

The phase coexistence in the system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$

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The phase coexistence has been determined in the system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ by means of X-ray powder diffraction, DTA, and hot-stage microscopy. There are three ternary compounds present in the system $\text{CaNa}_4(\text{PO}_3)_6$, $\text{CaNa}(\text{PO}_3)_3$, and $\text{MgNa}(\text{PO}_3)_3$. The existence of the further three ternary compounds reported in the literature has not been confirmed ($\text{MgNa}_4(\text{PO}_3)_6$, $\text{MgNa}_2(\text{PO}_3)_4$, $\text{Ca}_2\text{Mg}(\text{PO}_3)_6$). No quaternary phase is present.

The system $2\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ represents the section through the four-component system $\text{Na}_2\text{O—MgO—CaO—P}_2\text{O}_5$, at a constant content of 50 mole % of P_2O_5 . The terminology is related to the basic four-component system. The compounds NaPO_3 , $\text{Mg}(\text{PO}_3)_2$, and $\text{Ca}(\text{PO}_3)_2$ melt congruently. It can be expected that the system studied will be of quasi-ternary character.

In the literature only the data about phase equilibria in the partial systems $\text{NaPO}_3\text{—Ca}(\text{PO}_3)_2$ [1, 2], $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2$ [3], and $\text{Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ [4] of the system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ are available.

In the system $\text{NaPO}_3\text{—Ca}(\text{PO}_3)_2$ two intermediate compounds have been determined — $\text{CaNa}_4(\text{PO}_3)_6$, $\text{CaNa}(\text{PO}_3)_3$ — for which, from the crystallographic properties, the unit cell parameters and indexed powder diffraction patterns are given [1].

In the system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2$ three intermediate compounds $\text{MgNa}_4(\text{PO}_3)_6$, $\text{MgNa}_2(\text{PO}_3)_4$, and $\text{MgNa}(\text{PO}_3)_3$ are described [3]. For the compound $\text{MgNa}_2(\text{PO}_3)_4$ the unit cell parameters and the indexed pattern are given. This compound melts congruently. The other two compounds in the system melt incongruently and no diffraction characteristics are given for them.

In the system $\text{Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ the authors [4] judge upon the presence of one intermediate compound of the stoichiometry $2\text{Ca}(\text{PO}_3)_2 \cdot \text{Mg}(\text{PO}_3)_2$ ($\text{Ca}_2\text{Mg}(\text{PO}_3)_6$).

Experimental

The samples were prepared from the presynthesized binary and ternary compounds. The following starting materials were used: $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (anal. grade), CaHPO_4 (anal. grade), $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (chem. grade), $\text{NH}_4\text{H}_2\text{PO}_4$ (anal. grade).

The compound $\text{Ca}(\text{PO}_3)_2$ was prepared by the reaction of $\text{Ca}_2\text{P}_2\text{O}_7$ with $\text{NH}_4\text{H}_2\text{PO}_4$ (800°C/16 hrs). $\text{Ca}_2\text{P}_2\text{O}_7$ was prepared by heating CaHPO_4 (800°C/12 hrs), $\text{Mg}(\text{PO}_3)_2$ was prepared from $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{NH}_4\text{H}_2\text{PO}_4$ (800°C/12 hrs), and $\text{Mg}_2\text{P}_2\text{O}_7$ from $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (1000°C/10 hrs).

Table 1

Results of the phase analysis in subsystems of the system
 $\text{NaPO}_3 - \text{Mg}(\text{PO}_3)_2 - \text{Ca}(\text{PO}_3)_2$

