$Ca_3Al_2P_2Si_2O_{15}$: new data and discussion

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Abstract

The formula of $Ca_3Al_2P_2Si_2O_{15}$ is confirmed by electron microprobe anlaysis and synthesis. Electron diffraction discloses that the crystals are monoclinic, Pa or $P2/a$. Powder X-ray data (80 reflections, 53 indexed) are presented. The refined cell dimensions are $a = 24.212 \pm 0.008$Å, $b = 5.110 \pm 0.003$Å, $c = 10.698 \pm 0.003$Å; $\beta = 107.30 \pm 0.03°$.

During the course of studies of the reaction products obtained by heating mixtures consisting mainly of apatite, Na_2CO_3 and SiO_2, (Gunawardane and Glasser, 1979) we noted the possibility that feldspar might be present as an impurity and made a literature survey of compound formation in several relevant systems including $CaO–Al_2O_3–P_2O_5–SiO_2$. Simpson (1979) recently described the synthesis of a quaternary phase, $Ca_3Al_2P_2Si_2O_{15}$, in this system and presented data for its characterization. We confirm the existence of a phase at this composition but disagree with some of his data and its interpretation.

Experiments were made using basically the same methods and techniques as described by Simpson. Starting materials included chemically-pure grades of $CaCO_3$, Al_2O_3, $CaHPO_4$ and finely-divided quartz containing 0.08% material which is not volatile with HF. It was convenient to prepare anorthite, CAS_2, and C_2P[1] by firing weighed batches in Pt crucibles in air at ~1300°C and 900°C respectively. The firings were repeated until a homogeneous product was obtained, as judged by optical microscopy and X-ray powder diffraction. C_3APS_2 was readily made by direct reaction of CAS_2 and C_2P in equimolar quantities (~52 wt.% CAS_2). Preparations were also made containing 40 and 60 wt.% CAS_2.

The products obtained by heating were examined by using a petrographic microscope; X-ray powder diffraction with a Hägg-Guinier focussing camera; CORA, an electron microscope equipped for chemical analysis in the transmission mode with an energy dispersive attachment; and by electron diffrac-

tion using an AEI instrument equipped with a double-tilt stage developed by Gard (1976).

Preparations at the C_3APS_2 ratio appeared microscopically homogeneous at subsolidus temperatures. At 1325°C, the product consisted of small, anhedral to platy crystals of low birefringence, wavy or undulose extinction and a mean refractive index close to 1.57. Traces of glass were also found. At 1355°C, incongruent melting had occurred and the product consisted of C_3P and glass. Preparations containing 40 and 60 wt.% CAS_2 contained notably less C_3APS_2, and at 1260°C consistently contained C_3APS_2 and glass together with an excess of either C_3P or CAS_2, respectively. The crystals obtained from the C_3APS_2 batch were too small for single-crystal X-ray diffraction, and were analyzed by electron optical methods. Table 1 shows the analyses obtained from 20 crystals in the C_3APS_2 batch. The analytical results corroborate the formula for this phase proposed by Simpson. The glass produced by partial incongruent melting of the C_3APS_2 composition had the approximate ratio (based on 10 analyses) $C_{1.00}A_{1.33}P_{0.92}S_{2.78}$, and is thus enriched in Al_2O_3 and SiO_2 components as would be expected because incongruent melting to yield C_3P had occurred.

Electron diffraction measurements were made using Al as an internal standard. Projections of the reciprocal lattice were constructed from zones recorded while tilting crystals about various rows of spots, particularly those spaced at $(11.58$Å$)^{-1}$ and $(5.12$Å$)^{-1}$. Figure 1 shows four examples of these zones. Rotation around the $(5.12$Å$)^{-1}$ axis gave zones with spots on orthogonal meshes, including the zones shown in Figs. 1(c) and (d). The sharp spots on all the zones recorded could be indexed on a primitive monoclinic pseudo-cell with $a = 12.14$,

