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A misunderstood member of the nagelschmidtite family unveiled: structure of $Ca_5Na_2(PO_4)_4$ from X-ray powder diffraction data

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Abstract

During the development of procedures to synthesize carbonate hydroxyapatite with properties resembling those of biological material, a new phase was found to form after high temperature treatments in the presence of sodium. The compound was isolated and analytically characterized, leading to its identification as $Ca_5Na_2(PO_4)_4$: an analogous Ca–Na phosphate was previously described, but with rather poor diffraction data and uncertain stoichiometry. Accurate XRD powder patterns revealed a hexagonal cell, space group P6$_3$mc (186), $a = 10.64$ Å, $c = 21.71$ Å, $Z = 6$, $\rho = 2.93$ g/cm^3, with the a axis double and the c axis triple those of the subcell typical of α-phases in the well-known system A_2XO_4 (or $ABXO_4$). The complete structural determination was carried out and the relevant aspects and properties discussed.

Keywords: Apatite; Biomedical applications; Powders-chemical preparation; Powder structure determination; X-ray methods

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1. Introduction

Since the pioneering work of Bredig in the 1930s,[1–4] noticeable attention has been devoted to the class of A_2XO_4 compounds with their many possible versions, especially thanks to their occurrence in cement.

The first to be studied were the alkali sulfates (so called glaserite group), soon followed by single and double-cation silicates and phosphates:[5,6] usually such compounds show a characteristic dimorphism, i.e. a high-temperature phase (α) hexagonal or trigonal and a low-temperature phase (β) orthorhombic. Lattice parameters are in the ranges: (α) $a = 5.2$–5.7 Å, $c = 6.8$–7.8 Å; (β) $a = 5.4$–5.8 Å, $b = 9.2$–10.0 Å, $c = 6.8$–7.6 Å. It is easy to see that orthorhombic modifications, characterized by $b \approx a\sqrt{3}$, present a pseudo-hexagonal double cell. The involved space groups are generally P$\bar{3}$m1 (164) and P6$_3$mc (186) for the α forms and Pnma (62) for the β forms.

A particularly interesting example of the complex group $A_7^{II}(XO_4)_2^{III}(YO_4)_2^{IV}$ is $Ca_7(PO_4)_2(SiO_4)_2$ named after Nagelschmidt who described it in 1937:[7] his original hexagonal subcell (ICDD card No. 3–706) was afterwards amplified, to account for more detected reflections, up to multiples 48 times larger (ICDD card No. 11–676).

During a systematic study to synthesize partially carbonated hydroxyapatite (CHA), mainly substituted in phosphate positions to reproduce the composition of the biological material,[8] a new compound $Ca_5Na_2(PO_4)_4$ was obtained after high temperature (≈1400 °C) thermal treatment (allowing for the influence of atmosphere) of CHA powders prepared from Ca nitrate, Na (or NH_4) bicarbonate and NH_4 (or Na) diphosphate: in this paper the complete structural determination from powder diffraction data for this compound is reported. The phase appears roughly similar to $Ca_6Na_3(PO_4)_5$ formerly found by Ando,[9] but for which a very limited number (15) of observed lines, no specified cell and only generic structural indications were provided.

2. Experimental

Calcium based CHA, $Ca_{10-x/2}(PO_4)_{6-x}(CO_3)_x(OH)_2$ with $x < 3$, containing CO_3^{2-} groups in PO_4^{3-} position (B

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site) in different amounts (from 8 to 16 wt.%) was prepared by wet chemical synthesis starting from $Ca(NO_3)_2{\cdot}4H_2O$ (Sigma-Aldrich), $(NH_4)_2$- or Na_2-HPO_4 (Merck) and Na- or NH_4-HCO_3 (Merck).[10–12]

The thermal behaviour of the CHA powders was studied by simultaneous TG-DTA thermal analysis (STA 409 Netzsch Geratebau) in order to follow the decomposition process of the material and then to identify the best sintering conditions. The analyses were performed up to 1450 °C, both under flowing air and carbon dioxide, using a heating/cooling rate of 10 °C/min: mixed cycles with different atmospheres in heating and cooling were used as well.

