The phase equilibria study in the system $Mg_3(PO_4)_2$—Na_3PO_4

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The system $Mg_3(PO_4)_2$—Na_3PO_4 was studied by means of DTA, hot-stage microscopy, and X-ray diffraction analysis. The system is of quasi-binary character. There are two ternary compounds in it, $Mg_4Na(PO_4)_3$ and $MgNaPO_4$. The former compound melts incongruently (1165°C) and the latter one decomposes probably in the solid state.

The system $Mg_3(PO_4)_2$—Na_3PO_4 represents the section through the three-component system MgO—Na_2O—P_2O_5. Its study is a part of the investigation on the phase coexistence in the system MgO—CaO—Na_2O—P_2O_5. Within the system studied the existing literature data concern only single compounds $Mg_3(PO_4)_2$, $MgNaPO_4$, and Na_3PO_4.

$Mg_3(PO_4)_2$ melts, according to *Berak* [1], congruently at 1357°C and undergoes transition at 1055°C. *Sarver*, *Katnack*, and *Hummel* [2] did not confirm this transition. The crystal structure of $Mg_3(PO_4)_2$ is known [3]. Its powder pattern is given by [3, 4].

Na_3PO_4 melts congruently too. *Turkdogan* and *Maddocks* [5] determined its melting point and transition by DTA at 1583 and 1474°C respectively.

Osterheld and *Bahr* [6] determined melting point of Na_3PO_4 by means of hot-stage microscope at the temperature of 1512°C and the transition by DTA at 340°C. *Bergman* and *Shanzharova* [7] gave for Na_3PO_4 three transitions at 240, 320, and 420°C; all of them were determined by DTA. Two modifications of Na_3PO_4 have been up to now fully described by their powder diffraction patterns, low temperature-tetragonal modification [8], and high temperature-cubic modification [8, 9].

$MgNaPO_4$ was described by *Berul'* and *Voskresenskaya* [10] and *Kaprálik* [11]; in both cases during the study of $NaPO_3$—MgO system, representing other section through the three-component system MgO—Na_2O—P_2O_5. The authors [10] give for $MgNaPO_4$ one reaction at 800°C, whereas the author [11] shows DTA curve of $MgNaPO_4$ on which five endothermic effects exist.

Experimental

The diluted water solutions of $Mg(NO_3)_2$, $NaNO_3$, and $NH_4H_2PO_4$ were used for samples preparation. Individual solutions were mixed together in the volume proportions according to the desired concentrations. $Mg(NO_3)_2$ solution was prepared by dissolving the Mg metal (99.9%) in nitric acid. The solutions of $NaNO_3$ and $NH_4H_2PO_4$ were obtained by dissolution of $NaNO_3$ and $NH_4H_2PO_4$ (anal. grade chemicals) in water. The resulting solutions were slowly evaporated. After evaporation, the dry precursors were heated at 600°C to liberate the fluid components and to decompose nitrates. The final heating was accomplished at 800°C after 10 hours.

Slowly cooled samples were analyzed by X-ray powder diffraction. Powder patterns were taken on a Philips 1540 diffractometer (Ni filtered CuK_α radiation) at the rate 1°

2Θ/min. In some instances the silicon was used as an internal standard ($a_0 = 5.43062$ Å) and the patterns were taken at the scanning rate 1/4° 2Θ/min.

Each sample was subjected to DTA on the Netsch apparatus. Analyses were performed during heating at the heating rate 10°C/min. The temperature was measured by Pt/Pt—10% Rh thermocouple. 200 mg of the sample was taken into analysis.

Liquidus temperatures were determined by the direct observation of samples in a hot-stage microscope Griffin—Telin. The microscope is equipped with Pt—5% Rh/Pt—20% Rh thermocouple, which serves as a sample holder and heating element simultaneously [12, 13]. The thermocouple of the microscope was calibrated against melting points of NaCl and K_2SO_4 and the transition (573°C) of K_2SO_4. The reproducibility of temperature measurement was ±5°C in the case of hot-stage microscope and ±5—7°C in the case of DTA.

