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Phase Equilibria in the Ternary System MgO–Na_2O–P_2O_5. The Partial System MgO–Na_3PO_4–$Na_4P_2O_7$

by T. Podhajska-Kaźmierczak[*]

Faculty of Engineering and Economics, Department of Inorganic Chemistry, Wrocław University of Economics, Komandorska 118/120, 53-345 Wrocław, Poland

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A partial system of MgO–Na_3PO_4–$Na_4P_2O_7$ in the ternary system MgO–Na_2O–P_2O_5 was investigated and its phase diagram was obtained. Thermal analysis (heating and cooling), powder X-ray diffraction, and optical microscopy using reflected light were applied. In the composition range of interest two ternary compounds occur, which melt congruently and have the formulae $MgNa_4(PO_4)_2$ (m.p. 1655°C) and $MgNa_6P_2O_9$ (m.p. 1665°C). The phosphates compose a quasi-binary section with continuous solid solutions and exhibit a temperature minimum about 1520°C.

Key words: phase equilibria, magnesium-sodium phosphates, DTA, solid solutions

The aim of this investigation was to elaborate the phase diagram of the partial system MgO–Na_3PO_4–$Na_4P_2O_7$ in the composition range 0–40 wt % (0–67 mol. %) MgO up to 1800°C. The remaining part of the system was not examined because of the high melting point of the samples. The above composition range is limited by three binary side systems: (i) Na_3PO_4–$Na_4P_2O_7$, (ii) MgO–$Na_4P_2O_7$, and (iii) MgO–Na_3PO_4. Starting compounds of the partial system, *i.e.* MgO and sodium phosphates Na_3PO_4 and $Na_4P_2O_7$ as well as the phase diagrams of the two side systems, Na_3PO_4–$Na_4P_2O_7$ [1] and MgO–$Na_4P_2O_7$ [2,3] are known. The system Na_3PO_4–$Na_4P_2O_7$ is a simple eutectic system. The composition and temperature of eutectic point are: 50.2 wt % (69.8 mol. %) Na_2O, 49.8 wt % (30.2 mol. %) P_2O_5, and 944°C. In the MgO–$Na_4P_2O_7$ system an intermediate compound of $MgNa_4(PO_4)_2$ occurs. It melts congruently at 1655°C and shows three polymorphic modifications. The compound divides the side system MgO–$Na_4P_2O_7$ into two quasi-binary systems: 1) MgO–$MgNa_4(PO_4)_2$ [2] and 2) $MgNa_4(PO_4)_2$–$Na_4P_2O_7$ [3]. These two systems are simple eutectic systems, and the parent substances exhibit a perfect intersolubility in the subsolidus region. In the system MgO–$MgNa_4(PO_4)_2$ the parameters of the eutectic mixture are: 4.0 wt % (24.0 mol. %) MgO and 96.0 wt % (76.0 mol. %) $MgNa_4(PO_4)_2$, 1630°C. Composition and temperature of the eutectic in the system $MgNa_4(PO_4)_2$–$Na_4P_2O_7$ are: 58.0 wt % (54.5 mol. %) $MgNa_4(PO_4)_2$, 42.0 wt % (45.5 mol. %) $Na_4P_2O_7$ and 900°C.

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[*] E-mail: tesapk@credit.ae.wroc.pl