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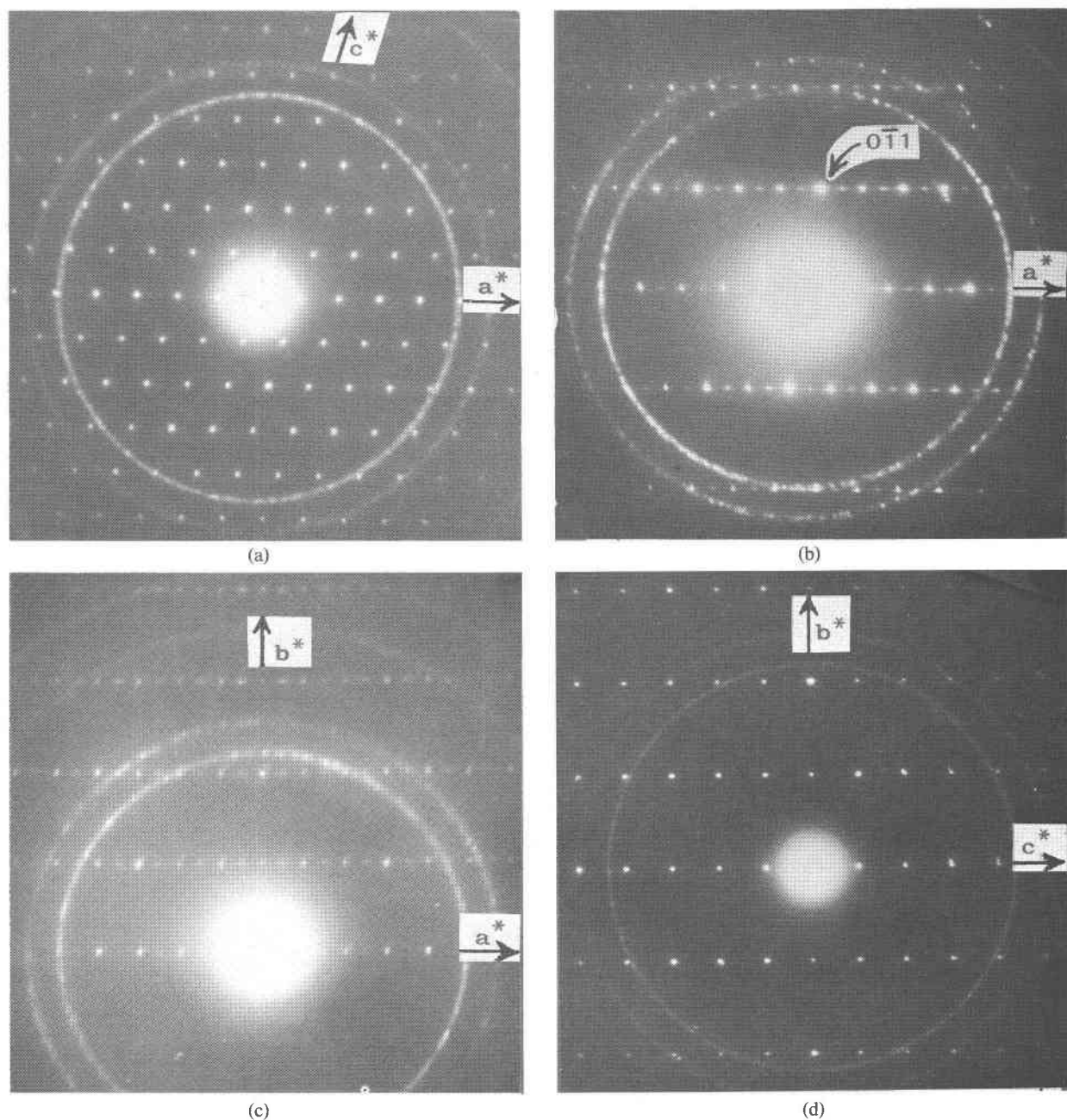[1] Shorthand nomenclature: C = CaO, A = Al_2O_3, S = SiO_2 and P = P_2O_5.

Fig. 1. Electron diffraction patterns of $Ca_3Al_2P_2Si_2O_{15}$, with the following zone axes parallel to the electron beam: (a) [010], (b) [011], (c) [001], (d) [100]. Note the elongated odd-h spots in (b) and (c). The rings are from Al ($d_{111} = 2.338$Å, $d_{020} = 2.025$Å).

