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Phase equilibria in the ternary system $MgO–Na_2O–P_2O_5$. The partial system $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$

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Abstract

The $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$ subsystem of the ternary system $MgO–Na_2O–P_2O_5$ was investigated using thermal analysis (heating and cooling), X-ray diffraction techniques and microscopy in reflected light. Three intermediate compounds: $Mg_4Na(PO_4)_3$, $MgNaPO_4$ and $MgNa_4(PO_4)_2$ occur in the partial system. $Mg_4Na(PO_4)_3$ melts incongruently at 1155 °C, $MgNa_4(PO_4)_2$ melts congruently at 1655 °C, whereas $MgNaPO_4$ exists only in the solid phase and decomposes at 950–960 °C. A phase diagram for the partial system is proposed. It has been established that the $MgNa_4(PO_4)_2$ phosphate forms a binary system with $Na_4P_2O_7$. A phase diagram of this system has been constructed. It has been found that a ternary peritectic ($t_P = 1145 \pm 3.0\,°C$) and two ternary eutectics ($t_{E_1} = 984 \pm 3.0\,°C$, $t_{E_2} = 732 \pm 1.5\,°C$) occur in the $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$ system. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Partial systems; Binary phosphates; Ternary systems

1. Introduction

In the present paper, the results of a study on the ternary system $MgO–Na_2O–P_2O_5$ are reported. The goal of the research was to construct a phase diagram of the $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$ subsystem.

The subsystem is bounded by four side systems: (1) $MgO–Mg_3(PO_4)_2$, (2) $Mg_3(PO_4)_2–Mg_4Na(PO_4)_3$, (3) $Mg_4Na(PO_4)_3–Na_4P_2O_7$ and (4) $MgO–Na_4P_2O_7$. The different substances are described in detail in the literature. Relevant information can be found, for instance, about MgO in [1–3], $Mg_3(PO_4)_2$ [4–12] and $Na_4P_2O_7$ [13–16]. Characteristic properties of the magnesium–sodium double phosphates which occur in the investigated composition range can also be found: $Mg_4Na(PO_4)_3$ [10–12,17–19], $MgNaPO_4$ [10,11,20–25] and $MgNa_4(PO_4)_2$ [11,18,26,27]. The three phosphates occur as intermediate compounds formed in the $Mg_3(PO_4)_2–Na_3PO_4$ system. The phase diagrams of the first three of the four side systems mentioned above are known.

The $MgO–Mg_3(PO_4)_2$ system is a simple eutectic system. Its phase diagram is given in [4]. The composition and temperature of the eutectic are 48 ± 1.0 wt.% MgO, and $1325 \pm 3.0\,°C$, respectively. The other two side systems have been worked out by the present author [11,12,28]. In the fourth side system, i.e. $MgO–Na_4P_2O_7$, an intermediate compound—$MgNa_4(PO_4)_2$ occurs. This phosphate melts congruently at 1655 °C and occurs in three polymorphic modifications. $MgNa_4(PO_4)_2$ divides the

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$MgO–Na_4P_2O_7$ system into two partial systems: (1) $MgO–MgNa_4(PO_4)_2$ and (2) $MgNa_4(PO_4)_2–Na_4P_2O_7$. The former partial system has been worked out within a composition range 60–100 wt.% $MgNa_4(PO_4)_2$ up to a temperature of 1800 °C [27]. The remaining part of the system was not examined because of the high melting point of the samples. The system is a simple eutectic system. The eutectic's composition is approximately 4 ± 1.0 wt.% MgO and 96 ± 1.0 wt.% $MgNa_4(PO_4)_2$ and its temperature is 1630 ± 30.0 °C. The $MgNa_4(PO_4)_2–Na_2P_2O_7$ system was unknown. It has been worked out by the present author and its phase diagram is presented in this paper.

The $MgO–Mg_4Na(PO_4)_3$ section occurs in the $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$ subsystem. The section's phase diagram can be found in [29]. The section has been worked out in a composition range 60–100 wt.% $Mg_4Na(PO_4)_3$ up to a temperature of 1800 °C. $Mg_4Na(PO_4)_3$ melts incongruently and as a result at high temperatures $MgO–Mg_4Na(PO_4)_3$ is multiphase, consisting of four phases: a liquid, $Mg_3(PO_4)_2$, $Mg_4Na(PO_4)_3$ and MgO. Below a temperature of 1145 °C only two phases coexist, i.e. MgO and $Mg_4Na(PO_4)_3$. In the subsolidus region, the section is a real binary system.