EXPERIMENTAL

Samples in the partial system MgO–Na_3PO_4–$Na_4P_2O_7$ were prepared from original reagents and home-synthesized compounds. The following analytically pure reagents were used: MgO, $MgHPO_4 \cdot 3H_2O$, $Na_2HPO_4 \cdot 2H_2O$, $Na_3PO_4 \cdot 12H_2O$. MgO was roasted at 1000°C for 1 h. Magnesium diphosphate $Mg_2P_2O_7$ was obtained *via* complete dehydration of $MgHPO_4 \cdot 3H_2O$ at 900°C for 1 h. Magnesium orthophosphate $Mg_3(PO_4)_2$ was synthesized from MgO and $Mg_2P_2O_7$ by sintering the parent substances (1:1) 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. Na_3PO_4 was obtained by slowly dehydration of $Na_3PO_4 \cdot 12H_2O$ at 200, 300 and finally 600°C. $MgNa_4(PO_4)_2$ was produced by solid state reaction (900°C for 72 h) from different parent substances, namely: 1) $Mg_3(PO_4)_2$ and Na_3PO_4 mixed in a molar ratio of 1:4 and 2) MgO and $Na_4P_2O_7$ mixed in the molar ratio 1:1. $MgNa_6P_2O_9$ was obtained from MgO and Na_3PO_4 mixed in the molar ratio 1:2, by heating the mixture at 900°C for 96 h.

The system MgO–Na_3PO_4–$Na_4P_2O_7$ was examined by differential thermal analysis during heating and cooling (DTA), powder X-ray diffraction, and microscopy in reflected light. Heating DTA was performed by a derivatograph Type 3427 (MOM, Hungary). The heating rate was 5°C/min between 20–1350°C. The standard substance was Al_2O_3 p.a. Platinum crucibles and air atmosphere were employed. Mass of a sample ranged from 0.2 to 0.9 g. DTA of cooling was carried out by a home-made resistance furnace with PtRh30 winding. Temperature was measured with a Pt/PtRh10 thermocouple, calibrated against the melting points of NaCl (801°C), K_2SO_4 (1070°C), $Ca_2P_2O_7$ (1353°C), and the polymorphic transition temperature of K_2SO_4 (583°C). Three-gram samples were used. Thermal examination at temperatures in excess of 1350°C was carried out by using a home-made, horizontal resistance furnace with molybdenum winding in argon. Samples pressed into pellets of 1–2-grams were placed into PtRh30 boats. Melting points were determined by an optical pyrometer calibrated by melting points of Na_3PO_4 (1583°C) and $Ca_3(PO_4)_2$ (1810°C). Accuracy of the temperature was ±30°C above 1350°C, ±3°C above 800°C, and ±1.5°C below 800°C.

The sample preparation in the binary systems as well as in the whole partial system was similar. The only difference was in the conditions of the presynthesis performed in the solid state, *i.e.* its temperature and sintering period. Parameters for the process of synthesis (temperature and time) were found experimentally according to the initial composition of a sample. The initial substances were weighed in fixed amounts and thoroughly mixed, then ground in an agate mortar to attain homogeneity. To improve the contact between the components of such mixtures, they were pressed into pellets and then heated in conditions suitable for obtaining equilibrated samples. Part of the samples, which were $Na_4P_2O_7$-rich and Na_3PO_4-rich, tended to glaze. In order to attain at least a partial crystallization, the samples melting below 1400°C were slowly cooled down (2°C/min) and applied to frequently grafting. Such alloys were used to produce microsections to be checked by microscopy in reflected light. The microscopy was helpful in determination of the phase purity as well as the phase structure of these alloys. X-ray structure analysis was performed by the powder method using a diffractometer type Siemens D-5000 and HZG-4 with CuK_α radiation and Ni filter.

RESULTS AND DISCUSSION

Experimental work in the composition range MgO–Na_3PO_4–$Na_4P_2O_7$ was started with investigation of phase dependences existing in the side system MgO–Na_3PO_4, which were investigated in the subsolidus region in the entire range of composition. However, the liquidus curve has been determined only in the Na_3PO_4-rich part, *i.e.* 60–100 wt % (26.9–100 mol. %) Na_3PO_4, since the rest of the samples melts above 1800°C. Fig. 1 shows the phase diagram of the MgO-Na_3PO_4 system, constructed on the basis of the results of DTA heating, powder X-ray diffraction and, in part, observations by microscopy in reflected light.

