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THE SYSTEM $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$

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Abstract

Phase equilibria in the partial system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ were examined by differential thermal analysis and powder X-ray diffraction. It was found that there are six sections in the composition range under investigation.

Keywords: phase equilibria, sodium–magnesium phosphates

Introduction

The present paper summarizes our investigations on the partial system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$. This is a part of the ternary system MgO–Na_2O–P_2O_5, rich in P_2O_5. Phase equilibria occurring within this composition range have been examined by several authors. However, the obtained results differ. The differences are attributed mainly to the stoichiometry of the sodium–magnesium phosphates existing in this part of the ternary system. The literature postulates the existence of the following metaphosphates: $NaMg(PO_3)_3$ [1–6], $Na_2Mg(PO_3)_4$ [1, 6] and $Na_4Mg(PO_3)_6$ [1, 6]. Analogous discrepancies exist regarding the sodium–magnesium pyrophosphates, to which the following formulas have been ascribed: $Na_2MgP_2O_7$ [4, 7, 8], $Na_{12}Mg_4(P_2O_7)_5$ [8], $7Na_4P_2O_7{\cdot}9Mg_2P_2O_7$ [9] and $Na_8Mg_6(P_2O_7)_5$ [10]. An additional mixed phosphate $Na_3Mg_2P_5O_{16}$ has also been claimed to exist [4, 11, 12]. According to Ustiancev *et al.* [4], this phosphate melts incongruently at 1003 K, forming a liquid and solid pyrophosphate $Na_2MgP_2O_7$. Our investigations [14] showed that $Na_3Mg_2P_5O_{16}$ is thermally unstable. At approximately 948 K, it melts peritectically and decomposes. The decomposition proceeds without mass decrement, through several stages. In the last stage, a mixture of sodium–magnesium metaphosphates and $Mg_2P_2O_7$ is formed.

The partial system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ is limited by four side-systems: (1) $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$, (2) $Mg_2P_2O_7$–$Mg(PO_3)_2$, (3) $Mg(PO_3)_2$–$NaPO_3$ and (4) $Na_8Mg_6(P_2O_7)_5$–$NaPO_3$. The phase diagrams of the first three systems are known. However, it should be pointed out that be-

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cause of the differences mentioned above, the phase equilibria occurring in the side-systems $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$ and $Mg(PO_3)_2$–$NaPO_3$ have been presented differently.

Experimental

Samples of the system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ were prepared from the following parent compounds: $MgHPO_4{\cdot}3H_2O$ (p.a., Belgium), $Na_2HPO_4{\cdot}2H_2O$ (p.a.), $NaH_2PO_4{\cdot}H_2O$ (p.a.) and H_3PO_4 (85% p.a.). The experiments were carried out by differential thermal analysis (DTA) during heating and by X-ray powder diffraction (XRD). DTA was performed by means of a C-derivatograph (MOM, Hungary). The phases formed in the system were identified by XRD with an HZG-4 diffractometer (Guinier camera) and a SIEMENS D 5000 diffractometer. CuK_α radiation was used.

Results and discussion

The partial system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ is limited on one side by the system $Na_8Mg_6(P_2O_7)_5$–$NaPO_3$. The previously unknown phase diagram of this system is described in this paper. Samples for investigations were prepared from the initial phosphates. The analysed samples were presynthesized at subsolidus temperatures. The phase diagram of the system is presented in Fig. 1. The initial phosphates form a simple binary eutectic system. The eutectic temperature is 843 K (570°C), and the composition is 82.5 wt% $NaPO_3$, 17.5 wt% $Na_8Mg_6(P_2O_7)_5$. Samples rich in $NaPO_3$ crystallize with difficulty and have a tendency to form glasses. This also holds true for all other samples of the whole partial system, particularly if they are rich in