2. Experimental

The samples were prepared from ready-made reagents and in-house synthesized compounds. The ready-made reagents included the following analytical grade materials: magnesium oxide MgO, $MgHPO_4 \cdot 3H_2O$, $Na_2HPO_4 \cdot 2H_2O$, $Na_3PO_4 \cdot 12H_2O$ and Na_2CO_3. MgO was annealed at 1000 °C for 1 h. Na_2CO_3 was annealed at 200 °C for 3 h. Magnesium diphosphate $Mg_2P_2O_7$ was obtained by completely dehydrating $MgHPO_4 \cdot 3H_2O$ at 900 °C for 1 h. Orthophosphate $Mg_3(PO_4)_2$ was synthesized from $Mg_2P_2O_7$ and MgO by annealing the initial components at 1200 °C for 20 min. $Na_4P_2O_7$ was synthesized by heating $Na_2HPO_4 \cdot 2H_2O$ at 200 °C for 1 h. Orthophosphate Na_3PO_4 was obtained by slowly dehydrating $Na_3PO_4 \cdot 12H_2O$ at a 200 °C and subsequently at 300 and 600 °C. $Mg_4Na(PO_4)_3$ was obtained by heating the $Mg_3(PO_4)_2–Na_3PO_4$ mixture (with a molar ratio of 4:1) at 900 °C for 72 h. $MgNa_4(PO_4)_2$ was synthesized via a solid state reaction (at 900 °C for 72 h) from different parent substances, namely: (1) $Mg_3(PO_4)_2$ and Na_3PO_4 mixed in a 1:4 molar ratio, (2) MgO and $Na_4P_2O_7$ mixed in a 1:1 molar ratio, (3) $Mg(PO_3)_2$ and Na_2CO_3 mixed in a 1:2 molar ratio. $MgNaPO_4$ was synthesized via a conventional solid state reaction (600–900 °C, 72–96 h) from different initial materials such as $Mg_3(PO_4)_2$ and Na_3PO_4, MgO and $NaPO_3$, and $Mg_2P_2O_7$ and Na_2CO_3.

The samples were investigated using differential thermal analysis (DTA) for heating and cooling, X-ray diffraction analysis, and microscopy in reflected light. DTA for heating was performed by means of a type-C derivatograph (MOM, Hungary); the heating rate was 5 °C/min in a temperature range 20–1350 °C. The standard substance was Al_2O_3. Platinum crucibles in an air atmosphere were used. Samples weighing 0.2–0.9 g were used for derivatography. DTA for cooling was carried out using a resistance furnace (an in-house design) with a PtRh30 winding. The temperature was measured by a Pt/PtRh10 thermocouple standardized for the melting points of the following substances: NaCl (801 °C), K_2SO_4 (1070 °C) and $Ca_2P_2O_7$ (1353 °C) and for the K_2SO_4 polymorphic transition temperature (583 °C). Three gram samples crystallized with grafting were used. Above 1350 °C, the thermal investigations were conducted in an atmosphere of argon in a horizontal resistance furnace with a molybdenum winding. The samples were pressed into 1–2 g pellets and placed into small boats made of PtRh30 melt. The temperature was read out by an optical pyrometer calibrated against the melting points of Na_3PO_4 (1583 °C) and $Ca_3(PO_4)_2$ (1810 °C). In the thermal analysis, the temperature read-out accuracy was ± 1.5 °C in a temperature range up to 800 °C, ± 3 °C above 800 °C, and ± 30 °C when the temperature was read out by the optical pyrometer. The composition of the samples was determined with an accuracy of ± 1.0 wt.% for the binary system and ± 3.0 wt.% for the ternary system.