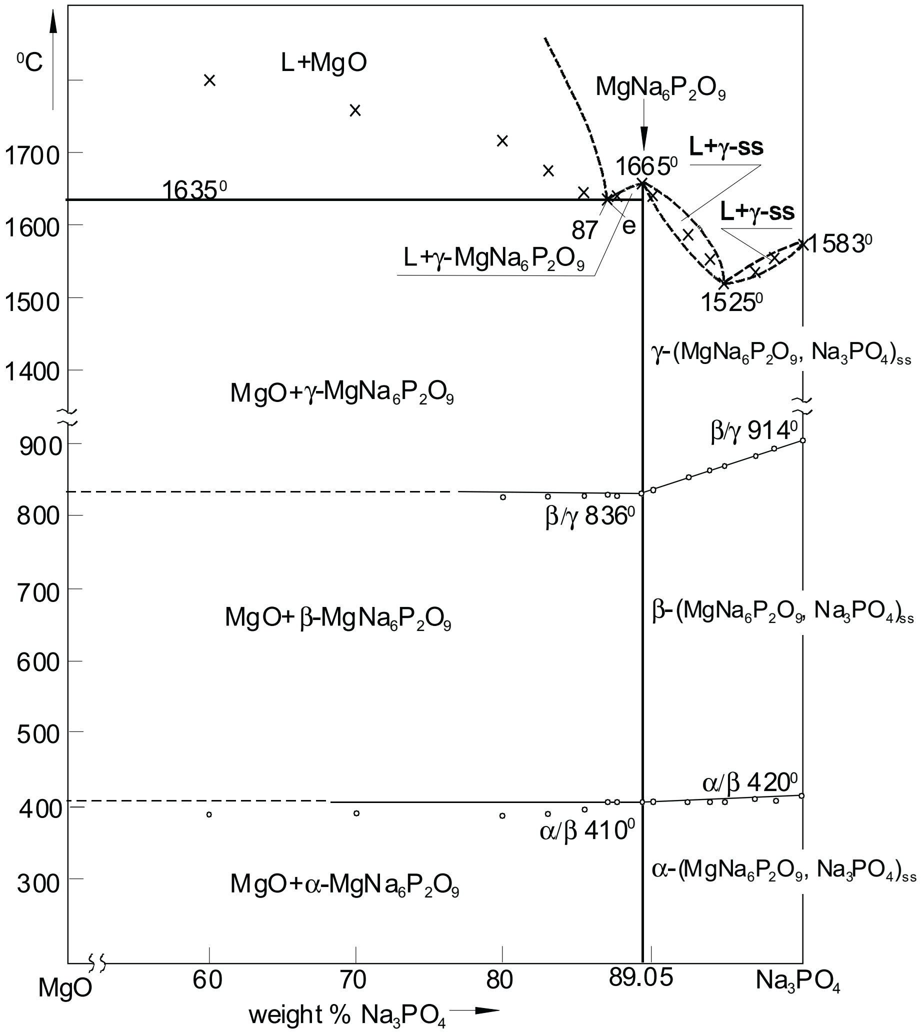

Figure 1. Phase diagram of MgO–Na$_3$PO$_4$ system; L = liquid, ○ – DTA of heating, x – optical.

Samples for investigation of the MgO–Na$_3$PO$_4$ system were obtained from starting substances. Their mixtures of different ratios were heated at 900°C for 72 h to ensure equilibrium conditions. The sinters obtained were cooled down to room temperature and anew rubbed thoroughly. In the composition range 95–100 wt % (82.4–100 mol. %) Na$_3$PO$_4$ investigated were both melted and sintered samples. In the remaining, MgO-rich composition range investigated were samples both of sintering and partial melting.

It has been found that in the system MgO–Na$_3$PO$_4$ an unknown so far, intermediate compound occurs: MgNa$_6$P$_2$O$_9$. It is formed in the molar ratio 1:2 of MgO:Na$_3$PO$_4$.