Representative point ^a	Starting compounds (molar ratio) ^b	Thermal treatment [°C/hrs]	Identified phases ^c
System $\text{NaPO}_3 - \text{Mg}(\text{PO}_3)_2$			
MN_2P_3	$\text{MP} + 2\text{NP}$	650/24	M_2NP_3 , NP
M_2NP_3	$2\text{MP} + \text{NP}$	800/24	M_2NP_3
MNP_2	$\text{MP} + \text{NP}$	600/30	M_2NP_3 , NP
		800/5	M_2NP_3 , NP
M_5NP_6	$5\text{MP} + \text{NP}$	800/18	M_2NP_3 , MP
System $\text{Mg}(\text{PO}_3)_2 - \text{Ca}(\text{PO}_3)_2$			
CM_2P_3	$\text{CP} + 2\text{MP}$	800/16	MP, CP
CMP_2	$\text{CP} + \text{MP}$	800/16	MP, CP
C_2MP_3	$2\text{CP} + \text{MP}$	800/16	CP, MP
System $\text{MgNa}(\text{PO}_3)_3 - \text{Ca}(\text{PO}_3)_2$			
$\text{C}_3\text{M}_2\text{NP}_6$	$3\text{CP} + \text{M}_2\text{NP}_3$	650/24	M_2NP_3 , CP
$\text{C}_3\text{M}_4\text{N}_2\text{P}_9$	$3\text{CP} + 2\text{M}_2\text{NP}_3$	600/24	M_2NP_3 , CP
CM_2NP_4	$\text{CP} + \text{M}_2\text{NP}_3$	650/24	M_2NP_3 , CP
$\text{CM}_4\text{N}_2\text{P}_7$	$\text{CP} + 2\text{M}_2\text{NP}_3$	600/20	M_2NP_3 , CP (?)
		700/24	M_2NP_3 , CP (?)
System $\text{MgNa}(\text{PO}_3)_3 - \text{CaNa}_4(\text{PO}_3)_6$			
$\text{CM}_2\text{N}_3\text{P}_6$	$\text{CN}_2\text{P}_3 + \text{M}_2\text{NP}_3$	600/16	M_2NP_3 , CN_2P_3
System $\text{MgNa}(\text{PO}_3)_3 - \text{CaNa}(\text{PO}_3)_3$			
$\text{C}_6\text{M}_2\text{N}_4\text{P}_{12}$	$3\text{C}_2\text{NP}_3 + \text{M}_2\text{NP}_3$	750/15	C_2NP_3 , M_2NP_3
System $\text{MgNa}(\text{PO}_3)_3 - \text{CaNa}(\text{PO}_3)_3 - \text{CaNa}_4(\text{PO}_3)_6$			
$\text{C}_4\text{M}_3\text{N}_8\text{P}_{15}$	$4\text{CN}_2\text{P}_3 + 3\text{MP}$	600/20	CN_2P_3 , M_2NP_3
$\text{CM}_2\text{N}_2\text{P}_5$	$\text{CN}_2\text{P}_3 + 2\text{MP}$	600/20	M_2NP_3 , CN_2P_3 , C_2NP_3 (?)
		700/24	M_2NP_3 , CN_2P_3 , C_2NP_3 (?)
$\text{C}_3\text{M}_2\text{N}_4\text{P}_9$	$3\text{CNP}_2 + \text{M}_2\text{NP}_3$	700/24	M_2NP_3 , C_2NP_3 , CN_2P_3 (?)
$\text{CM}_2\text{N}_2\text{P}_5$	$\text{CNP}_2 + \text{M}_2\text{NP}_3$	700/24	M_2NP_3 , CN_2P_3 , C_2NP_3 (?)

a) Representative points refer to molar ratios of oxides. The symbols M, N, P represent MgO , Na_2O , and P_2O_5 respectively.

b) The symbol CNP_2 introduced in the last two lines of the Table 1, contrary to the other cases does not represent the individual phase but only the stoichiometry of the material used.

c) The ternary compounds in the system do not undergo any transitions. The compound NaPO_3 was in all samples present as $\text{Na}_3\text{P}_3\text{O}_9$ [5]. The compound $\text{Mg}(\text{PO}_3)_2$ was identified according to [6]. The compound $\text{Ca}(\text{PO}_3)_2$ was in all samples present as β modification [7, 8].

The compounds $\text{CaNa}_4(\text{PO}_3)_6$ and $\text{CaNa}(\text{PO}_3)_3$ were prepared from $\text{Ca}(\text{PO}_3)_2$ and NaPO_3 taken in the appropriate proportions (700°C/48 hrs).

The compound NaPO_3 was prepared by dehydration of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and by heating the product at 600°C for 50 hrs.