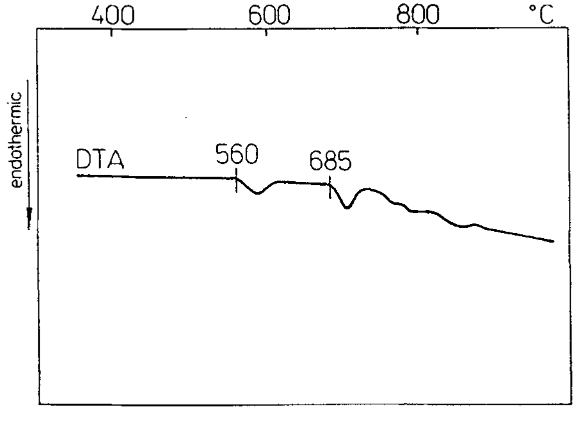

Fig. 1 DTA curve of a sintered sample containing 60 wt% $Na_3Mg_2P_5O_{16}$ – 40 wt% $Na_4Mg(PO_3)_6$

P_2O_5. This fact, and also the thermal instability of $Na_3Mg_2P_5O_{16}$ in the region under investigation, have an important influence on the formation of the phase equilibria.

Earlier investigations have proved that in the system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ there are four sections:

(1) $Mg_2P_2O_7$–$NaMg(PO_3)_3$

(2) $Mg_2P_2O_7$–$Na_2Mg(PO_3)_4$

(3) $Mg_2P_2O_7$–$Na_4Mg(PO_3)_6$

(4) $Mg_2P_2O_7$–$NaPO_3$.

Their phase diagrams have been published [13–14]. It has now been found that two further sections exist: (1) $Na_8Mg_6(P_2O_7)_5$–$Na_3Mg_2P_5O_{16}$, and (2) $Na_3Mg_2P_5O_{16}$–$Na_4Mg(PO_3)_6$. They have been examined by DTA on heating of samples sintered at subsolidus temperatures. Cooling curves were excluded mainly because of the thermal instability of $Na_3Mg_2P_5O_{16}$.

In the DTA heating curves of sintered samples from the system $Na_8Mg_6(P_2O_7)_5$–$Na_3Mg_2P_5O_{16}$, an endothermal peak occurs at 923–963 K (650–690°C) within the composition range 20–100 wt% $Na_3Mg_2P_5O_{16}$. The peak is large for samples rich in $Na_3Mg_2P_5O_{16}$. With decreasing content of this phosphate, the peak becomes smaller. Several other small endothermal effects appear in the temperature interval 973–1273 K (700–1000°C). As an example, the DTA heating curve for a mixture of 40 wt% $Na_8Mg_6(P_2O_7)_5$ and 60 wt% $Na_3Mg_2P_5O_{16}$ is presented in Fig. 2. The results obtained by DTA were supported by XRD measurements. Both samples sintered in the solid state and samples melted and cooled slowly with grafting down to room temperature were examined. It was found that all sintered samples are a mixture of the initial

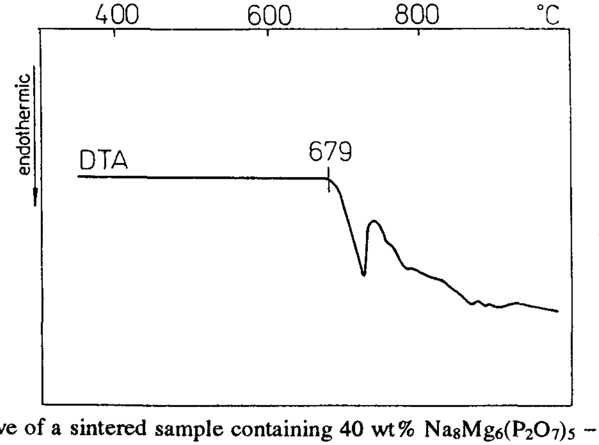

Fig. 2 DTA curve of a sintered sample containing 40 wt% $Na_8Mg_6(P_2O_7)_5$ – 60 wt% $Na_3Mg_2P_5O_{16}$

phosphates: $Na_8Mg_6(P_2O_7)_5$ and $Na_3Mg_2P_5O_{16}$. The phase composition of molten samples without annealing was more complex and differentiated. Since it must be assumed that these are non-equilibrium states, these results were not considered.