Results and discussion

DTA study

On the basis of DTA results the phase diagram of the system $Mg_3(PO_4)_2$—Na_3PO_4 was constructed (Fig. 1). The usual abbreviated notation is used in the paper: M — MgO, N — Na_2O, P — P_2O_5.

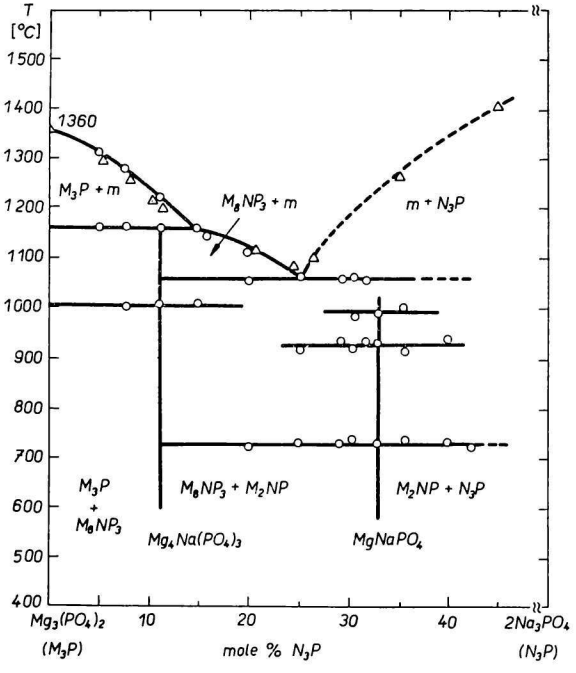

Fig. 1. The phase diagram of the system $Mg_3(PO_4)_2$—$2Na_3PO_4$ (M_8NP_3 — $Mg_4Na(PO_4)_3$, M_2NP — $MgNaPO_4$).
△ hot-stage microscopy; ○ DTA.

The samples which contained more than 50.0 mole % $2Na_3PO_4$ exhibited no thermal effects in the whole temperature interval. The temperatures of isothermal reactions in the system were read from the maxima of DTA signals. The liquidus temperatures were deduced from the points at which extrapolated base lines and tangents to the steep-descending portions of peaks intersected. These temperatures are in Fig. 1 denoted by open circles.

According to the phase diagram two ternary phases are present in the system. The first of them, $Mg_4Na(PO_4)_3$ (M_8NP_3), melts incongruently at 1165°C and undergoes a transition at 1005°C. Its chemical composition was deduced from the intensities of endothermic signals accompanying the incongruent melting. The second compound, $MgNaPO_4$ (M_2NP), undergoes transitions at 580, 725, 925, and 990°C. The transition at 990°C was accompanied by a minute thermal effect observed only in the case of three samples. The behaviour of this compound above 990°C has not been as yet clarified. It is possible that already the reaction at 920°C represents the decomposition of Na_3PO_4 in the solid state. The thermal effects associated with the end of a primary field of crystallization were in the case of the sample of $MgNaPO_4$ composition and the neighbouring samples below the limit of detection. On the DTA curve of $Mg_3(PO_4)_2$, in agreement with [2] no thermal effect was observed corresponding to the transition of this compound.

X-ray diffraction analysis

The concentrations of samples analyzed on the presence of phases are shown in Table 1. The concentrations are expressed also by the figurative points the samples would attain in the three component system $MgO-Na_2O-P_2O_5$.

In the last colum of Table 1 the identified phases are listed, together with their informatively estimated quantity. The compound $Mg_4Na(PO_4)_3$ was identified in agreement with DTA results. The list of its powder diffraction lines is shown in Table 2.

Table 1

The results of X-ray diffraction phase analysis in the system $Mg_3(PO_4)_2-Na_3PO_4$

Chemical composition [mole % $2Na_3PO_4$]	Figurative point in the system M—N—P	Identified phases [quantity in %]*	
0	M_3P	M_3P (100)	
5.11	$M_{17}NP_6$	M_8NP_3 (60),	M_3P (40)
11.11	M_8NP_3	M_8NP_3 (100)	
22.22	$M_7N_2P_3$	M_2NP (60),	M_8NP_3 (40)
30.61	$M_{27}N_{12}P_{13}$	M_2NP (90),	M_8NP_3 (10)
33.33	M_2NP	M_2NP (100)	
36.36	$M_{21}N_{12}P_{11}$	M_2NP (100)	
44.44	$M_5N_4P_3$	α-N_3P (100)	
66.66	MN_2P	α-N_3P (100)	
98.00	$MN_{49}P_{50/3}$	α-N_3P (100)	

* The quantity of phases identified is of informative character. M — MgO, N — Na_2O, P — P_2O_5.

