Phase coexistence in the system $Mg_3(PO_4)_2$—$Ca_3(PO_4)_2$—Na_3PO_4

J. MAJLING and F. HANIC

Institute of Inorganic Chemistry, Slovak Academy of Sciences,
809 34 Bratislava

Received 12 May 1975

Accepted for publication 15 August 1975

The phase coexistence in the subsolidus region of the title system was determined by X-ray powder diffraction (at 800°C). Crystallographic data are given for one ternary ($Mg_4Na(PO_4)_3$) and one quaternary phase ($Mg_7CaNa_2(PO_4)_6$).

The former compound, $Mg_4Na(PO_4)_3$, crystallizes in the orthorhombic system with unit cell parameters $a = 9.875(2) \times 10^{-10}$ m, $b = 15.234(4) \times 10^{-10}$ m, $c = 6.346(1) \times 10^{-10}$ m. $Mg_7CaNa_2(PO_4)_6$ (designated as a phase Q) crystallizes in the rhombohedral system ($a = 16.616 \times 10^{-10}$ m, $\alpha = 53.43°$). Corresponding hexagonal parameters are: $a = 14.938(7) \times 10^{-10}$ m, $c = 42.61(2) \times 10^{-10}$ m.

Рентгенофазовым анализом было определено существование фаз под линией солидуса указанной системы (при температуре 800°C). В работе приводятся кристаллографические данные для одной тройной ($Mg_4Na(PO_4)_3$) и одной четверной ($Mg_7CaNa_2(PO_4)_6$) фаз.

Соединение $Mg_4Na(PO_4)_3$ кристаллизуется в орторомбической системе с параметрами решетки $a = 9{,}875(2) \times 10^{-10}$ м, $b = 15{,}234(4) \times 10^{-10}$ м, $c = 6{,}346(1) \times 10^{-10}$ м. $Mg_7CaNa_2(PO_4)_6$ кристаллизуется в ромбоэдрической системе ($a = 16{,}616 \times 10^{-10}$ м, $\alpha = 53{,}43°$). Соответствующие гексагональные параметры $a = 14{,}938(7) \times 10^{-10}$ м, $c = 42{,}61(2) \times 10^{-10}$ м.

The present paper is a part of the study of phase coexistence in the quaternary oxide system MgO—CaO—Na_2O—P_2O_5 [1—3] and it deals specifically with the section at 25 mole % of P_2O_5. The oxide systems of such complexity, containing P_2O_5 as one component have not yet been studied systematically.

The phase composition of the following subsystems has already been investigated.

In the subsystem $Mg_3(PO_4)_2$—$Ca_3(PO_4)_2$ there exists an intermediate phase of variable composition. According to the crystal structure analysis [9] its formula is given by $Mg_9Ca_7(Mg,Ca)_2(PO_4)_{12}$. The intermediate phase was referred to compositions $Mg_3Ca_3(PO_4)_4$ [4—7] (Fig. 1) and $Mg_5Ca_4(PO_4)_6$ [8]. The first composition corresponds to the end member of the solid solution series, the second one is an intermediate member as it is implicated by the formula given above.

On the $Ca_3(PO_4)_2$ side of this subsystem, another solid solution is formed with a boundary composition $Ca_7Mg_2(PO_4)_6$ at 1150°C. This end member of the solid solution was designated as an individual compound, Mg-whitlockite [10]. According to [11] whitlockite exists up to 960°C. Therefore it is necessary to distinguish between β-$Ca_3(PO_4)_2$ and whitlockite which represent two distinct compounds [11—13].

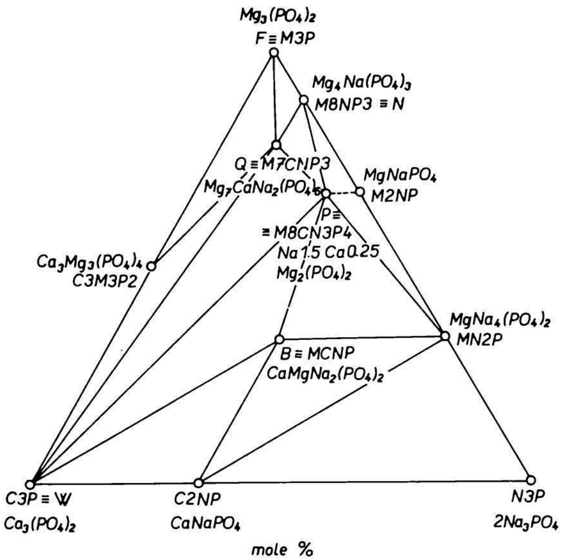

Fig. 1. Phase coexistence in the system $Mg_3(PO_4)_2$—$Ca_3(PO_4)_2$—Na_3PO_4 (symbols *F, Q, P, B, W* denote phases according to key to Table 1).