The samples for phase investigations in both the binary systems and the whole partial system were prepared in a similar way. The initial substances were weighed out in fixed amounts, then thoroughly mixed and ground in an agate mortar to attain their homogeneity. To improve the contact area between the substances, the weighed portions were pressed into pellets. Then the samples were presynthesized by sintering (in the solid phase). The sintering temperature and the presynthesis time in relation to the initial composition of the samples were determined experimentally. Some of the samples showed a tendency to glaze. To promote the crystallization (at least partial) of the samples, slow cooling (2 °C/min) with frequent grafting was employed. Microsections of the melts were prepared and examined by microscopy in reflected light. Also visual observation of the samples during heating was conducted. The observation consisted in the recording of the temperature at which the first traces of liquid appeared and the temperature at which the sample became transparent. On the basis of the microscopic examinations, the purity of the substances and the phase constitution of the melts were estimated. The phases in the partial system were identified and the phase purity of the substances was determined by X-ray powder diffraction using Siemens diffractometers D 5000 and HZG 4 with Cu Kα radiation and a Ni-filter.

3. Results

The $MgNa_4(PO_4)_2$–$Na_4P_2O_7$ binary system in the MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system was investigated and the phase diagram was constructed for the whole range of composition and temperature. Samples of the $MgNa_4(PO_4)_2$–$Na_4P_2O_7$ system were presynthesized at 600 °C for 72 h and then melted. The phase diagram of the $MgNa_4(PO_4)_2$–$Na_4P_2O_7$ binary system is shown in Fig. 1. The components form a simple eutectic system. The eutectic point composition and temperature are 58.0 ± 1.0 wt.% $MgNa_4(PO_4)_2$, 42.0 ± 1.0 wt.% $Na_4P_2O_7$ and 900 ± 3.0 °C. Since the samples rich in $MgNa_4(PO_4)_2$ melted at high temperatures, an optical pyrometer (with an accuracy of ±30 °C) was used to read the temperatures. The approximate liquidus curve in this region is marked by a dashed line in the phase diagram.

Sodium diphosphate ($Na_4P_2O_7$) shows three polymorphic transitions. In the pure compound, the transition occurs at: 390 °C for α/β-$Na_4P_2O_7$, 512 °C for β/γ-$Na_4P_2O_7$ and 550 °C for γ/δ-$Na_4P_2O_7$. Magnesium sodium phosphate ($MgNa_4(PO_4)_2$) shows two polymorphic transitions which occur at: 396 °C for α/β-$MgNa_4(PO_4)_2$ and 821 °C for β/γ-$MgNa_4(PO_4)_2$. The low-temperature, polymorphic α/β transitions of both phosphates produce a clearly visible, joint thermal effect in the heating DTA curves. Whereas the cooling DTA curves show two successive thermal effects. The thermal effects corresponding to high-temperature transitions β/γ-$Na_4P_2O_7$ and γ/δ-$Na_4P_2O_7$ occur in a composition range 20–100 wt.% $Na_4P_2O_7$. The β/γ-$MgNa_4(PO_4)_2$ transition (at 821 °C) hardly proceeds in the system and leads to visible thermal effects in the DTA curves only in the $MgNa_4(PO_4)_2$-rich composition range. One can infer that a high $Na_4P_2O_7$ content inhibits the β/γ-$MgNa_4(PO_4)_2$ polymorphic transition.

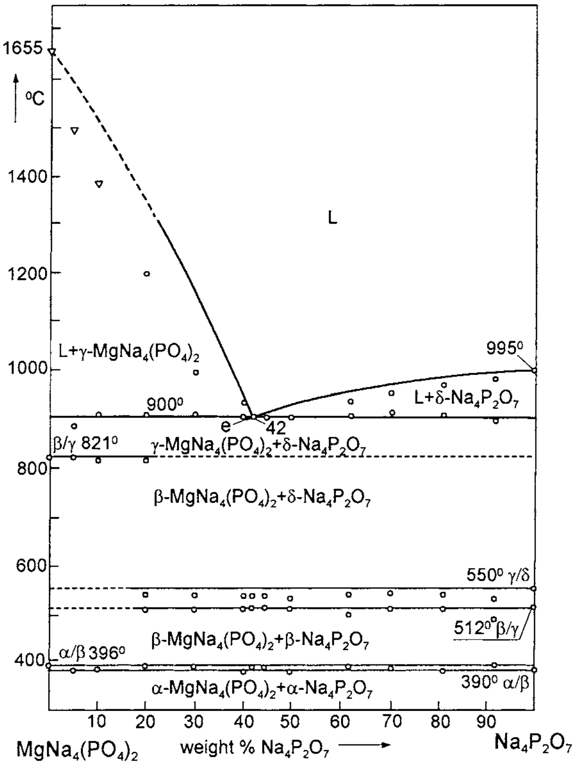

Fig. 1. Phase diagram of $MgNa_4(PO_4)_2$–$Na_4P_2O_7$ system; (L) liquid, (○) DTA of cooling, (△) optical.