$b = 5.12$, $c = 10.72$Å, $\beta = 107.3°$, with no extinctions. From the [010] orientation giving the distorted hexagonal zone shown in Figure 1(a), however, tilting about the a^*-axis gives zones (*e.g.*, Figs. 1(b) and (c)) in which elongated weaker spots interspace the sharp spots in all rows parallel to a^* (odd $h00$ spots are extinctions, but these spots are present due to multiple diffraction). This shows that the true

unit cell is also primitive monoclinic, with $a = 24.28$, $b = 5.12$, $c = 10.72$Å, $\beta = 107.3°$, with some stacking disorder. Absence of the weak spots with h odd from the $h0l$ zone (Fig. 1(a)) indicates an a-glide normal to b, corresponding to possible space groups Pa (No. 7) or $P2/a$ (No. 13).

The indexing of the powder pattern was initiated with the approximate pseudocell dimensions ob-

Table 1. Transmission electron microscope analyses of C_3APS_2 crystals

Cation	Abundance [†]	S.D. (σ) [‡]	SE [*]
P	0.68	0.028	0.006
Si	0.68	0.035	0.008
Al	0.65	0.053	0.012

[†] Abundance relative to Ca = 1.00
[‡] S.D. = Standard deviation
[*] SE = Standard error, $\dfrac{\sigma}{\sqrt{n-1}}$

Table 2. Powder X-ray data for $Ca_3Al_2P_2Si_2O_{15}$ [†]

hkl	d_{calc}(Å)	d_{obs}(Å)	I	hkl	d_{calc}(Å)	d_{obs}(Å)	I
200	11.56	11.57	81	810	2.5152	2.5121	19
001	10.21	10.23	10	612	2.3957		
$\bar{2}01$	9.12	9.15	16	$\bar{1}0\cdot02$	2.3898	2.3936	18
201	6.725	6.729	5	221	2.3883		
$\bar{4}01$	5.827	5.831*	14	$\bar{2}14$	2.3636	2.3644	5
400	5.779	5.780*	10	420	2.3367		
$\bar{2}02$	5.289	5.293	20	$\bar{8}13$	2.3320	2.3313	6
010	5.110	5.114	20	413	2.3266		
002	5.107			$\bar{1}0\cdot00$	2.3116	2.3091	3
011	4.570	4.568	81	811	2.3075		
$\bar{4}02$	4.558			022	2.2849		
401	4.490	4.496*	30	014	2.2841	2.2831	12
$\bar{2}11$	4.457	4.460*	12	$\bar{8}04$	2.2790		
202	4.229	4.233	17	802	2.2450		
$\bar{6}01$	4.021	4.026	24	$\bar{6}14$	2.2440	2.2410	6
600	3.853			603	2.2418		
$\bar{4}11$	3.842	3.841	22	421	2.2205	2.2174	7
410	3.828			$\bar{1}0\cdot11$	2.1830	2.1776	4
$\bar{2}12$	3.675	3.675	11	$\bar{6}21$	2.1564	2.1545	4
012	3.612	3.613	22	$\bar{4}05$	2.1359		
$\bar{2}03$	3.566	3.563	5	214	2.1354	2.1307	12
$\bar{4}03$	3.410			620	2.1292		
003	3.405	3.405	16	$\bar{6}22$	2.0911	2.0891	8
$\bar{4}12$	3.401			423	2.0447		
402	3.3627	3.3638	24	023	2.0435	2.0427	24
212	3.2581	3.2596	18	005	2.0428		
$\bar{6}11$	3.1600	3.1858	24	$\bar{1}0\cdot04$	2.0423		
610	3.0763	3.0759	44	$\bar{1}2\cdot02$	2.0106	2.0072	19
203	3.0307	3.0306	21	$\bar{1}2\cdot01$	2.0047		
$\bar{8}01$	3.0261			414	1.9540		
$\bar{6}12$	2.9645	2.9637	51	223	1.9532	1.9522	19
802	2.9135	2.9105	24	821	1.9522		
800	2.8895	2.8880	36	$\bar{8}22$	1.9209		
$\bar{4}13$	2.8366	2.8344	100	205	1.9163	1.9186	29
013	2.8333			820	1.9140		
611	2.7696	2.7683	5	015	1.8968	1.8949	10
602	2.7122	2.7120	5	$\bar{1}0\cdot14$	1.8964		
$\bar{2}04$	2.6659	2.6647	3	604	1.8858	1.8798	1
$\bar{8}03$	2.6209			622	1.8597	1.8585	7
403	2.6132	2.6143	5	$\bar{4}24$	1.8374		
$\bar{6}13$	2.6118			$\bar{8}15$	1.8351	1.8329	7
801	2.5863	2.5862	19[‡]	$\bar{8}23$	1.8294		
020	2.5548	2.5534	52	423	1.8268		
004	2.5535						

