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THE SYSTEM $Mg_2P_2O_7$–$NaPO_3$

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Abstract

In the ternary system MgO–Na_2O–P_2O_5, the system $Mg_2P_2O_7$–$NaPO_3$ has been examined by thermal and X-ray methods and its phase diagram has been determined. The intermediate compound $Na_3Mg_2P_5O_{16}$ exists in this system. It melts peritectically at 948 K and decomposes to mixtures of sodium-magnesium metaphosphates and magnesium pyrophosphate $Mg_2P_2O_7$.

Keywords: compound $Na_3Mg_2P_5O_{16}$, magnesium pyrophosphate, phase equilibria, sodium metaphosphate

Introduction

Studies on the system $Mg_2P_2O_7$–$NaPO_3$ comprise another stage of the systematic research on the ternary system MgO–Na_2O–P_2O_7 in our laboratory. The literature on sodium-magnesium phosphates is extensive. In this group of compounds, a mixed phosphate with the formula $Na_3Mg_2P_5O_{16}$ [1–3] is known. In 1976, Ustiancev *et al.* [1] published their work on phase equilibria in the ternary system Na_2O–MgO–P_2O_5. By thermal and X-ray analyses, a sodium magnesium phosphate with the formula $Na_3Mg_2P_5O_{16}$ was found. According to [1], this compound lies at the intersection of two sections, namely $Mg_2P_2O_7$–$NaPO_3$ and $Na_2MgP_2O_7$–$NaMg(PO_3)_3$. The phosphate $Na_3Mg_2P_5O_{16}$ melts incongruently at 1003 K, giving a liquid and sodium-magnesium pyrophosphate $Na_2MgP_2O_7$. In 1978, Smolin *et al.* [2] published the results of an X-ray structural analysis of $Na_3Mg_2P_5O_{16}$. It crystallizes in the monoclinic system: $a=18.617\pm0.005$, $b=6.844\pm0.003$, $c=5.174\pm0.003$ Å, $\beta=90.15°$. According to Majling [3], $Na_3Mg_2P_5O_{16}$ is monoclinic, $P2_1/c$, with unit-cell parameters $a=5.177(1)$, $b=6.853(1)$, $c=18.628(5)$ Å, $\beta = 90.00(4)°$.

According to its composition, the phosphate $Na_3Mg_2P_5O_{16}$ occurs in the system $Mg_2P_2O_7$–$NaPO_3$. Because this system is not yet known in the literature, we have determined its phase diagram.

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Experimental

Samples for measurements in the system $Mg_2P_2O_7$–$NaPO_3$ were prepared from initial phosphates synthesized in our laboratory. Magnesium diphosphate, $Mg_2P_2O_7$, was obtained by dehydration of $MgHPO_4 \cdot 3H_2O$ (p.a. Belgian) for 1 h at 1173 K, and sodium metaphosphate, $NaPO_3$, by dehydration of $NaH_2PO_4 \cdot H_2O$ p.a. for 0.5 h at 573 K and for 2 h at 773 K.

Test samples were synthesized in a Pt cup by reaction in the solid phase. The investigations were carried out by differential thermal analysis (DTA) and X-ray analysis. DTA in the heating mode was performed by using a C derivatograph (MOM, Hungary), within the temperature range 293–1473 K. The heating rate was 5 deg·min^{-1}. High-purity Al_2O_3 was used as the standard substance. Typical sample mass varied from 200 mg to 600 mg.

Resistance furnaces with a platinum winding, constructed in our laboratory, were used to perform the thermal analysis of cooling. The temperature was measured with a Pt/PtRh 10 thermocouple, which was calibrated against the melting points of NaCl (1073 K), K_2SO_4 (1343 K) and $Ca_2P_2O_7$ (1626 K) and the temperature of the polymorphic transition of K_2SO_4 (856 K).

The identification of the phases in the binary system was performed by an X-ray method. Powder patterns at ambient temperature were taken on an HZG-4 diffractometer or a SIEMENS D 5000 diffractometer with CuK_α radiation. High-temperature X-ray studies were made on a DRON 2.0 diffractometer.