The residual material after thermal tratment was analysed by XRD (Rigaku Miniflex, CuK_α radiation, 2θ from 20 to 60°, step width 0.04°, counting time 1 s) in order to check the decomposition products and to determine the influence of the different atmospheres during the thermal analysis. For the new phase identified, accurate XRD patterns for structure analysis were recorded by a Siemens D-500 diffractometer (CuK_α radiation, tube power 3 times higher) at 2θ from 3 to 120°, step width 0.02°, counting time 6 s.

Different experiments were also carried out after varying the Na-based reagent amount: in fact the new phase does not form, either under air or carbon dioxide, when the Na ions partially substituting for Ca ions in the starting CHA are less than 5 wt.%.

Quantitative chemical analysis of Ca, Na and P was performed by ICP (Varian Liberty 200) and the possible presence of C verified by EPS equipped SEM (Leica Cambridge).

The mixtures containing appreciable quantity of the new phase were dispersed in 0.01 M HCl solution, then centrifuged and the residue was washed three times in order to eliminate CaO and make easier the identification of the useful lines by XRD.

The citric solubility of the compound was also tested by the method employing 100 ml of 2% citric acid for 1 g of sample (shaking for half an hour) to verify the chemical analogy with the phase described in outline by Ando.[9]

3. Results and discussion

Many structures assignable to nagelschmidtite type have been found, often containing three different cations and two anions and with cells multiple of the elementary ones: a stimulating investigation of the system $2CaO{\cdot}SiO_2$–$2CaO{\cdot}Na_2O{\cdot}P_2O_5$ has been performed by Kapràlik and Hanic.[13] Even restricting the discussion to compounds with two cations and one anion, a variety of stoichiometries has been identified in the past: in particular Ando, studying important systems in phosphate fertilizers, described in 1958[9] a compound with integer formula $Ca_6Na_3(PO_4)_5$ [allowing a stoichiometry range from $Ca_{4.8}Na_{2.4}(PO_4)_4$ up to $Ca_{5.2}Na_{1.6}(PO_4)_4$] characterized by an XRD powder pattern whose main features were very similar to those of the phase analyzed in this paper. No cell was reported to index the few observed reflections, but it was stated that the compound had an α-rhenanite ($CaNaPO_4$) type structure, this high-temperature modification being stabilized by partial substitution of CaO for Na_2O, mostly when nearly half of Na_2O was replaced by CaO (i.e. $Ca_{1.25}Na_{0.5}PO_4$).

In our case the nagelschmidtite-type phase always appears together with considerable amount of CaO and a small residual of HA (usually slightly carbonated), more seldom with a moderate quantity of TeCP ($Ca_4(PO_4)_2O$) too. Sometimes it may occur that the synthesis reaction, neglecting for simplicity secondary phases present as minor impurities, proceeds in accordance with:

$$\begin{aligned}&4Ca(NO_3)_2{\cdot}4H_2O + NaHCO_3 + 2(NH_4)_2HPO_4\\&= Ca_4Na(PO_4)_2CO_3OH + 4NH_4NO_3 + 4HNO_3\\&+ 15H_2O\end{aligned}$$

(actually the desired CHA should be Na-free, i.e. $Ca_{5-x/2}(PO_4)_{3-x}(CO_3)_xOH$ with $1/2 \leqslant x \leqslant 1$); then the solid product during thermal treatment undergoes the transformation:

$$\begin{aligned}&2Ca_4Na(PO_4)_2CO_3OH = Ca_5Na_2(PO_4)_4 + 3CaO\\&+ 2CO_2 + H_2O.\end{aligned}$$

If the thermal cycle up to 1400 °C and back is performed completely in air, the predominant final phase is HA, with limited amounts of $Ca_5Na_2(PO_4)_4$ and CaO; if the cycle is carried out entirely in CO_2 flux, the atmosphere causes a shift towards higher temperature (about 950 °C instead of 800 °C) in the carbonate decomposition and modifies the TG curve in terms of shape and total weight loss, leaving as the only detected phase well crystallized CHA (almost totally restored carbonate content); if heating occurs in a CO_2 flux and cooling without such flux, $Ca_5Na_2(PO_4)_4$ remains dominant, with CaO and CHA (lowered carbonate content) as secondary phases (occasionally traces of TeCP). From these synthesis conditions, it appears that in the presence of Na the new competing phase is less stable than HA, but more stable than CHA: its citric solubility was almost complete, confirming a chemical affinity with the phase perceived by Ando.[9]