In the subsystem $Mg_3(PO_4)_2$—Na_3PO_4 three ternary compounds are present: $Mg_4Na(PO_4)_3$, $MgNaPO_4$ [14], and $MgNa_4(PO_4)_2$ [15]. The crystallographic data for the first compound are given in this paper. The second compound exhibits polymorphic transformations and decomposes probably in the solid state [14].

In the subsystem $Ca_3(PO_4)_2$—Na_3PO_4 up to the temperature of *ca.* 990°C only the single compound $CaNaPO_4$ is present [16 – 18]. Above this temperature (990—1350 °C) there is also stable phase *A*, coexisting with β-, α-$Ca_3(PO_4)_2$ and α-, β-$CaNaPO_4$ [16, 18]. From among the phases, present in the system, two phases can be found in the nature as mineral species: $Mg_3(PO_4)_2$, farringtonite [8] and $Ca_{18}Mg_2H_2(PO_4)_{14}$, Mg-whitlockite [11]. The later phase can be present in the system depending on the sample preparation and external conditions.

Another two quaternary phases of stoichiometries $MgCaNa_2(PO_4)_2$ and (Na, Ca)$_2$(Mg,Fe)$_2$(PO$_4$)$_2$ belong into the section studied. These phases were isolated from the meteorite "Dayton", identified as individual compounds and named as minerals brianite and panethite, respectively [19]. Their presence in the earth crust was not stated yet. The former compound, $MgCaNa_2(PO_4)_2$, as a synthetic phase was also studied in [20].

Experimental

The samples were prepared by the evaporation of diluted aqueous solutions of $Mg(NO_3)_2$, $Ca(NO_3)_2$, $NaNO_3$, and $NH_4H_2PO_4$ as described in [14] and by heating the dried precursors at 800°C in the air. The phases present in samples were identified by X-ray powder diffractometry. The powder patterns were taken on Philips standard diffractometer using CuK_α radiation. As diffraction standards, the data, published in [8] and the data, published in [14, 15, 19] were used.

Table 1

Concentration of analyzed samples and results of the phase analysis

No.	Composition	Present phases	No.	Composition	Present phases
1	M16CNP6	*Q*, *F*	*17*	M2CN3P2	α-N3P, *B*
2	M15CN2P6	*Q*, *X*	*18*	M3CN5P3	α-N3P, α-C2NP, *W*
3	M7CNP3	*Q*	*19*	M2C6NP3	*W*
4	M6C2NP3	*Q*	*20*	M2C5N2P3	α-C2NP, *W*, *B*
5	M20C2N5P9	*Q*	*21*	M2C3N4P3	α-C2NP
6	M17C9NP9	C3M3P2, *Q*	*22*	M2C3N4P3	α-C2NP, α-N3P
7	M14C3N4P7	*Q*, *P*, *W*	*23*	M2C2NP	α-N3P, α-C2NP
8	M5C3NP3	*Q*, *W*	*24*	M2CN6P3	α-N3P
9	M5C2N2P3	*B*, *P*, *W*	*25*	MC3N2P2	α-C2NP
10	M21CN5P9	*P*, *X*	*26*	MC2N3P2	α-N3P, α-C2NP
11	M15CN5P6	*P*, *X*, α-N3P	*27*	MC6N2P3	α-C2NP, *W*
12	M9C2N4P5	*P*, *B*, α-N3P	*28*	MC5N3P3	α-C2NP
13	M9CN5P5	*P*, *B*, α-N3P	*29*	MC4N4P3	α-C2NP, N3P
14	M3CN2P2	*B*	*30*	MC3N5P3	α-N3P (disordered structure)
15	MCNP	*B*	*31*	MC2N6P3	α-N3P
16	M3C2N4P3	α-N3P			

Phases present at 800°C.