Results and discussion

The system $Mg_2P_2O_7$–$NaPO_3$ was investigated across the full range of composition and temperature by DTA and X-ray analyses. The melting points were additionally estimated visually. It was discovered in preliminary investigation, that molten samples crystallize with difficulty over the full composition range of the system. The tendency to form glasses dominates in the $NaPO_3$–rich part of the system. Over the whole range of composition, the content of the amorphous phase depended on the speed of cooling. Since few thermal effects occurred in the DTA cooling curves and they were weak as well as broadened, only DTA heating curves were used.

To obtain a full picture of the phases transitions occurring in the system $Mg_2P_2O_7$–$NaPO_3$, DTA analysis of heating was performed for two series of samples:

(1) samples that had been melted or only partially melted were slowly cooled (with grafting) down to room temperature,

(2) samples were sintered in the temperature range 773–923 K for 2.5–7 days.

A comparison of the results obtained for the two series of samples revealed that the distribution temperature and the sizes of the thermal effects in the DTA heating curves, even for samples with the same stoichiometric composition, depend on the way in which the samples were prepared. As an example of this phenomenon, DTA heating curves obtained for a mixture of 40 wt% $NaPO_3$ and 60 wt% $Mg_2P_2O_7$ are presented in Fig. 1. It should be pointed out that the thermal effects in the DTA_1 and DTA_2 curves are not accompanied by any mass loss (TG analysis). Therefore, an attempt was made to explain these divergences.

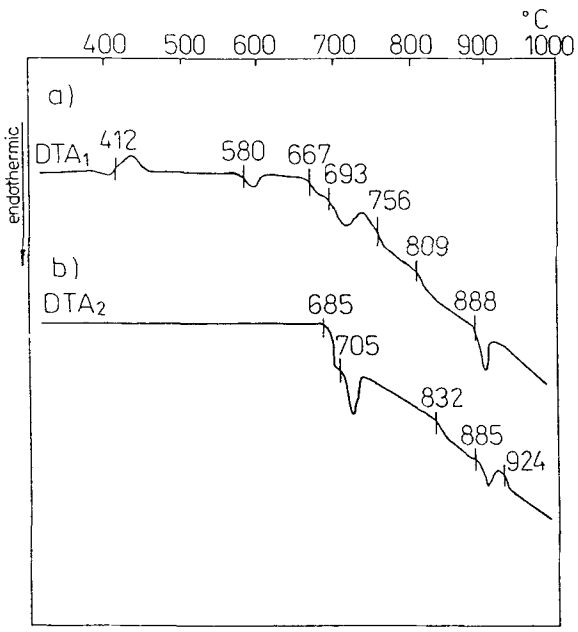

Fig. 1 DTA curves of a sample containing: 40 wt% $NaPO_3$, 60 wt% $Mg_2P_2O_7$; a) sample only partially melted; b) sample sintered

There is an exothermic peak at 685 K (412°C) in the DTA_1 curve. Analogous peaks, but with different size, can be observed in all DTA heating curves of samples melted across the full composition range of the system. These exothermic peaks are sometimes more or less split. One more phenomenon was observed as well. When the DTA heating analysis was stopped a little over the temperature at which an exothermic peak comes to an end (i.e. at approx. 773 K), and the sample was then cooled down to room temperature, the above-mentioned peak did not appear, when the heating curve was measured again. High-temperature X-ray examinations in the temperature interval 293–823 K proved that the exothermic peaks are generated by the transition from the metastable amorphous state to the stable crystalline state. When the crystallization

proceeds in several stages, this is reflected in a larger number of exothermic peaks in the DTA curve. They are separated according to the kinetics of the particular stages. The size of a peak reflects the content of the vitreous phase.