4. Discussion

The phase diagram of the MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system, with solidification isotherms, is shown in Fig. 2. The composition range can be divided into three partial ternary systems: (1) MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$, (2) MgO–$Mg_4Na(PO_4)_3$–$MgNa_4(PO_4)_2$ and (3) $Mg_4Na(PO_4)_3$–$MgNa_4(PO_4)_2$–$Na_4P_2O_7$. Since there are five phosphates, five fields

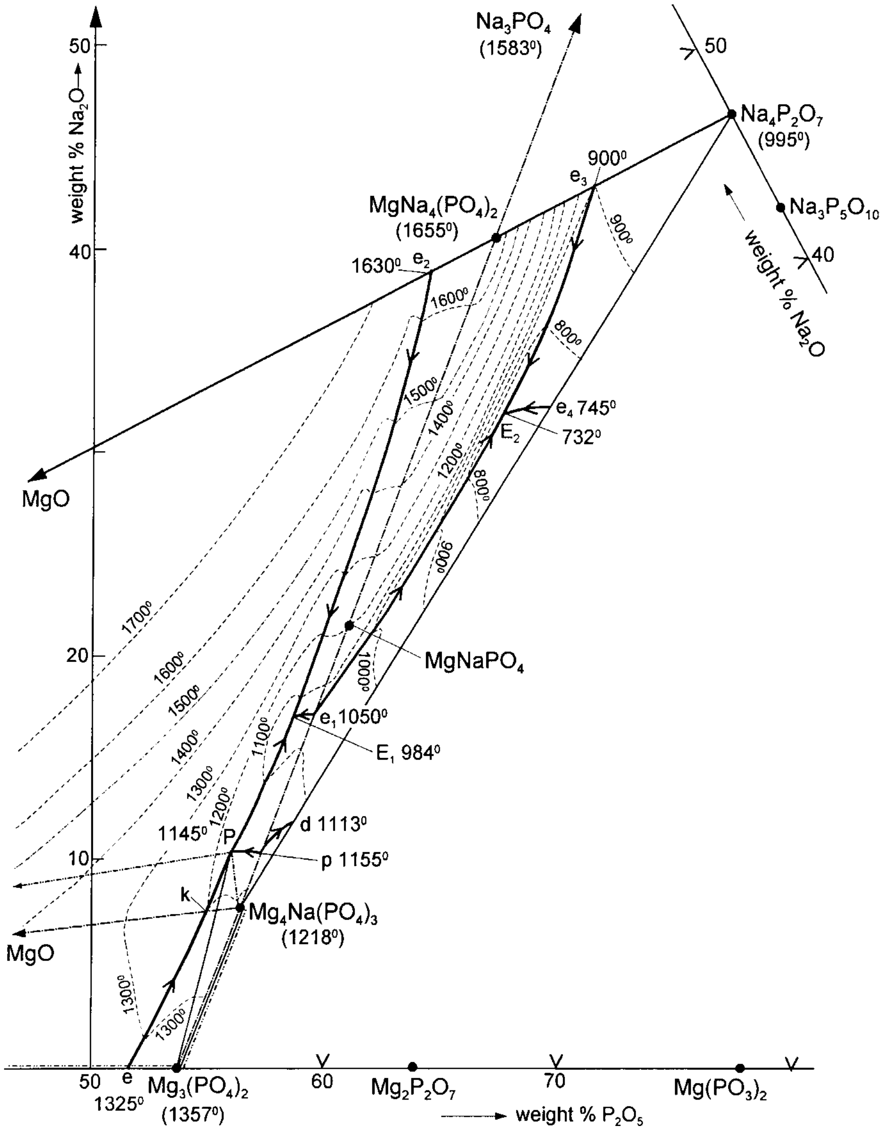

Fig. 2. Phase diagram of MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system including solidification isotherms.