The phosphate $MgNa_6P_2O_9$ melts congruently at 1665°C and appears in three polymorphic modifications. In the pure compound the polymorphic transitions proceed at 410°C (α/β transition) and 836°C (β/γ transition). The processes are manifested by small peaks on the DTA curves. The transitions are reversible and occur both during heating and cooling. High temperature modifications β- and γ-$MgNa_6P_2O_9$ cannot be stabilized at room temperature upon quenching.

It is found, on the basis of DTA and powder X-ray diffraction, that the phosphate $MgNa_6P_2O_9$ and MgO form a simple eutectic system. Composition and temperature conditions of the eutectic point are 13.0 wt % (37.8 mol. %) MgO, 87.0 wt % (62.2 mol. %) Na_3PO_4, and 1635°C. This system shows a slight decrease in temperature of the polymorphic transition α/β-$MgNa_6P_2O_9$ with increasing MgO content. In contrast, the β/γ-transition proceeds at a constant temperature (836°C).

Phase equilibria in the composition range $MgNa_6P_2O_9$ were determined with finding the melting points of the samples composed of heteromolar mixtures of the phosphates. The lowest melting point was found for a sample of the composition 95.0 wt % (82.4 mol. %) Na_3PO_4. This suggests that $MgNa_6P_2O_9$ forms an eutectic system with Na_3PO_4, too. However, it results from the X-ray analysis that the above phosphates form continuous solid solutions in the entire range of composition and temperature with a minimum melting point at 1525°C. Thermal investigation in the subsolidus region, in turn, shows that appropriate polymorphic modifications of the phosphates $MgNa_6P_2O_9$ and Na_3PO_4 yield joint thermal effects, in the whole range of composition, which is typical for systems with continuous solid solutions. The samples from the system MgO–Na_3PO_4, rich in sodium orthophosphate, crystallize with difficulty and readily form glasses. The samples crystallized in this region are hygroscopic, the glasses are resistant to moisture. In the system MgO–Na_3PO_4–$Na_4P_2O_7$ an unknown quasi-binary section of $MgNa_6P_2O_9$–$MgNa_4(PO_4)_2$ has been identified. It is elaborated in the entire range of composition and temperature, and its phase diagram is shown in Fig. 2. Samples for investigation of this quasi-binary section were obtained from initial substances. Their mixtures of different ratios were heated at 900°C for 96 h. Such samples were examined by DTA and X-ray analyses. Microscopy of melted samples was difficult, because of their easy glazing during cooling.

In order to determine the liquidus curve, the samples of the $MgNa_6P_2O_9$–$MgNa_4(PO_4)_2$ section were melted under argon in a horizontal furnace with PtRh30 winding. It has been found that the sample of the composition 78.0 wt % (81.0 mol. %) $MgNa_4(PO_4)_2$ shows the lowest melting point about 1520°C. This suggests that the system has an eutectic character. On the other hand, the results of X-ray structure analysis of samples both melted and sintered have shown the existence of continuous solid solutions in the whole range of composition. Both initial phosphates melt congruently, $MgNa_6P_2O_9$ at 1665°C and $MgNa_4(PO_4)_2$ at 1655°C. Each of them appears in three polymorphic modifications. Based on the DTA results, it was found that the respective (*i.e.* α/β - and β/γ -) polymorphic modifications $MgNa_6P_2O_9$ and $MgNa_4(PO_4)_2$ give joint thermal effects in the whole range of composition.