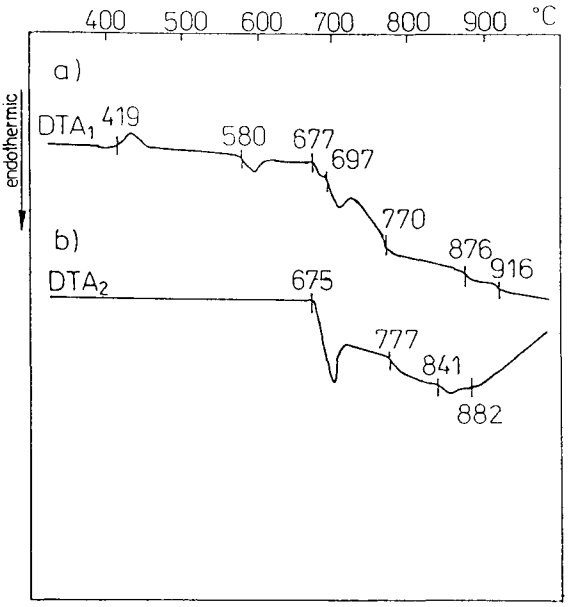

Fig. 2 DTA curves of a sample containing: 57.87 wt% $NaPO_3$, 42.13 wt% $Mg_2P_2O_7$, i.e. $Na_3Mg_2P_5O_{16}$; a) sample only partially melted; b) sample sintered

In order to interpret other endothermic peaks which occur at temperatures higher than 948 K, it was necessary to examine the thermal stability of the phosphate $Na_3Mg_2P_5O_{16}$. Literature data [1] show that $Na_3Mg_2P_5O_{16}$ melts incongruently at 1003 K, giving a liquid and sodium-magnesium pyrophosphate, $Na_2MgP_2O_7$. However, the different authors disagree on the stoichiometric composition of sodium-magnesium pyrophosphates. According to Klement [4] and Ustiancev [1], a pyrophosphate with the formula $Na_2MgP_2O_7$ exists. Berul *et al.* [5] reported the existence of two pyrophosphates: $Na_2MgP_2O_7$ and $Na_{12}Mg_4(P_2O_7)_5$. According to Majling [6], a compound with the composition $7Na_4P_2O_7{\cdot}9Mg_2P_2O_7$ exists. Our investigations [7] have proved the existence of a pyrophosphate with the composition $6Na_4P_2O_7{\cdot}9Mg_2P_2O_7$, i.e. $Na_8Mg_6(P_2O_7)_5$.

The compound $Na_3Mg_2P_5O_{16}$ was synthesized in our laboratory by means of a reaction in the solid phase, using the methods described in Refs [1, 3]. TG, DTG and DTA (heating) experiments were performed with sintered samples and with samples which had been melted (or partially melted) and then slowly cooled with grafting down to room temperature. Representative DTA curves for

the compound $Na_3Mg_2P_5O_{16}$, heated in air in an open cup, are shown in Fig. 2. X-ray phase analysis proved necessary to interpret the results obtained during thermal examinations properly. Mixtures with the stoichiometric composition $Na_3Mg_2P_5O_{16}$, sintered at different temperatures (in the solid phase) and then quenched to ambient temperature, were analysed by X-ray diffraction. Samples which were partially melted (i.e. heated up to 973–1023 K) and then cooled slowly with grafting down to room temperature, were analysed in the same way. High-temperature X-ray examinations of $Na_3Mg_2P_5O_{16}$ were also performed. Both the molten preparation and the one synthesized by means of reaction in the solid phase were subjected to these investigations. The results obtained were quite unexpected. Their interpretation was possible with the help of previously determined phase equilibria of the P_2O_5-rich part of the system MgO–Na_2O–P_2O_5.