Table 2

The list of X-ray powder diffraction lines for $Mg_4Na(PO_4)_3$ and $MgNaPO_4$

$Mg_4Na(PO_4)_3$				$MgNaPO_4$			
d_{hkl} [Å]	I/I_0	d_{hkl} [Å]	I/I_0	d_{hkl} [Å]	I/I_0	d_{hkl} [Å]	I/I_0
7.61	100	2.865	10	4.43	5	2.23	5
5.84	40	2.763	20	4.22	2	2.13	2
5.03	10	2.727	3	3.92	80	2.07	2
4.67	2	2.658	30	3.83	5	1.96	5
4.125	75	2.622	3	3.53	2	1.89	2
3.975	15	2.559	5	3.07	70	1.86	3
3.760	3	2.511	40	2.79	40	1.79	15
3.573	5	2.466	30	2.52	100	1.77	5
3.539	4	2.448	15	2.45	2	1.70	5
3.164	40	2.335	5	2.39	2	1.65	10
3.089	5	2.268	5	2.32	20	1.64	5
3.003	60	2.181	10	2.27	5	1.59	-

The sample of composition corresponding to $MgNaPO_4$, also in agreement with DTA results, represented an individual phase and accordingly in its powder pattern no lines of $Mg_4Na(PO_4)_3$ and Na_3PO_4 were present. Modification changes of $MgNaPO_4$ are reversible [11] and the list of the diffraction lines in Table 2 represents the low-temperature modification.

It was found out that small amounts of $Mg_3(PO_4)_2$ (1—2 wt %) stabilize Na_3PO_4 in its cubic modification (α-Na_3PO_4). This modification can be stabilized also by additions of MgO [9] and CaO. The powder pattern given for Na_3PO_4 by [14] represents also this modification of Na_3PO_4.

In the concentration region of the system from 66.7 mole % $2Na_3PO_4$ the cubic modification of Na_3PO_4 is present as the only crystalline phase (α-$Na_3PO_{4\,ss}$). In the concentration region 50.0—66.7 mole % $2Na_3PO_4$ one phase is also present, which is, as seen from the profiles of diffraction lines, characterized by the lesser degree of ordering. The powder pattern characteristic of this phase includes all diffraction lines of the cubic modification of Na_3PO_4 and a few of the other, unidentified lines of low intensities.

Hot-stage microscopy

The equilibrium between primary crystalline phases and the melt was determined by means of a hot-stage microscope. According to the results achieved the system appeared to be stable only in its concentration region from $Mg_3(PO_4)_2$ to the eutectic composition (25 mole % $2Na_3PO_4$).

In this concentration region liquidus temperatures (triangles in Fig. 1) are in sufficient agreement with DTA results. In the concentration range of the system, from the eutectic composition to Na_3PO_4, it was not possible to measure the equilibrium liquidus temperatures, but only the liquidus temperatures in their instantaneous values, depending on the heating rate of samples. The system in this concentration region does not satisfy the requirements imposed on the condensed systems and the more exact results can be achieved when conducting the experiments within a closed system.

The liquidus temperatures determined in this region during rapid heating of samples

(heating rate 20—50°C/s) were continuously lowered, because of the change in chemical composition taking place as a result of evaporation. From the lowering of liquidus temperatures the preferred evaporation of the melt constituents with a stoichiometry close to that of Na_3PO_4 can be judged.

The primary crystalline phase (α-Na_3PO_4) exhibited in the whole concentration region the same character; optical isotropy and skeletal crystal growth.

The melting point temperature of the pure Na_3PO_4 was, in agreement with *Osterheld* and *Bahr* [6], determined at 1510°C.

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