of primary crystallization exist, see Fig. 3. The three ternary invariants, corresponding to one ternary peritectic and two ternary eutectics are as follows:

1. Ternary peritectic P at 1145 ± 3.0 °C corresponds to the reaction:

   $$\text{liq. P} + Mg_3(PO_4)_2 \leftrightarrow Mg_4Na(PO_4)_3 + MgO$$

   The composition of P: 39.0 ± 3.0 wt.% MgO, 10.6 ± 3.0 wt.% Na_2O, 50.4 ± 3.0 wt.% P_2O_5.

2. Ternary eutectic E_1 at 984 ± 3.0 °C corresponds to the equilibrium:

   $$MgO + Mg_4Na(PO_4)_3 + MgNa_4(PO_4)_2 \leftrightarrow \text{liq. } E_1$$

   The composition of E_1: 17.5 ± 3.0 wt.% MgO, 31.9 ± 3.0 wt.% Na_2O, 50.6 ± 3.0 wt.% P_2O_5.

3. Ternary eutectic E_2 at 732 ± 1.5 °C corresponds to the equilibrium:

   $$Mg_4Na(PO_4)_3 + Na_4P_2O_7 + MgNa_4(PO_4)_2 \leftrightarrow \text{liq. } E_2$$

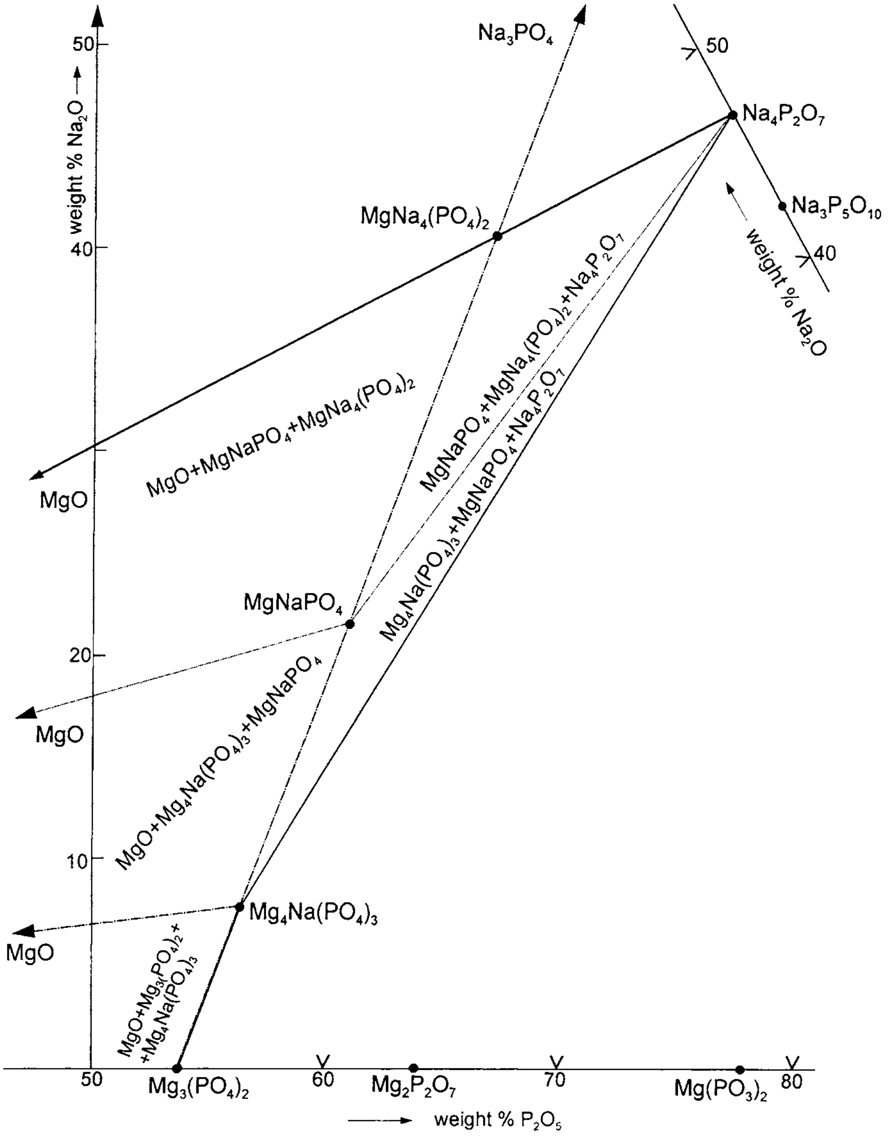

Fig. 3. Isothermal section of MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system at room temperature.