After the purification procedures and the accurate determination of stoichiometry by analytical techniques supported by thermoanalysis, our phase was confirmed to be just $Ca_5Na_2(PO_4)_4$, with no residual carbonate and with perfect correspondence to nagelschmidtite

$Ca_7(PO_4)_2(SiO_4)_2$ (the main difference being 2 cations + 1 anion kinds instead of 1 cation + 2 anions). All the observed lines were indexed on the basis of a hexagonal (trigonal) cell with $a = 10.64$ Å, $c = 21.71$ Å ($Z = 6$, $\rho = 2.93$ g/cm^3): a is double and c triple in respect to the above mentioned elementary cell (volume 12 times).

Analogous behaviour was found in the $Ca_2KNa(PO_4)_2$ compound,[14] whose small α-type hexagonal cell (stable from 670 °C upwards) yields at room temperature a hexagonal superlattice (volume 27 times) by tripling both a and c axes. Recently, for such a compound, the uncommon permanence of simple α modification at room temperature was claimed.[15]

Moreover, the appearance of these large commensurate "superstructure" cells, necessary to index the numerous observed lines (not all weak as usually the case when not belonging to the small subcell), has to be considered as evidence to question the conclusion of Bredig that the majority of such complex compounds are pure solid solutions.[5,16,17]

The first problem to be faced in structural determination (not easy from powder data with large cells containing several tens of atoms in the asymmetric unit), was the choice between trigonal ($P\bar{3}m1$) space group and hexagonal ($P6_3mc$) one: the former is centrosymmetric and implies PO_4^{3-} tetrahedra in the cell pointing in opposite directions, while the latter is non-centrosymmetric and involves tetrahedra all pointing in the same direction (vertices all up or all down along c axis). Systematic absences were not conclusive because all discriminating reflections were too weak and moreover with overlapping terns of indexes: consequently this fundamental result could only be achieved during the structural analysis.

The starting structural model was supplied by the atomic arrangement discussed in detail by Kapràlik and Hanic[13] for the hexagonal (trigonal) subcell typical of the α modification and then by introducing the displacements necessary to justify the recourse to a multiple cell: from the beginning it was clear that the $P\bar{3}m1$ space group would have implied a strong (003) reflection with $d = 7.24$ Å not observed experimentally. Consequently further efforts were focused on the $P6_3mc$ space group in which (00l) reflections with $l = 2n + 1$ are forbidden.

Direct methods to solve the structure (programme EXPO)[18] were discarded because the ratio between the number of independent observed reflections and that of the parameters to be refined was unfavourable.

After various "trial and error" attempts it was realized that the ideal model was unable to reproduce satisfactorily the observed intensities, so fundamental adjustments were inserted including the shifts of Ca atoms originally placed right at the midpoints of the a axis and of Ca and Na atoms at $x = 5/6$, $y = 1/6$, together with general deformation of PO_4 tetrahedra and suitable modification of z coordinates. A few tests with limited introduction of CO_3 planar groups replacing PO_4 tetrahedra in accordance with recent findings[19–21] always resulted in a worsening of the overall discrepancy factor, confirming the practical absence of carbonate in the structure.