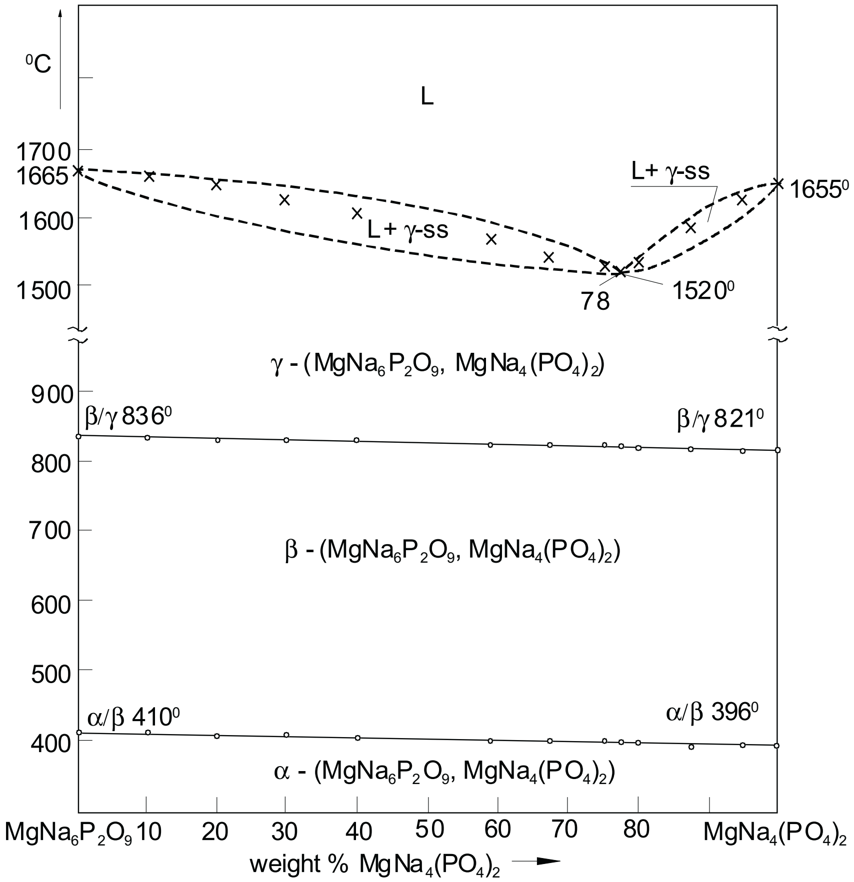

Figure 2. Phase diagram of $MgNa_6P_2O_9$–$MgNa_4(PO_4)_2$ system; L = liquid, ○ – DTA of heating, x – optical.

The phase diagram of the system MgO–Na_3PO_4–$Na_4P_2O_7$ with solidification isotherms is presented in Fig. 3.

In the system the three binary compounds MgO, Na_3PO_4 and $Na_4P_2O_7$, as well as the two ternary compounds $MgNa_6P_2O_9$ and $MgNa_4(PO_4)_2$, occur, crystallizing from the liquid phase. 1) The primary crystallization field of MgO is bounded by the points e_1 e_2 MgO. 2) The primary crystallization field of $Na_4P_2O_7$ is bounded by the points e_3 e_4 $Na_4P_2O_7$. 3) The primary crystallization field of the solid solutions $MgNa_6P_2O_9$–$MgNa_4(PO_4)_2$ occurs in the range e_1 $MgNa_6P_2O_9$ $MgNa_4(PO_4)_2$ e_2. 4) The primary crystallization field of the solid solutions $MgNa_4(PO_4)_2$–Na_3PO_4 occurs in the range e_4 $MgNa_4(PO_4)_2$ Na_3PO_4 e_3. 5) The primary crystallization field of the solid solutions Na_3PO_4–$MgNa_4(PO_4)_2$–$MgNa_6P_2O_9$ occurs in the range Na_3PO_4–$MgNa_4(PO_4)_2$–$MgNa_6P_2O_9$. It follows from the above that the phosphates Na_3PO_4, $MgNa_4(PO_4)_2$, and $MgNa_6P_2O_9$ do not posses their own primary crystallization fields. This is because they produce continuous solid solutions, therefore, they have joint primary