The composition of E_2: 33.0 ± 3.0 wt.% MgO, 17.5 ± 3.0 wt.% Na_2O, 49.5 ± 3.0 wt.% P_2O_5.

The peritectic reaction occurs during the solidification of the molten mixtures corresponding to points in the $Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–P–MgO area (the triple peritectic quadrangle). The reaction ends the solidification of the mixtures corresponding to points within the triple peritectic quadrangle.

As a result of the peritectic reaction, excess of liquid L remains in the molten mixtures representing the $Mg_4Na(PO_4)_3$–P–MgO area.

Thus the further solidification of the molten mixtures proceeds at a varying (from 1145 to 984 °C) temperature along line PE_1 and consists in the separation of the binary eutectic ($Mg_4Na(PO_4)_3$ + MgO). The lines originating from binary eutectics e_1 and e_2 intersect at the point of ternary eutectic E_1. When

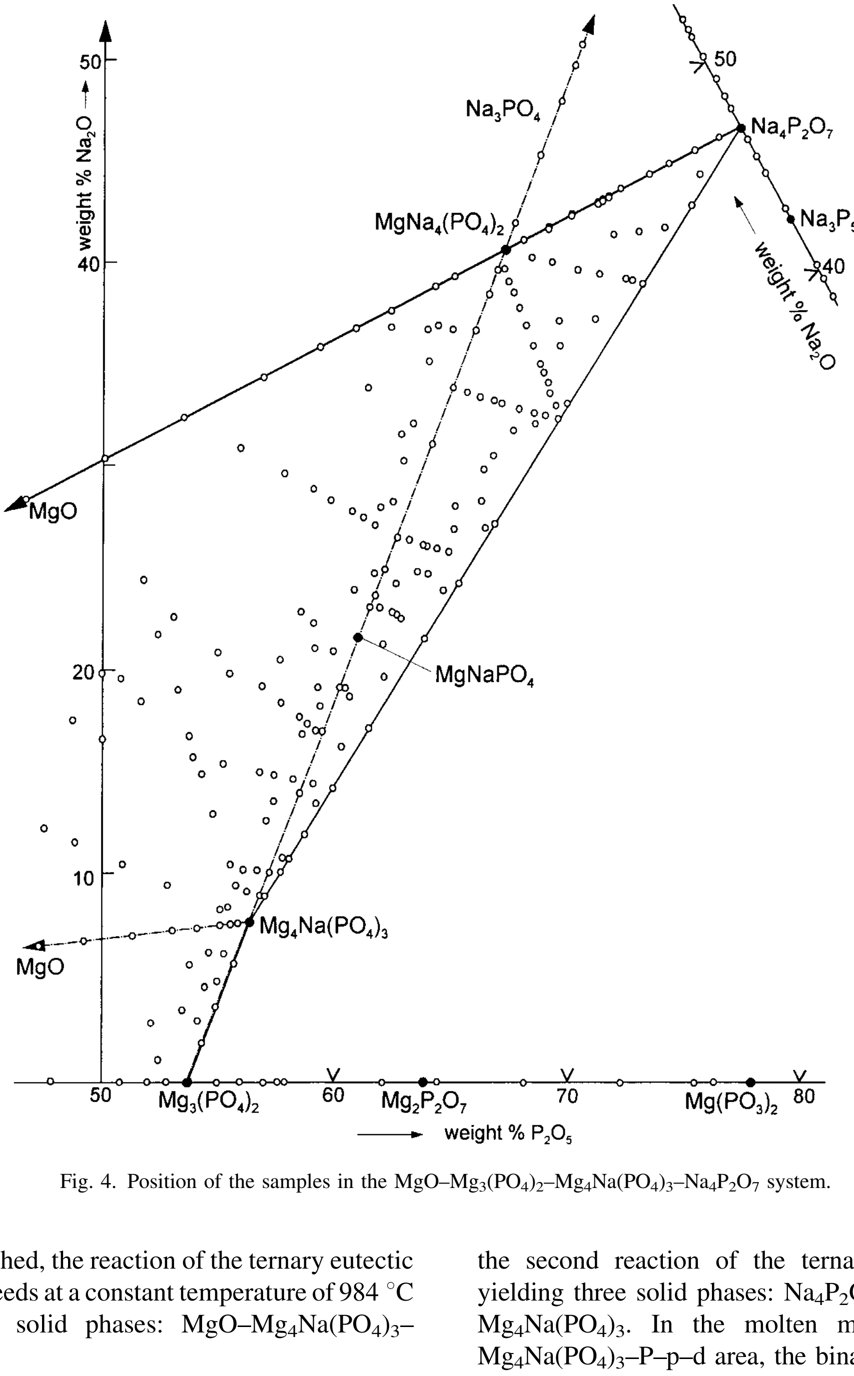

Fig. 4. Position of the samples in the $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$ system.

point E_1 is reached, the reaction of the ternary eutectic starts and proceeds at a constant temperature of 984 °C yielding three solid phases: $MgO–Mg_4Na(PO_4)_3–MgNa_4(PO_4)_2$.

In the ternary system $Mg_4Na(PO_4)_3–MgNa_4(PO_4)_2–Na_4P_2O_7$, the components make up a pseudo-binary system of the eutectic type. The lines originating from binary eutectics e_1, e_3 and e_4 intersect at point E_2 corresponding to a temperature of 732 °C at which the second reaction of the ternary eutectic starts, yielding three solid phases: $Na_4P_2O_7–MgNa_4(PO_4)_2–Mg_4Na(PO_4)_3$. In the molten mixtures from the $Mg_4Na(PO_4)_3$–P–p–d area, the binary peritectic reaction: $Mg_3(PO_4)_2 + L_{Ppd} \rightarrow Mg_4Na(PO_4)_3$ was found to occur. L_{Ppd} denotes liquids whose composition corresponds to points on the P–p–d line.