As far as the presence of different modifications (of the same substance) was not relevant for the participant phases, the identified phases are denoted as follows: *Q* — ($Mg_7CaNa_2(PO_4)_6$), *F* — farringtonite ($Mg_3(PO_4)_2$), *X* — $Mg_4Na(PO_4)_3$, C3M3P2 — $Mg_9Ca_7(Mg,Ca)_2(PO_4)_{12}$, *W* — whitlockite, *B* — brianite, *P* — panethite. In the system there are further present modification of $CaNaPO_4$ (α-C2NP) and α modification of Na_3PO_4 (α-N3P). α-N3P is a common name for the solid solution of $MgNa_4(PO_4)_2$ and Na_3PO_4 (at 800°C). Symbol *W* does not differentiate between whitlockite and Mg-whitlockite. In reality, the partially transformed Mg-whitlockite with a presence of Na^+ ions are to be encountered in the system.

Table 2

Crystallographic data for compounds $Mg_4Na(PO_4)_3$ and $Mg_7CaNa_2(PO_4)_6$

$Mg_4Na(PO_4)_3$	$Mg_7CaNa_2(PO_4)_6$
$a = 9.875(2)\times10^{-10}$ m	$a_r = 16.616\times10^{-10}$ m
$b = 15.234(4)\times10^{-10}$ m	$\alpha_r = 54.43°$
$c = 6.346(1)\times10^{-10}$ m	$a_h = 14.939(9)\times10^{-10}$ m
	$c_h = 42.58(3)\times10^{-10}$ m
$V = 954.7\times10^{-30}$ m^3	$V = 8234.2\times10^{-30}$ m^3
$Z = 4$	$Z_h = 18$
SG: *Pnam*	—
$D_x = 2790$ kg m^{-3}	$D_x = 2998$ kg m^{-3}
$D_m = 2820(20)$ kg m^{-3}	$D_m = 2990(20)$ kg m^{-3}
	$M_{calc} = 823.87$

Unit cell parameters of phases were measured from the Weissenberg and precession photographs of single crystals and refined by the method of least squares from powder data [21]. The density was measured by flotation method [22]. The liquidus temperatures were measured using the Griffin hot-stage microscope [23, 24].

Results and discussion

The results of phase analysis for certain selected samples are listed in Table 1. The majority of them was later found to lie in the two phase regions. Those samples, which correspond to three phase regions, contain the phases in such ratios, that the presence of each one of them could be unambiguously detected.

The compositions of samples were selected in order to keep the constituent oxides in simple molar proportions (the ratio of integers) (Table 1). Usual abbreviated notation is used (Table 1, Fig. 1), where M = MgO, C = CaO, N = Na_2O, P = P_2O_5. Fig. 1 contains all types of notation.

The deduced diagram of the phase coexistence is shown in Fig. 1. In the system, already at 800°C solid solutions are formed within broad limits. The tie lines in Fig. 1 represent the phase relationship only qualitatively.

Besides the known phases we have identified in the system the presence of a further quaternary phase, denoted as the phase *Q*. This phase is of a variable composition in broad limits and we give its representative formula as $Mg_7CaNa_2(PO_4)_6$. The samples *3, 4, 5* listed in Table 2 (corresponding representative points are depicted in Fig. 2) exhibit X-ray single phases.

According to liquidus temperatures the phase *Q* has its primary crystallization boundaries at following concentrations: in the section $Mg_3(PO_4)_2$—$CaNaPO_4$ from 21.9 to 31.6 mole % $2CaNaPO_4$, in the section $Mg_3(PO_4)_2$—"$Ca_3Na_6(PO_4)_4$" from 24.3 to 42.8 mole % $1/2Ca_3Na_6(PO_4)_4$ and in the section $Mg_3(PO_4)_2$—"$CaNa_4(PO_4)_2$" from 22.2 to 41.5 mole % of $CaNa_4(PO_4)_2$.