The syntheses of $\text{MgNa}_4(\text{PO}_3)_6$ and $\text{MgNa}_2(\text{PO}_3)_4$ compounds belonging to the system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2$ and of $\text{Ca}_2\text{Mg}(\text{PO}_3)_6$ belonging to the system $\text{Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ were not successful.

The temperatures and the reaction times reported showed themselves to suffice and the products represented X-ray single phases.

The compound NaPO_3 was identified as a trimer ($\text{Na}_3\text{P}_3\text{O}_9$ [5]). The calculated powder diffraction pattern was used for the identification [6]. Other synthesized compounds were identified according to their published powder diffraction data [1, 3, 7—9].

The powder patterns were taken on a Philips 1540 diffractometer with $\text{CuK}\alpha$ radiation. Some of the samples belonging to the sections $\text{Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$, $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2$, $\text{MgNa}(\text{PO}_3)_3\text{—CaNa}_4(\text{PO}_3)_6$ were investigated also by means of DTA (Derivatograph, MOM, Budapest) and by a hot-stage microscope (Griffin 6000 [10, 11]). In both last cases analyses were performed in the course of heating, in the case of DTA at a heating rate 10°C/min on 350 mg samples.

Results and discussion

The system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$ was studied in its particular sections. The results of the phase analysis are listed in Table 1.

The samples were allowed to react at subsolidus temperatures (except the sample MNP_2 ; Table 1). The prolonged heating did not lead to the change in the phase composition.

The symbols used in Table 1 represent: M — MgO , N — Na_2O , P — P_2O_5 . These symbols stand also for the representative points in Table 1 characterizing the stoichiometry of analyzed samples.

The system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2$

The phase diagram of the system proposed on the basis of hot-stage microscopy, X-ray powder diffraction, and some of the DTA measurements is shown in Fig. 1. This diagram differs significantly from the one described in the literature [3].

As mentioned above, the authors [3] described in the phase diagram of the system the presence of three compounds ($\text{MgNa}_4(\text{PO}_3)_6$, $\text{MgNa}_2(\text{PO}_3)_4$, $\text{MgNa}(\text{PO}_3)_3$). The phase diagram was determined on the basis of DTA results. For one of the compounds, $\text{MgNa}_2(\text{PO}_3)_4$, its unit cell parameters were given ($a = 14.343 \text{ \AA}$, $b = 14.258 \text{ \AA}$, $c = 14.198 \text{ \AA}$).

Our X-ray powder diffraction analysis revealed the presence of the only intermediate phase. We pursued the own phase equilibria study in the system only in an extent to clarify the contradiction.

According to our results (Fig. 1) the stoichiometry of the only intermediate phase can be derived from the composition corresponding to $\text{MgNa}(\text{PO}_3)_3$. This phase is characterized by the powder diffraction pattern and unit cell parameters which the authors [3] ascribed to the compound $\text{MgNa}_2(\text{PO}_3)_4$. The compound of this stoichiometry as well as of $\text{MgNa}_4(\text{PO}_3)_6$ stoichiometry we did not detect and the phases present in the samples of relevant composition (Table 1) are consistent with Fig. 1.

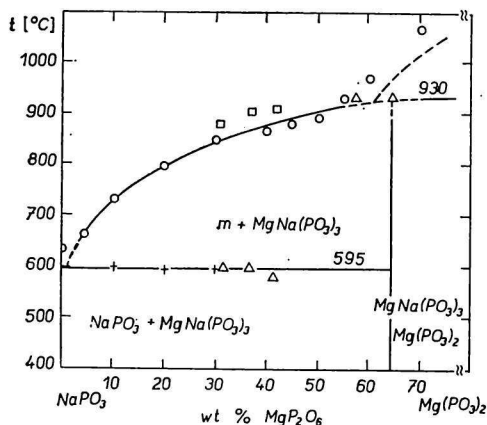


Fig. 1. Phase diagram of the system $\text{NaPO}_3\text{--Mg}(\text{PO}_3)_2$.

- liquidus temperatures determined by the hot-stage microscope;
- + "collapse" temperatures of samples according to the hot-stage microscope;
- △ temperatures of isothermal reactions determined by DTA;
- liquidus temperatures according to DTA.

