYMANN, H. & HEINKE, R. (1969). J. Amer. Ceram. Soc. 52, 346–347.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.
GOSSNER, B. (1928). Neues Jb. Miner. Mh. 57A, 89–116.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 72. Birmingham: Kynoch Press.
LENHERT, P. G. (1975). J. Appl. Cryst. 8, 568–570.
MACKAY, A. L. (1953). Acta Cryst. 6, 743–744.
NURSE, R. W., WELCH, J. H. & GUTT, W. (1959). J. Chem. Soc. pp. 1077–1083.
ROUSE, K. D., COOPER, M. J., YORK, E. J. & CHAKERA, A. (1970). Acta Cryst. A26, 682–691.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY system – version of June 1972. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

TRÖMEL, G. & MOLLER, H. (1951). Silic. Ind. 16, 300–301.
VAN VALKENBURG, A. JR & McMURDIE, H. F. (1947). J. Res. Natl. Bur. Stand. 38, 415–418.

Disodium Zincosilicate, Na₂ZnSi₃O₈

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The structure of synthetic Na₂ZnSi₃O₈ [monoclinic $P2_1$; $a = 6.660$ (6), $b = 8.629$ (6), $c = 6.411$ (8) Å, $\beta = 103.70$ (7)°; $Z = 2$, $D_m = 2.94$, $D_x = 2.95$ g cm⁻³] has been refined to $R = 0.033$ for 1077 independent reflexions from Mo $K\alpha$ radiation. Corner-sharing [SiO₄] tetrahedra form chains with three tetrahedra in the identity period of the chain. These Dreierketten form tetrahedral layers $_\infty^2[Si_3O_8]$. Together with [ZnO₄] tetrahedra the [SiO₄] groups constitute a framework resembling that of paracelsian, BaAl₂Si₂O₈. The sodium ions occupy irregular cavities: Na(1) is seven-coordinated (mean bond length 2.718 Å) with two additional oxygens at 3.4 Å; Na(2) may be regarded as seven or eight-coordinated (mean bond lengths 2.529 or 2.600 Å). The structure of Na₂ZnSi₃O₈ shows remarkable similarities to the sodic plagioclase feldspars, (Na,Ca)-(Al,Si)₄O₈, and other framework aluminosilicates. The formula

$$Si{-}O = 1.571 - 0.068\,\Delta Zn_{br} + 0.067[\Sigma\,1/(Na{-}O)^2] - 0.025/\cos(T{-}O{-}T),$$

whose constants were derived by multiple linear regression analysis for feldspars and modified to account for the substitution of Zn for Al, gives an excellent estimation of the 12 individual Si–O bond lengths in this compound.

Introduction

Disodium zincosilicate, Na₂ZnSi₃O₈, was first described by Litvin, Mel'nikov, Ilyukhin & Nikitin (1965). In the present study single crystals were synthesized by heating a mixture of 5.0 g gel of composition Na₂O . ZnO . 3SiO₂ . nH₂O [prepared by the method of Hamilton & Henderson (1968)] and 1.4 g pure SiO₂ (Riedel–de Haën) in sealed silver tubes for several days at 1 kbar and 450°C. Chemical, electron microprobe, and thermogravimetric analyses and IR spectra reveal a partial replacement of Na by H in agreement with the formula Na₂₋ₓHₓZnSi₃O₈ with $x \le 0.25$.

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The cell dimensions were obtained by a least-squares analysis of 19 peaks from a Guinier powder photograph (Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å). Intensities of 1077 independent reflexions from a crystal of dimensions 0.08 × 0.17 × 0.22 mm were collected from θ–2θ scans on a Siemens four-circle diffractometer with Mo $K\alpha$ radiation ($\mu = 40.3$ cm⁻¹). Lorentz, polarization and absorption corrections were applied. From systematic absences of $0k0$ reflexions with $k = 2n + 1$ and an $N(z)$ test (Howells, Phillips & Rogers, 1950) the space group $P2_1$ was deduced.

Approximate atomic coordinates were determined from a three-dimensional Patterson synthesis and were refined by least-squares and Fourier methods with scattering factors for half-ionized atoms. For the final coordinates in Table 1 the unweighted residual, using all