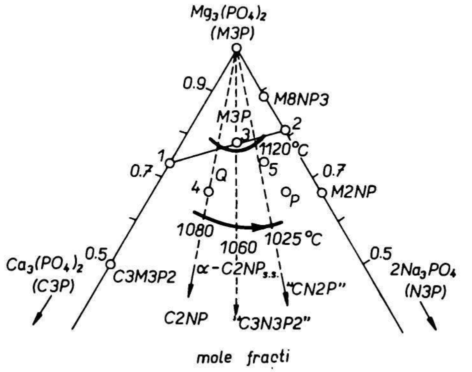

Fig. 2. Boundary curves of primary crystallization fields of $Mg_3(PO_4)_2$, *Q* phase and $CaNaPO_{4\,s.s.}$ as determined by the hot-stage microscope.

The straight line $\overline{1\;2}$ — the set of "isomolecular weights" with a value equal to the molecular weight of the phase *Q*, determined experimentally (Table 2).

The resulting liquidus surface is shallow in its course with a maximum temperature of 1120°C in a broader zone at its contact with the field of primary crystallization of $Mg_3(PO_4)_2$ (Fig. 2).

The alternative stoichiometry M6C2NP3 ($Mg_3CaNa(PO_4)_3$) as a stoichiometry, representing (in the first approximation by integer indices) the chemical composition of the quaternary phase was neglected for two reasons: The temperature of the liquidus surface of the phase *Q* continuously descends from the side of its boundary with $Mg_3(PO_4)_2$. The sample M14C3N4P7, the representative point of which lies on the join of two respective representative points M6C2NP3 and M8CN3P4 (the later representative point corresponds to the X-ray single panethite phase), contains three phases, the third phase being "whitlockite"

Table 3

List of diffraction lines of $Mg_7CaNa_2(PO_4)_6$

hkl	d_{hkl} (obs)	d_{hkl} (calc)	I/I_0
0 0 3	14.16	14.20	8
0 1 2	11.02	11.06	11
1 0 4	8.222	8.223	2
0 2 4	5.519	5.529	9
0 1 8	4.917	4.925	17
0 2 7	4.435	4.433	17
3 0 0	4.316	4.312	18
2 1 5	4.234	4.241	9
3 0 3	4.118	4.126	18
3 0 5*	3.850	3.848	16
0 3 6	3.681	3.686	100
2 1 8	3.607	3.602	7
3 1 2	3.537	3.538	55
1,1,11*	3.443	3.438	17
3 1 4 2 1 9	3.396	3.400 3.400	9
2 0 11	3.322	3.323	7
1 0 13	3.182	3.177	12
4 0 4	3.098	3.095	20
**	3.012	—	20
3 2 1	2.959	2.962	40
2 2 9	2.935	2.932	50
4 0 7	2.856	2.856	17
4 0 8	2.768	2.764	43
3 0 12	2.742	2.741	100
4 1 6	2.625	2.623	12
5 0 1 2 1 14	2.584	2.583 2.583	12
3 3 0	2.488	2.490	38
3 3 6	2.349	2.349	27

The phase panethite melts incongruently. It may be expected (according to Fig. 2) that its representative point lies below the liquidus surface of the phase *Q*. In Fig. 2 we arbitrarily represent this phase by the point corresponding to $Mg_2Ca_{0.25}Na_{1.5}(PO_4)_2$. The sample of this composition represents a single phase.

At the composition corresponding to M2NP ($MgNaPO_4$), which is the composition of a possible end member of the solid solution "panethite" ($(Na,Ca)_2(Mg,Fe)_2(PO_4)_2$ [19]) this phase is still not formed. The sample of this composition at temperatures up to 730°C, represents an individual phase, $MaNaPO_4$, different from panethite.

Table 4

List of diffraction lines of $Mg_4Na(PO_4)_3$

hkl	d_{hkl} (obs)	d_{hkl} (calc)	I/I_0
020	7.602	7.617	37
011	5.852	5.858	33
111	5.039	5.038	5
200	4.939	4.938	2
210	4.695	4.697	3
121	4.370	4.372	3
220	4.141	4.143	44
031	3.965	3.965	30
201	3.892	3.897	5
211	3.773	3.775	5
140	3.548	3.553	6
221	3.469	3.471	3
002	3.171	3.173	30
231	3.089	3.092	5
320	3.016	3.021	100
112	2.963	2.963	20
311	2.867	2.870	3
122	2.807	2.808	9
051	2.747	2.747	10
241	2.7238	2.7237	3
202	2.6687	2.6693	18
151	2.6462	2.6462	2
212	2.6292	2.6293	1
331	2.5327	2.5325	15
222	2.5190	2.5191	37
340	2.4907	2.4905	4
160	2.4590	2.4593	28
042	2.4374	2.4378	16
410		2.4371	
251	2.3995	2.4003	10
420	2.3488	2.3486	4
312	2.2583	2.2592	2
322	2.1880	2.1881	5
261	2.1269	2.1730	2