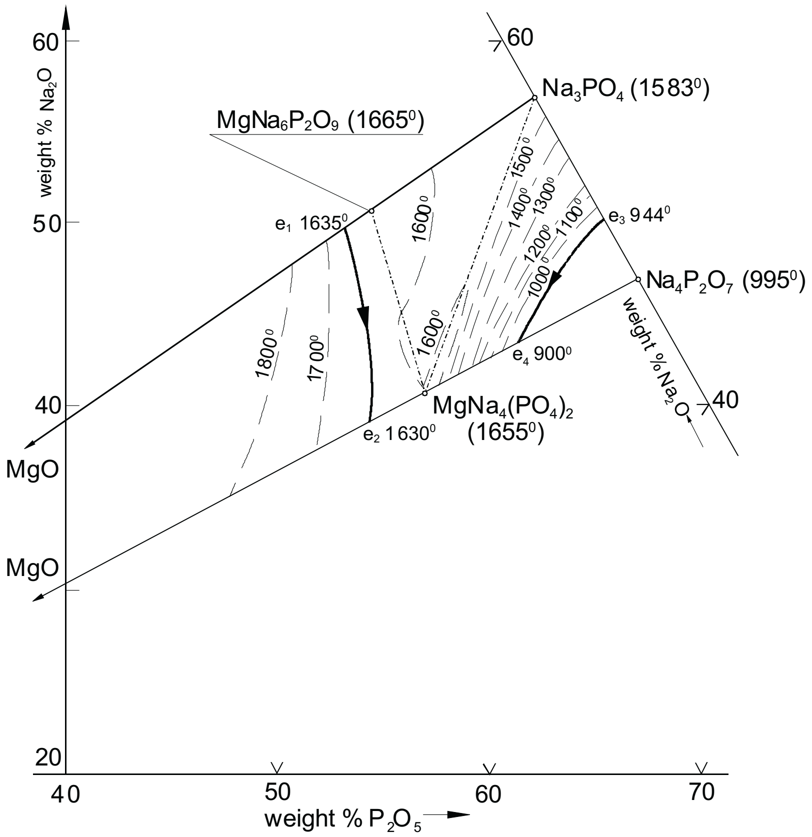

Figure 3. Phase diagram of $MgO–Na_3PO_4–Na_4P_2O_7$ system, including solidification isotherms.

crystallization fields. In the case of Na_3PO_4 this area is bounded by the points $MgNa_6P_2O_9$ Na_3PO_4 e_3 e_4 $MgNa_4(PO_4)_2$.

The composition range under investigation can be divided into the following three partial ternary systems, existing at room temperature, namely: 1) $MgO–MgNa_6P_2O_9–MgNa_4(PO_4)_2$. 2) $MgNa_6P_2O_9–Na_3PO_4–MgNa_4(PO_4)_2$, 3) $MgNa_4(PO_4)_2–Na_3PO_4–Na_4P_2O_7$.

In the partial system $MgO–MgNa_6P_2O_9–MgNa_4(PO_4)_2$ the components form two side systems of an eutectic type ($MgO–MgNa_6P_2O_9$ and $MgO–MgNa_4(PO_4)_2$), as well as another with continuous solid solutions ($MgNa_6P_2O_9–MgNa_4(PO_4)_2$). Along curve e_1 e_2, between 1635–1630°C, a binary eutectic crystallizes, which is composed of MgO crystals and continuous solid solutions ($MgNa_6P_2O_9–MgNa_4(PO_4)_2$), according to:

$$L\ e_1\ e_2 = MgO + (MgNa_6P_2O_9,\ MgNa_4(PO_4)2)_{ss}.$$

In the partial system $MgNa_6P_2O_9–Na_3PO_4–MgNa_4(PO_4)_2$ its side systems are binary systems with continuous solid solutions ($MgNa_6P_2O_9–Na_3PO_4$, $Na_3PO_4–$

$MgNa_4(PO_4)_2$ [4] and $MgNa_6P_2O_9$–$MgNa_4(PO_4)_2$. Hence, in these triangle crystallize continuous solid solutions, which are composed of the $MgNa_4(PO_4)_2$, $MgNa_6P_2O_9$ and Na_3PO_4 crystals.