An intermediate compound $MgNaPO_4$ occurs in the $MgO–Mg_3(PO_4)_2–Mg_4Na(PO_4)_3–Na_4P_2O_7$ system.

This double phosphate forms in the $Mg_3(PO_4)_2$–Na_3PO_4 system at an equimolar ratio of the initial phosphates [11]. It exists in the solid phase only and decomposes in the temperature range 950–960 °C. The present study indicates that the compound occurs in three polymorphic modifications. As a result of presynthesis a mixture of the polymorphs is obtained at room temperature. High-temperature modifications of $MgNaPO_4$ cannot be stabilized at room temperature by freezing with ice. A pure low-temperature modification of $MgNaPO_4$ can be obtained by subjecting the presynthesized compound with an addition of 2–3 wt.% $Na_4P_2O_7$ to prolonged heating at 500–600 °C. The presence of $MgNaPO_4$ plays an essential role in the formation of the phase dependencies in the subsolidus region of the MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system. In this region, the above phosphate forms two hypothetical sections: one with magnesium oxide (MgO) and the other with sodium diphosphate ($Na_4P_2O_7$). The two sections together with the quasi-binary systems described above divide the investigated composition range into five partial ternary systems existing at room temperature, namely:

1. MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$,
2. MgO–$Mg_4Na(PO_4)_3$–$MgNaPO_4$,
3. MgO–$MgNaPO_4$–$MgNa_4(PO_4)_3$,
4. Mg_4Na-$(PO_4)_3$–$Na_4P_2O_7$–$MgNaPO_4$ and
5. $MgNaPO_4$ –$Na_4P_2O_7$–$MgNa_4(PO_4)_2$.

The isothermal section of the MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system at room temperature is shown in Fig. 3. Position of the samples in the MgO–$Mg_3(PO_4)_2$–$Mg_4Na(PO_4)_3$–$Na_4P_2O_7$ system is presented in Fig. 4.

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