On the basis of the above results, it must be concluded that the system $Na_8Mg_6(P_2O_7)_5$–$Na_3Mg_2P_5O_{16}$ is quasi-binary. In the subsolidus region, only compounds $Na_8Mg_6(P_2O_7)_5$ and $Na_3Mg_2P_5O_{16}$ exist. Above the decomposition temperature of $Na_3Mg_2P_5O_{16}$, this is a polyphase system.

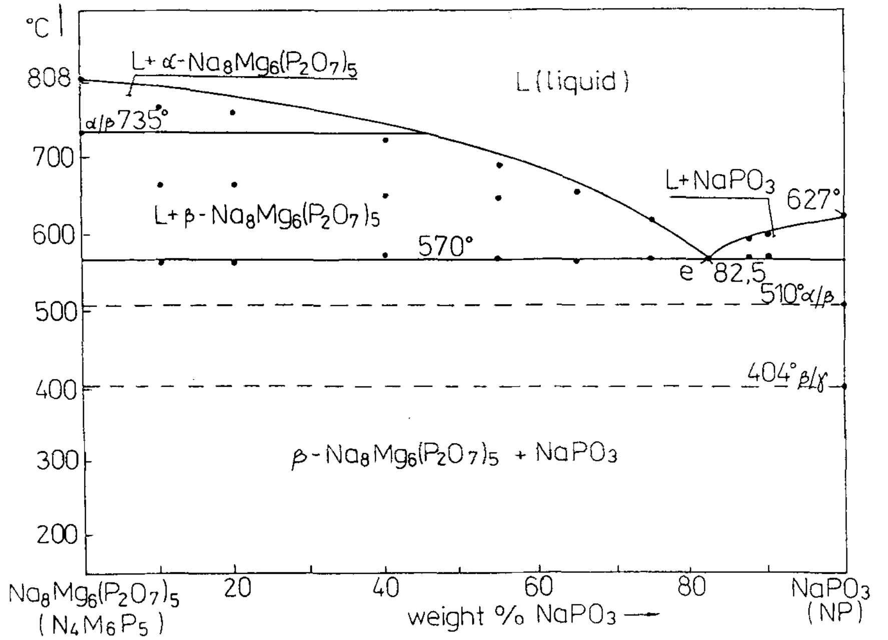

Fig. 3 Phase diagram of the system $Na_8Mg_6(P_2O_7)_5$–$NaPO_3$

The section $Na_3Mg_2P_5O_{16}$–$Na_4Mg(PO_3)_6$ is complex too. Both initial phosphates melt incongruently and $Na_3Mg_2P_5O_{16}$ is thermally unstable. In the DTA heating curves of sintered samples, a thermal effect occurs at approximately 833 K (560°C). It is very strong within the composition range 80–100 wt% $Na_4Mg(PO_3)_6$. In the other part of the section, it is of moderate size. The next endothermal effect occurs within the temperature interval 923–973 K (650–700°C). However, it appears in the DTA curves only within the composition range 45–100 wt% $Na_3Mg_2P_5O_{16}$. It is strong in samples rich in $Na_3Mg_2P_5O_{16}$ and decreases with decreasing content of this compound. Some other thermal effects occur at higher temperatures (up to 1273 K). A representative DTA heating curve for a mixture of 40 wt% $Na_4Mg(PO_3)_6$ and 60 wt% $Na_3Mg_2P_5O_{16}$ is shown in Fig. 3. To interpret the results obtained during the thermal investigations, X-ray phase analysis was used. XRD showed that sintered samples are a mixture of $Na_3Mg_2P_5O_{16}$ and $Na_4Mg(PO_3)_6$. X-ray photographs of molten samples display non-equilibrium reflections coming from mixed sodium–magnesium metaphosphates (mainly $Na_4Mg(PO_3)_6$) and $Mg_2P_2O_7$. The thermal and X-ray investigations revealed that the section $Na_3Mg_2P_5O_{16}$–$Na_4Mg(PO_3)_6$ is binary only at subsolidus temperatures. It is not stable at liquidus temperatures.