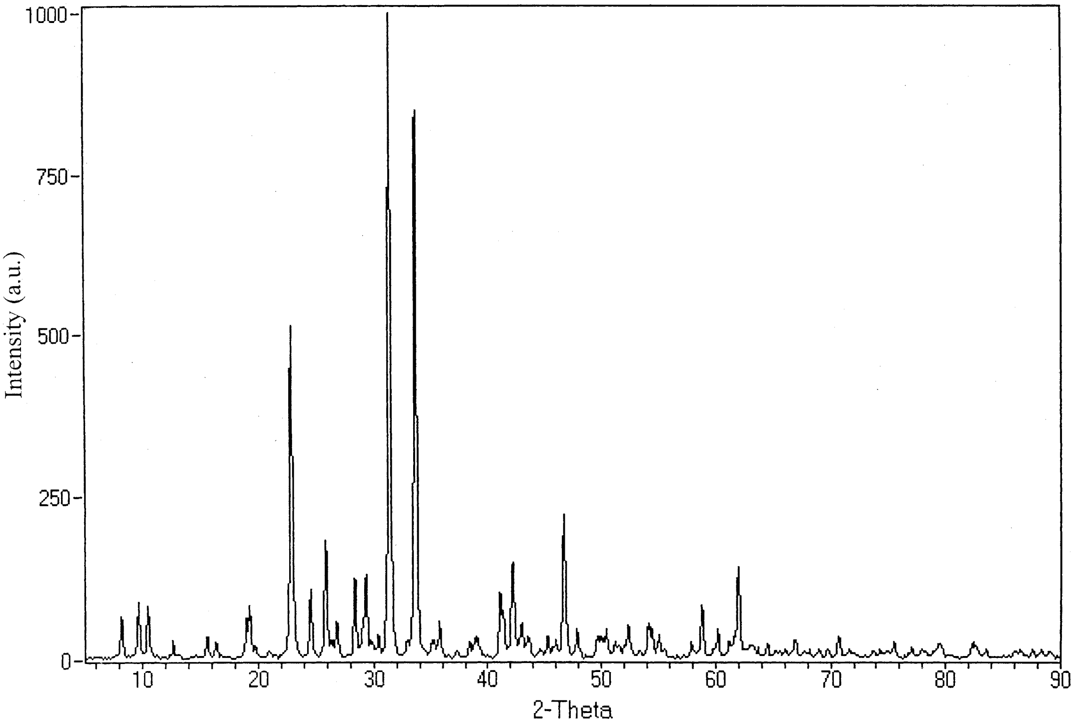

Fig. 1. Experimental XRD powder pattern of $Ca_5Na_2(PO_4)_4$ compound (CuK_α radiation).

However, a fair agreement between the observed and calculated intensities was obtained ($R_B = 25\%$) and judged sufficient to try whole pattern Rietveld refinement: DBWS programme[22] was employed and a remarkable improvement found ($R_B = 15\%$), but surprisingly at the expense of constraints on the logical atomic arrangement. All the time PO_4 tetrahedra were almost completely destroyed and unacceptable interatomic distances appeared. Consequently we were forced to continue the "trial and error" procedures, using as unique evaluation criterion the old method based on differences between observed and calculated peak intensities for all experimentally detected maxima. No attempt at pattern decomposition into a series of separate intensities was carried out, due to the difficulty and ambiguity of the available methods: instead, the less problematic composition of overlapping calculated intensities was applied. To appreciate the effects on calculated pattern due to adjustments in atomic coordinates the programme PowderCell[23] was employed: pseudo-Voigt analytical profile function with mixing parameter $\eta = 1/2$ and FWHM parameters $U = 0.09$, $V = -0.11$, $W = 0.10$ was used throughout.

In Fig. 1 the experimental XRD powder pattern of $Ca_5Na_2(PO_4)_4$ phase is reported, showing the typical features of few strong and many weak peaks; in Table 1 the final structural parameters are shown and in Table 2 the comparison between observed and calculated intensities is presented (a lower limit of 4 was selected to reasonably reduce the excessive number of faint data). In Fig. 2 the pattern evaluated using the parameters of Table 1 is displayed, while in Fig. 3a and b, the (001) and (110) projections of the determined structure are respectively sketched.

The intensity of the strongest line was set equal to 1000 and the others accordingly scaled: the overall discrepancy factor R_B amounts to 10.5%, rising to 11.0% if the absent reflections with calculated intensities larger than 4 and the observed ones with calculated intensities smaller than 4 are taken into account. These values can be considered quite satisfactory allowing for the quality of the observed pattern (about 100 lines detected up to $2\theta = 90°$ and only negligible ones beyond), the large cell size involved yielding a wide degree of line overlapping (more than 200 terns of indexes assignable to the observed lines) and the outstanding number of atoms to be rightly placed in the structure (162 in the unit cell generated by 30 in the asymmetric unit), moreover in the absence of heavy ones.