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(continuation of unindexed data)
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d_{obs} (Å)	I	d_{obs} (Å)	I	d_{obs} (Å)	I	d_{obs} (Å)	I
1.8206	18	1.6306	4	1.5030	4	1.3974	5
1.8064	21	1.6151	16	1.4916	3	1.3862	4
1.7939	18	1.5946	13	1.4817	3	1.3644	9
1.7820	12	1.5776	3	1.4677	4	1.3395	8
1.7666	7	1.5685	5	1.4607	4	1.3245	3
1.7231	10	1.5556	3	1.4393	8	1.3000	7
1.6824	5	1.5417	16	1.4320	8	1.2893	7
1.6685	10	1.5212	12	1.4149	3	1.2767	8
1.6483	7	1.5109	4	1.4055	4	1.2587	4

Refined pseudo cell dimensions (with e.s.d's) are: $a = 24.212 \pm 0.008$, $b = 5.110 \pm 0.003$, $c = 10.698 \pm 0.003$ (Å), $\beta = 107.30° \pm 0.03°$.

* Denote pairs of reflections resolved using a travelling vernier microscope.

[†] Four reflections, which are believed to be due to an impurity, were also observed: their d spacings and intensities, relative to the strongest reflection of C_3APS_2 at $d = 2.8344$ Å are

d (Å)	I
8.098	4
6.473	6
3.449	7
2.740	4

[‡] This reflection may contain a contribution from a tricalcium phosphate solid solution.

tained from electron diffraction and a powder pattern whose d spacings were read with an optical microdensitometer and corrected relative to a Si internal standard ($a = 3.1355$Å). A few closely-spaced pairs of reflections were resolved with the aid of a travelling vernier microscope. As the indexing was extended to include progressively more reflections and the cell parameters refined by successive least-squares cycles, it became apparent that even the purest preparation contained a small amount of an unidentified phase. Powder reflections from this phase were excluded from the refinement. The reflections thus excluded, relative to the strongest reflection of C_3APS_2 at 2.83Å corresponding to 100, had intensity ≤ 7: hence we are unable to rank them accurately in order of intensity, but reflections thus excluded were consistently observed at $d = 8.10, 6.47, 3.45$ and 2.74(Å). These reflections do not match the patterns of the starting materials (CAS_2, C_2P) or of likely impurities, *e.g.*, C_3P. The indexed pattern, containing only reflections due to C_3APS_2, is shown in Table 2.

The density of the purest C_3APS_2 preparation, determined using an air-comparison pycnometer, was 2.795 ± 0.003 g cm^{-3}. The volume of the unit cell, determined using the refined pseudocell parameters, is 631.46Å^3. Assuming that the empirical formula C_3APS_2 is correct, the number of formula units per cell, Z, = 1.998 (or 2).

The occurrence, composition, optical properties and melting point determined in the course of the present study are in reasonable agreement with those reported by Simpson. Thus it would appear that the same phase has been obtained in both studies. The agreement between the two sets of powder data is less satisfactory. For example, not only do the two sets of d spacings differ by a variable and often significant extent, but Simpson also finds reflections occurring at d values which are absent from our pattern, *e.g.*, at 7.74 and 6.23Å. It would appear that the triclinic cell was generated using a trial-and-error method, unassisted by single

crystal measurements or even optical measurements indicative of crystal symmetry. The indexing on the basis of a large triclinic cell is therefore highly suspect as it appears (1) that not all the reflections included in the refinement belong to C_3APS_2, and (2) that some reflections belonging to C_3APS_2 went unobserved and were not included.

It is not practicable to guess the structure type from the knowledge of the cell dimensions. The layer structure postulated by Simpson may or may not be correct, but in our experience cell dimensions alone are inadequate to admit sufficient deduction of even the general features of the structures of the chemically complex, low-symmetry phases.

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