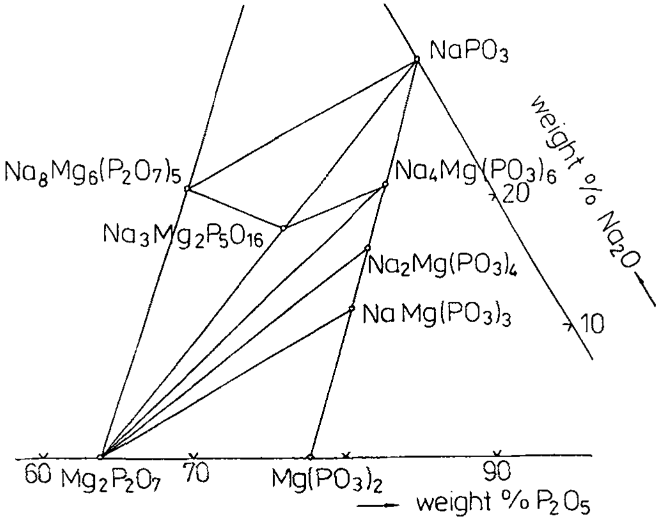

Fig. 4 The phase coexistence in the system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ at subsolidus temperatures

The coexistence of phases at subsolidus temperatures in the system $Mg_2P_2O_7$–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ is shown in Fig. 4. Determination of the phase equilibria at higher temperatures is not yet complete, especially in the part rich in Na_2O (upper part of the system – Fig. 4). It depends on the complex character of the double phosphates occurring within this region, on the thermal instability of $Na_3Mg_2P_5O_{16}$ and on the tendency to glass formation during the cooling of molten samples.

References

1 B. Thonnierieux, J. C. Grenier, A. Durif and C. Martin, Compt. Rend., 267 (1968) 968.
2 S. J. Volfkovits, T. D. Pozharskaya and L. V. Kubasova, Dokl. Akad. Nauk SSSR, 197 (1971) 583.
3 J. Majling, A. Vojteckova and J. Petrovic, Chem. Zvesti, 28 (1974) 289.
4 V. M. Ustiancev and M. G. Tretnikova, Ogneupory, 5 (1976) 53; ibid., 6 (1976) 52.
5 J. F. Shepielev, J. J. Smolin, Domanskij and A. V. Lavrov, Dokl. Akad. Nauk SSSR, 272 (1983) 610.

6 T. Podhajska-Kaźmierczak and T. Znamierowska, Polish J. Chem., 65 (1991) 1151.
7 R. Klement, Chem. Ber., 93 (1960) 2314.
8 S. I. Berul and N. K. Voskriesienskaya, Izv. Akad. Nauk SSSR, Neorg. Mat., 412 (1968) 2129.
9 J. Majling and F. Hanic, Solid State Chem., 7 (1973) 370.
10 T. Podhajska-Kaźmierczak and T. Znamierowska, Polish J. Chem., 66 (1992) 277.
11 J. I. Smolin, J. F. Shepielev, A. J. Domanskij and J. Majling, Krystallografija, 23 (1978) 1264.
12 J. Majling and F. Hanic, J. Appl. Cryst., 12 (1979) 244.
13 T. Podhajska-Kaźmierczak and T. Znamierowska, Prace Naukowe AE we Wrocławiu, 526 (1990) 255; ibid., 610 (1992) 299; ibid., 610 (1992) 303.
14 T. Podhajska-Kaźmierczak and T. Znamierowska, J. Thermal Anal., 44 (1995) 1195.

Zusammenfassung — Mittels Differentialthermoanalyse und Röntgen-Pulverdiffraktion wurde das Phasengleichgewicht im partiellen System Mg_2P_2O–$Na_8Mg_6(P_2O_7)_5$–$NaPO_3$–$Mg(PO_3)_2$ untersucht. Man fand die Existenz von sechs Abschnitten im untersuchten Zusammensetzungsbereich.