The isotropic thermal parameters leading to the best fit result remarkably high and, even if not unusual in Ca phosphates,[24] suggest a certain degree of statistical lattice disorder more than a low melting phase (remembering that it usually forms at 1400 °C).

Another interesting observation is the fact that the great majority of atoms lie in special positions: only 3/8 of oxygen atoms (corresponding to 2/9 of the total) occupy general positions. This is different from β-TCP ($Ca_3(PO_4)_2$), despite the geometrical analogies between the unit cells (if rhombohedral β-TCP is described in hexagonal axes): in fact the a axes are almost equal while the c axis of β-TCP is about $\sqrt{3}$ times that of the $Ca_5Na_2(PO_4)_4$ phase. Structural organization too presents some resemblance, exemplified by the two strongest reflections that, accounting for the differences in lattice parameters, have strictly corresponding indexes in the two phases: it is nevertheless important to remember that in this case no mixture of hexagonal (same orientation along *c* axis) and trigonal (opposite orientation) arrangement of PO_4 tetrahedra is allowed. Some analogy can be pointed out with high temperature α-TCP as well, even if its monoclinic cell (with volume almost exactly double that of $Ca_5Na_2(PO_4)_4$) does not exhibit simple relationships among the length of crystallographic axes: anyway the three strongest reflections of the two phases, apart from hardly correlated indexes, have interplanar spacings matching within few percent.

Furthermore, differently from HA (or CHA), in this phase the PO_4 tetrahedra never present faces parallel to

Table 1
Structural data for $Ca_5Na_2(PO_4)_4$ compound

Atom	Wyckoff	*x*	*y*	*z*	Occupancy	*B* (Å^2)
Ca(1)	2a	0	0	1	1	2
Ca(2)	2a	0	0	1/6	1	2
Ca(3)	2a	0	0	1/3	1	2
Ca(4)	6c	0.525	0.475	1	1	2
Ca(5)	6c	0.530	0.470	1/6	1	2
Ca(6)	6c	0.525	0.475	1/3	1	2
Ca(7)	6c	0.870	0.130	0.7675	1	2
Na(1)	6c	0.180	0.820	0.9342	1	5
Na(2)	6c	0.150	0.850	0.6008	1	5
P(1)	2b	1/3	2/3	0.255	1	4
P(2)	2b	1/3	2/3	0.585	1	4
P(3)	2b	1/3	2/3	0.920	1	4
P(4)	6c	5/6	1/6	0.585	1	4
P(5)	6c	1/6	5/6	0.755	1	4
P(6)	6c	5/6	1/6	0.920	1	4
O(1)	2b	1/3	2/3	0.320	1	8
O(2)	2b	1/3	2/3	0.653	1	8
O(3)	2b	1/3	2/3	0.997	1	8
O(4)	6c	0.5933	0.4067	0.722	1	8
O(5)	6c	0.1033	0.8967	0.719	1	8
O(6)	6c	0.930	0.070	0.549	1	8
O(7)	6c	0.4267	0.5733	0.549	1	8
O(8)	6c	0.5933	0.4067	0.379	1	8
O(9)	6c	0.1033	0.8967	0.379	1	8
O(10)	6c	1/6	5/6	0.820	1	8
O(11)	6c	5/6	1/6	0.653	1	8
O(12)	6c	5/6	1/6	0.997	1	8
O(13)	12d	0.4067	0.100	0.560	1	8
O(14)	12d	0.4367	0.1033	0.220	1	8
O(15)	12d	0.340	0.4267	0.379	1	8

Space group: $P6_3mc$ (186), $a = 10.64$ Å, $c = 21.71$ Å, $Z = 6$, $\rho = 2.932$ g/cm^3.