In the partial system $MgNa_4(PO_4)_2$–Na_3PO_4–$Na_4P_2O_7$ its components form two side systems of an eutectic type ($MgNa_4(PO_4)_2$–$Na_4P_2O_7$ and Na_3PO_4–$Na_4P_2O_7$) and another with continuous solid solutions ($MgNa_4(PO_4)_2$–Na_3PO_4). Along curve e_3 e_4, between 944–900°C, a binary eutectic crystallizes, which is composed of $Na_4P_2O_7$ crystals and continuous solid solutions ($MgNa_4(PO_4)_2$–Na_3PO_4):

$$L\ e_3\ e_4 = Na_4P_2O_7 + (MgNa_4(PO_4)_2,\ Na_3PO_4)_{ss}.$$

Special points from the MgO–Na_3PO_4–$Na_4P_2O_7$ system are presented in Tables 1 and 2.

Table 1. Special points from the MgO – Na_3PO_4 – $Na_4P_2O_7$ system presented in Fig. 3.

Special points in the ternary system MgO–Na_2O–P_2O_5	Composition of samples					
	in weight %			in molar %		
	MgO	Na_2O	P_2O_5	MgO	Na_2O	P_2O_5
Na_3PO_4	–	56.7	43.3	–	75.0	25.0
$Na_4P_2O_7$	–	46.2	53.4	–	66.7	33.3
$MgNa_6P_2O_9$	10.9	50.5	38.6	20	60	20
$MgNa_4(PO_4)_2$	13.2	40.5	46.3	25	50	25
eutectic e_1	13.0	49.3	37.7	23.3	57.5	19.2
eutectic e_2	16.6	38.9	44.5	30.5	46.3	23.2
eutectic e_3	–	50.2	49.8	–	69.8	30.2
eutectic e_4	7.6	42.3	50.1	15.5	55.7	28.8

Table 2. Special points from the MgO – Na_3PO_4 – $Na_4P_2O_7$ system presented in Fig. 3.

Special points on respective binary sections of the ternary system MgO–Na_2O–P_2O_5	Composition of samples			
	in weight %		in molar %	
$MgNa_6P_2O_9$ (MgO–Na_3PO_4)	10.9 MgO	89.1 Na_3PO_4	33.3 MgO	66.7 Na_3PO_4
$MgNa_4(PO_4)_2$ ($Mg_3(PO_4)_2$–Na_3PO_4)	28.6 $Mg_3(PO_4)_2$	71.4 Na_3PO_4	20.0 $Mg_3(PO_4)_2$	80.0 Na_3PO_4
eutectic e_1 (MgO–Na_3PO_4)	13.0 MgO	87.0 Na_3PO_4	37.8 MgO	62.2 Na_3PO_4
eutectic e_2 (MgO–$MgNa_4(PO_4)_2$)	4.0 MgO	96.0 $MgNa_4(PO_4)_2$	24.0 MgO	76.0 $MgNa_4(PO_4)_2$
eutectic e_3 (Na_3PO_4–$Na_4P_2O_7$)	35.5 Na_3PO_4	64.5 $Na_4P_2O_7$	47.2 Na_3PO_4	52.8 $Na_4P_2O_7$
eutectic e_4 ($MgNa_4(PO_4)_2$–$Na_4P_2O_7$)	58.0 $MgNa_4(PO_4)_2$	42 $Na_4P_2O_7$	54.5 $MgNa_4(PO_4)_2$	45.5 $Na_4P_2O_7$

REFERENCES

1. Berak J. and Znamierowska T., *Roczn. Chem.*, **46**, 1967 (1972).
2. Podhajska-Kaźmierczak T., Prace Naukowe Akad. Ekonomicznej – Wrocław, **729**, 93 (1996) (in Polish).
3. Podhajska-Kaźmierczak T., *Thermochim. Acta*, **385**, 163 (2002).
4. Podhajska-Kaźmierczak T. and Znamierowska T., *Polish J. Chem.*, **73**, 279 (1999).