The presence of the phase "whitlockite"/β-$Ca_3(PO_4)_2$ requires a further attention. The wide concentration range of existence of this phase can be seen in Fig. 1. As mentioned in [11] the first change in the whitlockite structure takes place at 780°C. Another change, associated with a more pronounced heat absorption follows at *ca*. 960°C. The products of heating above 960°C can be suggested as phases derived from β-$Ca_3(PO_4)_2$. From [10] it follows that solid solutions are formed in the system $Ca_3(PO_4)_2$—$Mg_3(PO_4)_2$ at 1150°C with a boundary at a composition $Ca_7Mg_2(PO_4)_6$ (C7M2P3). In our case, the structure of phases, formed at 800°C, is closer to that of the phase whitlockite. The substitution did not proceed in such broad limits, as in [10]. The samples of stoichiometries C7M2P3 and C5MP2 contained also $Ca_7Mg_9(Ca,Mg)_2(PO_4)_{12}$ (in Fig. 1 denoted as C3M3P2).

Whitlockite and β-$Ca_3(PO_4)_2$ can be distinguished mutually on the basis of powder diffraction according to the 006 diffraction line [12]. In the case of whitlockite this line is barely observable, however, in the case of β-$Ca_3(PO_4)_2$ it attains *ca*. a fourfold intensity. In our case, the 006 diffraction was present only in the sample of stoichiometry M2C5N2P3 (Table 1). In other samples (also in samples from the two phase regions) its relative intensity reached 3—4% due to the partial transformation of whitlockite.

The compound $MgNa_4(PO_4)_2$ was synthesized as a monohydrate ($MgNa_4(PO_4)_2 \cdot H_2O$) [15]. Further it was found that anhydride exists in three distinct phases (α, β, γ modification). This is in agreement with work [25] where a congruent maximum on the liquidus curve was found in the system $Mg_3(PO_4)_2$—Na_3PO_4 at the composition $MgNa_4(PO_4)_2$.

The γ modification of $MgNa_4(PO_4)_2$ and the α modification of Na_3PO_4 [14] form continuous series of solid solutions.

Crystallographic data

The phase (Q) identified in this study as well as the $Mg_4Na(PO_4)_3$ compound belonging to the investigated section [14] were prepared in form of single crystals.

The single crystals of the phase Q were prepared by slow cooling the melt of the composition M6C2NP3 (point *2*, Fig. 2) from the temperature 1150°C. Unit cell parameters were derived from precession photographs. This phase crystallizes in rhombohedral system. Refined rhombohedral and hexagonal unit cell parameters are listed in Table 2. The powder diffraction pattern was taken at scanning rate of $1/4°2\theta$/min. Intensities were measured from peak heights. The powder pattern indexed on the basis of hexagonal symmetry, includes two lines in the list of its diffraction lines (Table 3, diffractions 305; 1,1, 11(*)) whose indices do not satisfy the condition $-h+k+l=3n$, *i.e.* they cannot be transformed into the corresponding indices in the rhombohedral system. No indices (Table 3 (**)) could be ascribed to the diffraction having $d = 3.012 \times 10^{-10}$ m. This diffraction may correspond to the strongest diffraction (320, Table 4) of $Mg_4Na(PO_4)_3$.

According to the observation by the hot-stage microscope, the crystals of the phase Q exhibit idiomorphic growth with a prevailing column-like habitus. The crystals are little soluble in diluted inorganic acids.

The following reasons led us to describe the phase Q by the formula $Mg_7CaNa_2(PO_4)_6$: On the account that the phase Q lies in the section of compounds $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$, and Na_3PO_4 the following relationship is valid in limits of an experimental error

$$\frac{M(Q)}{k} = a\,M(\mathrm{M3P}) + b\,M(\mathrm{C3P}) + c\,M(\mathrm{N3P})\,,$$

where $M(Q)$ is molecular weight of the phase Q, calculated from the known unit cell volume and the known density of crystals (formally at 1 formula unit in the unit cell); a, b, c are mole fractions of components M3P, C3P, N3P; k is the integer constant.