Table 2
Comparison between observed and calculated powder pattern intensities for $Ca_5Na_2(PO_4)_4$ compound

hkl	d (Å)	I_{obs}	I_{calc}
002	10.85	64	71
100	9.21	76	84
101	8.48	81	115
102	7.02	23	17
103	5.69	31	24
004	5.43	15	28
110	5.32	–	6
104	4.68	53	39
200	4.61	73	116
201	4.51	7	8
202	4.24	7	9
105	3.93	23	33
203	3.88	518	478
006	3.62	95	89
211	3.44	189	180
106	3.37	22	26
212	3.32	53	42
213	3.14	123	108
300	3.07	37	47
301	3.04	121	111
116	2.992	24	31
302	2.955	–	8
107	2.939	26	16
214	2.931		6
206	2.846	1000	1000
303	2.827		24
215	2.717	15	16
304	2.673	863	4
220	2.660		830
108	2.603	6	5
310	2.556	23	43
311	2.538	16	17
305	2.507	49	76
313	2.410	5	–
306	2.342	17	6
109	2.334		9
217	2.316	18	38
400	2.304	15	23
401	2.291	4	5
403	2.195	96	116
307	2.182	46	44
226	2.143	152	83
218	2.141		8
209	2.137		93
320	2.114	13	16
321	2.104	53	67
316	2.087	13	15
322	2.075	34	31
323	2.029	9	8
411	2.002	32	33
219	1.9830	7	7
317	1.9723	16	8
324	1.9698		6
406	1.9432	229	229
413	1.9374		–
325	1.9007	39	25
309	1.8971		16
501	1.8363	27	31
326	1.8253	33	20
415	1.8246		18
502	1.8169	4	4
0.0.12	1.8092	40	40
503	1.7859	18	19
330	1.7733	15	21
416	1.7576	6	8
332	1.7501	39	4
327	1.7468		30
504	1.7451		5
420	1.7414	10	6
2.1.11	1.7171	13	14
505	1.6964	48	10
423	1.6931		45
417	1.6872	35	13
2.0.12	1.6840		25
328	1.6677	29	11
409	1.6660		19
510	1.6550	5	8
336	1.5924	16	11
329	1.5899		6
507	1.5843	12	16
426	1.5691	76	71
515	1.5465	10	5
419	1.5445		7
600	1.5358	37	37
3.2.10	1.5146	15	5
431	1.5112		13
516	1.5050	22	26
2.2.12	1.4960	150	154
433	1.4827	7	8
3.1.12	1.4766	10	5
520	1.4755		5
521	1.4721	9	10
3.0.13	1.4672	7	9
517	1.4601	4	4
523	1.4458	18	4
3.2.11	1.4426		16
435	1.4303	8	5
4.0.12	1.4228	10	10
606	1.4137	14	5
429	1.4119		12
525	1.3970	30	30
2.0.15	1.3808	5	9
3.2.12	1.3745	4	4
437	1.3612	6	6
5.0.11	1.3470	12	13
527	1.3324	33	7
440	1.3300		28
530	1.3164	13	9
701	1.3140		5
3.2.13	1.3104	8	5
616	1.3099		4
4.1.13	1.2847	4	5
621	1.2756	4	6

(*continued on next page*)

Table 2 (*continued*)

hkl	d (Å)	I_{obs}	I_{calc}	hkl	d (Å)	I_{obs}	I_{calc}
3.3.12	1.2664	6	7	4.3.11	1.2017	6	5
529	1.2587	20	6	6.0.12	1.1708	21	21
623	1.2584		18	2.0.18	1.1668	22	21
536	1.2370	22	28	716	1.1565	6	7
4.0.15	1.2255	9	12	629	1.1292	5	5
5.1.12	1.2211	14	7	721	1.1242	5	4
710	1.2205		10	4.2.15	1.1131	4	5
707	1.2117	4	4	5.2.13	1.1057	8	8
0.0.18	1.2061	19	5	2.2.18	1.0985	4	4
626	1.2049		13				

$R_B = 0.105$; $R_e = 0.085$; $R_w = 0.182$ (both expected and weighed values are adapted versions, to be considered as merely indicative, evaluated over the limited number of experimental points corresponding to peak intensities and not on all those representing the whole pattern, about 40 times more numerous).