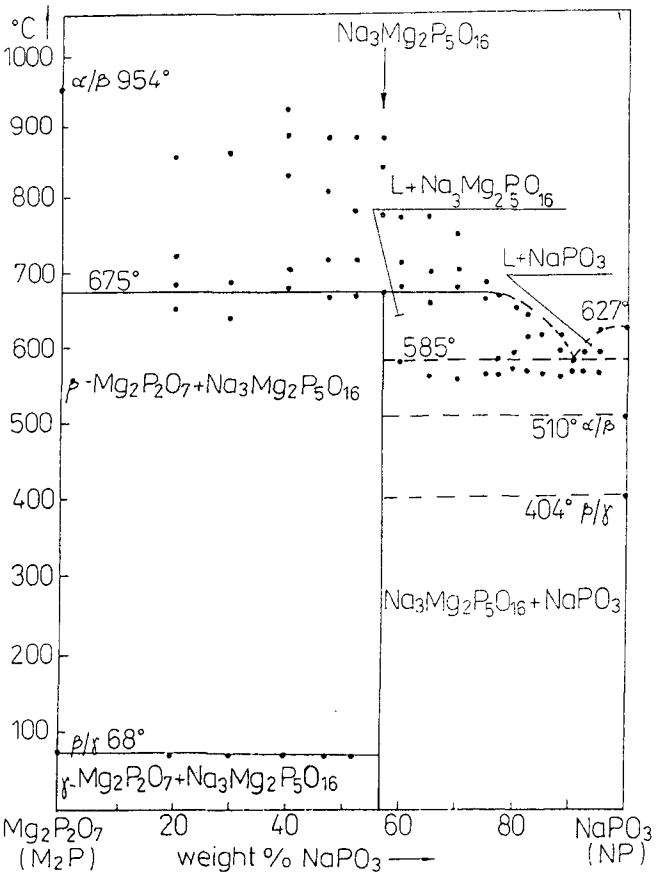

Fig. 3 Phase diagram of the system $Mg_2P_2O_7$–$NaPO_3$

Detailed analysis of the results obtained led to the following conclusions:

The phosphate $Na_3Mg_2P_5O_{16}$ is a thermally unstable compound. It exists only in the solid phase. At approximately 948 K (675°C), it melts peritectically and decomposes. The process of decomposition proceeds without mass decrement, through several stages. Some unstable intermediate products are formed; however, it is impossible to identify them exactly. In the last stage, a mixture of sodium-magnesium metaphosphates and the pyrophosphate $Mg_2P_2O_7$ is formed. Samples from the system $Mg_2P_2O_7$–$NaPO_3$ behave in the same way within the composition range from approximately 10 to approximately 80 wt% $NaPO_3$. The quantitative ratio of phases formed as a result of a peritectic reaction and a decomposition depends on the initial composition of the sample and the thermal treatment. This is confirmed by the number and sizes of the peaks observed in the DTA curves at higher temperature.

Figure 3 presents the suggested phase diagram of the system $Mg_2P_2O_7$–$NaPO_3$, constructed on the basis of the investigations described in this study. The circles which can be seen in Fig. 3 indicate thermal effects in the DTA heating curves of samples synthesized by means of a reaction in the solid phase. In the system, one intermediate compound of stoichiometry $Na_3Mg_2P_5O_{16}$ has been found. The system $Mg_2P_2O_7$–$NaPO_3$ is quasi-binary. In the subsolidus region of the system, only the compounds $Mg_2P_2O_7$ and $Na_3Mg_2P_5O_{16}$ are present from 0 to 57.87 wt% $NaPO_3$; $Na_3Mg_2P_5O_{16}$ and $NaPO_3$ exist in the composition range 57.87–100 wt% $NaPO_3$. The system is not stable above the temperatures of decomposition of $Na_3Mg_2P_5O_{16}$. On the basis of the high-temperature thermal effects occurring in the DTA curves of samples rich in $NaPO_3$, the shape of the liquidus curve within the composition range 80–100 wt% $NaPO_3$ is given by the broken line in Fig. 3. The liquidus curve has its minimum at approximately 90 wt% $NaPO_3$, at approximately 585°C. This suggests that a eutectic occurs in this part of the system. X-ray phase analysis could make interpretation of that minimum easier. However, it does not give a definite answer because most samples rich in $NaPO_3$, after being melted and cooled down to room temperature, are amorphous.

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Zusammenfassung — Im ternären System $MgO–Na_2O–P_2O_5$ wurde mittels thermischen und Röntgenmethoden das System $Mg_2P_2O_7–NaPO_3$ untersucht und das entsprechende Phasendiagramm erstellt. In diesem System existiert das Intermediär $Na_3Mg_2P_5O_{16}$. Es schmilzt peritektisch bei 948 K und zersetzt sich zu einem Gemisch aus Natriummagnesiummetaphosphat und Magnesiumpyrophosphat $Mg_2P_2O_7$.