The isolated crystals of the intermediate compound were chemically analyzed on the presence of MgO and P_2O_5 . The following results were obtained: MgO — 14.8 wt %, P_2O_5 — 74.9 wt %. The theoretical content of MgO and P_2O_5 in $\text{MgNa}(\text{PO}_3)_3$ gives the value: MgO — 14.2 wt %, P_2O_5 — 74.9 wt %.

The pycnometrically determined density of the crystals (D_m) equals 2.54 g cm^{-3} . This value is consistent with the molecular weight of $\text{MgNa}(\text{PO}_3)_3$, its unit cell parameters (see above) and 16 formula units in the unit cell ($D_x = 2.59 \text{ g cm}^{-3}$). The X-ray density, D_x , calculated for the formula $\text{MgNa}_2(\text{PO}_3)_4$ gives the value 2.64 g cm^{-3} .

Crystals of the intermediate compound were prepared by cooling the melt of composition 50 wt % of $\text{Mg}(\text{PO}_3)_2$ from the temperature close to liquidus temperature (900°C) and by dissolving the free NaPO_3 after cooling in water.

The system $\text{NaPO}_3\text{--Mg}(\text{PO}_3)_2$ according to the hot-stage microscopy appeared to be stable only in the concentration region up to 55 wt % $\text{Mg}(\text{PO}_3)_2$. The liquidus temperatures (empty circles in Fig. 1) in the other concentration part were appreciably higher with a prolonged heating.

The system $\text{Mg}(\text{PO}_3)_2\text{--Ca}(\text{PO}_3)_2$

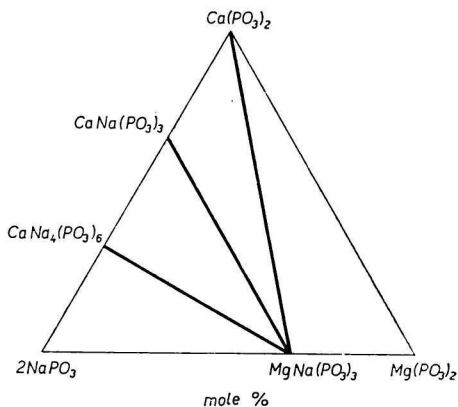
According to the DTA and the powder diffraction the system is of quasi-binary character. Analyzed samples (10, 20, 30, ..., 60 wt % $\text{Mg}(\text{PO}_3)_2$) exhibited on DTA records the only endothermic reaction, according to the starts of deflections at 950°C .

According to the hot-stage microscopy the system is not stable at liquidus temperatures. In the subsolidus region of the system only the phases $\text{Mg}(\text{PO}_3)_2$ and $\beta\text{-Ca}(\text{PO}_3)_2$ were present. The existence of the compound $\text{Ca}_2\text{Mg}(\text{PO}_3)_6$ [4] was not confirmed.

The system $\text{MgNa}(\text{PO}_3)_3\text{--CaNa}_4(\text{PO}_3)_6$

In the subsolidus part of the system the phases $\text{MgNa}(\text{PO}_3)_3$ and $\text{CaNa}_4(\text{PO}_3)_6$ were present. In the whole concentration region only one isothermal reaction was observed, according to the starts of deflections at 720°C . The start and the end of the endothermic deflection accompanying melting of $\text{MgNa}(\text{PO}_3)_3$ lie at the temperatures 930 and 970°C , respectively. The melting point of $\text{MgNa}(\text{PO}_3)_3$, according to the start of the deflection is in good agreement with the melting point determined by the hot-stage microscope.

Fig. 2. The phase coexistence in the system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$.



The system $\text{NaPO}_3\text{—Mg}(\text{PO}_3)_2\text{—Ca}(\text{PO}_3)_2$

The coexistence of phases present in the system is depicted in Fig. 2. Contrary to the results reported in the literature [3, 4], the existence of the compounds described as $\text{MgNa}_4(\text{PO}_3)_6$, $\text{MgNa}_2(\text{PO}_3)_4$, and $\text{Ca}_2\text{Mg}(\text{PO}_3)_6$ was not confirmed. No quaternary phase was detected to be present.

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