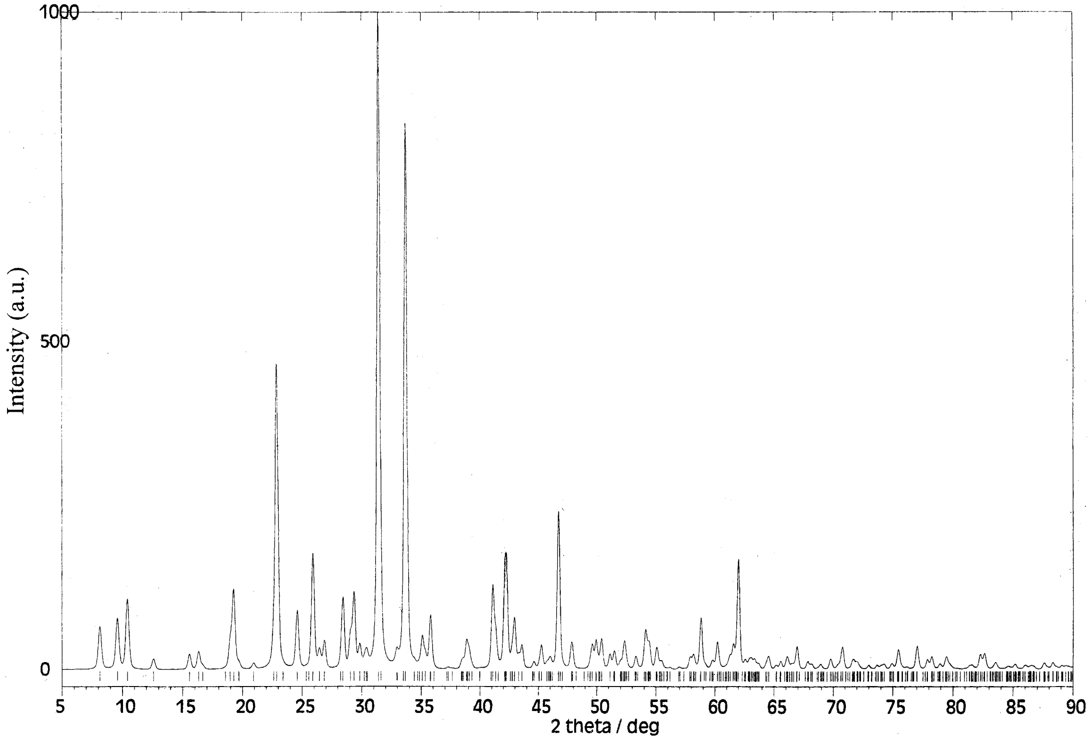

Fig. 2. Calculated XRD powder pattern: the structural coordinates of Table 1 and the profile parameters specified in the text were used. Short vertical bars beneath represent all possible interplanar spacings.

the c axis (the others making to it an angle close to 54.7°) nor do all faces make with the same axis angles of approximately 35.3°, but one face is nearly perpendicular and the others make an angle of about 19.5° to it: this alters substantially the arrangement of ninefold and sevenfold Ca coordination polyhedra previously found in reference compounds.[20] Ca and Na coordinations are basically in agreement with the layout met in α polymorphs, including fluctuations due to the rather severe tetrahedra distortion and occasional misplacement of cations.

By the classical method of mixtures[25] the scattering power $I = \left(1/V^2\right)\mathrm{mLP}|F|^2$ referred to corundum (α-Al_2O_3) was evaluated as $I/I_{cor} = 0.81$; if one takes into account the higher linear absorption coefficient this value goes down to 0.46. We can recall that investigated calcium and sodium orthophosphates exhibit I/I_{cor} lying (neglecting absorption) between 0.3 and 1.1.[1]

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[1] The value 7.30 reported in ICDD card No. 25–1137 for $Ca_4(PO_4)_2O$ (TeCP) is only a mistake: the correct one, carefully measured, turns out to be as low as 0.32.