The set of points satisfying the above-mentioned relationship lies on the straight line $\overline{1\ 2}$ (Fig. 2). It can be deduced from this figure that the experimental value $M(Q)$ is most satisfactorily approximated by the ratio (integral and low coefficients) of constituing orthophosphates corresponding to the formula $Mg_7CaNa_2(PO_4)_6$. This stoichiometry does not contradict the results of X-ray phase analysis and is consistent with the results of phase equilibria study using the hot-stage microscope.

The single crystals of $Mg_4Na(PO_4)_3$ were prepared by a slow cooling of the melt containing 20 mole % $2Na_3PO_4$ (with regard to the join $Mg_3(PO_4)_2$—Na_3PO_4) from the temperature 1000°C. This temperature is close to the liquidus temperature in the region of the primary crystallization field of $Mg_4Na(PO_4)_3$ [14]. Single crystals were hand-picked from the disintegrated sample after cooling. Refined unit cell parameters are given in Table 2 and the powder diffraction pattern is shown in Table 4. The powder pattern was taken at conditions as indicated in the previous case.

The single crystals of this compound were also flux grown from the NaCl melt. The single crystals obtained were needle-like in the former case and plate-like in the case of flux growing.

References

1. Majling, J., Vojtečková, A., and Petrovič, J., *Chem. Zvesti* ***28***, 289 (1974).
2. Majling, J., Kaprálik, I., and Mikloš, D., *Silikáty* ***2***, 125 (1974).
3. Majling, J. and Hanic, F., *Paper Presented at 2nd (IUPAC) Conference on Inorganic Phosphorus Compounds*, Prague, 1974.
4. Ando, J., *Bull. Chem. Soc. Jap.* ***31***, 201 (1958).
5. Bobrownicki, K. and Slawski, K., *Rocz. Chem.* ***33***, 201 (1966).
6. Slawski, K., *Chem. Stosow.* ***3A***, 305 (1966).
7. McCauley, R. A., Hummel, F. A., and Hoffman, M. V., *J. Electrochem. Soc.* ***118***, 755 (1971).
8. *Joint Committee on Powder Diffraction Standards: Powder Diffraction File*, Philadelphia, 1967.
9. Dickens, B. and Brown, W. E., *Tschermaks. Mineral. Petrol. Mitt.* ***16***, 79 (1971).
10. Ito. J., *J. Res. Nat. Bur. Stand.* ***72A***, 355 (1968).
11. Gopal, R., Calvo, C., Ito, J., and Sabine, W. K., *Can. J. Chem.* ***52***, 1155 (1974).
12. Gopal, R. and Calvo, C., *Nature Phys. Sci.* ***237***, 30 (1972).
13. Calvo, C. and Gopal, R., *Amer. Mineral.* ***60***, 120 (1975).
14. Majling, J., *Chem. Zvesti* ***27***, 732 (1973).
15. Ghorbel, A., d'Yvoire, F., and Dorémieux-Morin, C., *Bull. Soc. Chim. Fr.* ***1974***, 1239.
16. Ando, J. and Matsuno, S., *Bull. Chem. Soc. Jap.* ***41***, 342 (1968).
17. Kubicki, J., *Chem. Stosow.* ***3A***, 287 (1966).
18. Berak, J. and Znamierowska, T., *Rocz. Chem.* ***47***, 1137 (1973).
19. Fuchs, L. H., Olsen, E., and Henderson, E. P., *Geochim. Cosmochim. Acta* ***31***, 1711 (1967).
20. Kaprálik, I. and Potančok, M., *Chem. Zvesti* ***25***, 266 (1971).
21. Lindqvist, O. and Wengelin, F., *Ark. Kemi* ***28***, 179 (1967).
22. Proks, I., unpublished results.
23. Welch, J. H., *J. Sci. Instrum.* ***31***, 458 (1954).
24. Welch, J. H., *J. Sci. Instrum.* ***38***, 402 (1961).
25. Majling, J., *Thesis*. Slovak Academy of Sciences, Bratislava, 1971.

Translated by J. Majling