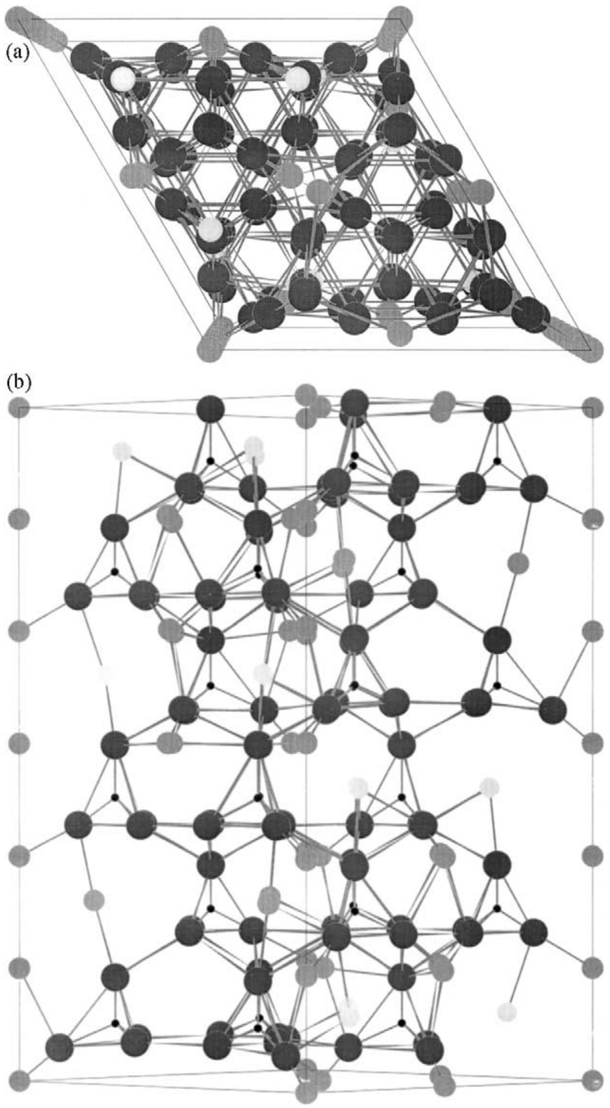

Fig. 3. Fundamental projections of the determined structure: (a) (001); (b) (110). Only atoms contained in the unit cell are shown with size reduced to 1/3 for clarity (medium dark circles: Ca; medium light circles: Na; small black circles: P; large dark circles: O). Lines connecting atoms are drawn for all interatomic distances $\leqslant 3$ Å and not only for real chemical bonds.

4. Conclusions

High-temperature treatments ($\approx$1400 °C) of bone-like carbonate hydroxyapatite prepared from Ca nitrate, Na (or NH_4) bicarbonate and NH_4 (or Na) diphosphate lead to the formation (somewhat stimulated by CO_2 atmosphere during heating alone) of a Ca–Na phosphate with composition $Ca_5Na_2(PO_4)_4$. The presence of many reflections characterised by relatively high intensities absent in Ando experimental pattern,[9] leads to believe that our compound, even if with undeniable similarity, is not properly the same described by this author: probably the main difference, connected to the unlike preparative conditions, lies in the close but distinct stoichiometries. No carbonate is retained in this phase and its structure can be interpreted on the basis of a hexagonal cell ($P6_3mc$) with the a axis double and the c axis triple the typical values found for the α modification subcell in the extensively studied systems $(A,B)_m[(X,Y)O_4]_n$. The features of the observed pattern made it necessary to abandon the alternative trigonal hypothesis ($P\bar{3}m1$), often hard to discriminate. After the unpredictable failure of Rietveld refinement, which was not able to converge at any acceptable atomic disposition, the classical structural analysis performed only on the peak intensities instead of the whole pattern was adopted and, even if lengthy and laborious, a satisfactory result was attained: the final discrepancy factor R_B amounted to 10.5%, satisfactory in consideration of the number of observed reflections, the size of the cell and the quantity of atoms to be located. The atomic arrangement presents a noticeable degree of distortion in PO_4 tetrahedra, besides significant displacements in the cations "ideal" positions (defined as those occupied in the simple subcell) and considerably high thermal factors: all indications of an irregular structure, with frozen-in localized disorder after the formation within a fairly complex environment and in conditions far from equilibrium, possibly characterized by a certain degree of physico-chemical instability that justifies its infrequent detection.

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