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The system YPO_4–Na_3PO_4–$Na_4P_2O_7$

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Abstract

The ternary system YPO_4–Na_3PO_4–$Na_4P_2O_7$ was investigated by differential thermal analysis, powder X-ray diffraction and microscopy in reflected light. Its phase diagram and isothermal section at room temperature were determined. The system contains two double phosphates which are formed at the 1:1 and 2:1 molar ratios of YPO_4 and Na_3PO_4, i.e. $Na_3Y(PO_4)_2$ and $Na_3Y_2(PO_4)_3$.

INTRODUCTION

The present paper is the second part of our studies on binary sodium–yttrium orthophosphates. The binary system YPO_4–Na_3PO_4 has been examined before and its phase diagram has been determined [1]. Two mixed orthophosphates, $Na_3Y_2(PO_4)_3$ and $Na_3Y(PO_4)_2$, occur in this system. They melt congruently and form simple eutectic systems with each other and with the orthophosphates YPO_4 and Na_3PO_4.

The partial ternary system YPO_4–Na_3PO_4–$Na_4P_2O_7$ was previously unknown. It is surrounded by the binary side-systems: YPO_4–Na_3PO_4, Na_3PO_4–$Na_4P_2O_7$ and YPO_4–$Na_4P_2O_7$. The phase diagram of the first two systems are known [1,2]. Phase equilibria in the binary system YPO_4–$Na_4P_2O_7$ are not known.

EXPERIMENTAL

Samples for investigations of the YPO_4–Na_3PO_4–$Na_4P_2O_7$ system were prepared from the following starting compounds: Y_2O_3, (99.99%), H_3PO_4 (85%) (analytical grade), $Na_3PO_4 \cdot 12H_2O$ (analytical grade), NaH_2PO_4 (analytical grade), Na_2HPO_4 (analytical grade) and Na_2CO_3 (analytical grade).

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YPO_4, $Y_2P_4O_{13}$, Na_3PO_4, $Na_4P_2O_7$, $NaPO_3$, $Na_3Y(PO_4)_2$ and $Na_3Y_2(PO_4)_3$ were obtained in our laboratory. Yttrium orthophosphate YPO_4 was obtained from solution by the method given in ref. 1. $Y_2P_4O_{13}$ was prepared from Y_2O_3 and $NH_4H_2PO_4$ according to ref. 3. Sodium orthophosphate Na_3PO_4 was obtained by slow dehydration of $Na_3PO_4 \cdot 12H_2O$ at 200°C, 300°C and, further, at 600°C.

Sodium pyrophosphate $Na_4P_2O_7$ was obtained from Na_2HPO_4 by heating at 150°C for 1 h and at 500°C for 12 h. Sodium metaphosphate $NaPO_3$ was prepared from NaH_2PO_4 by heating at 500°C for 1 h. Double sodium–yttrium orthophosphates were obtained by one of the methods described in ref. 1. $Na_3Y(PO_4)_2$ phosphate was synthesized from $Y_2P_4O_{13}$ and Na_2CO_3 in 1:3 molar ratio. $Na_3Y_2(PO_4)_3$ phosphate was prepared from Y_2O_3 and $NaPO_3$ in 1:3 molar ratio.

The ternary system YPO_4–Na_3PO_4–$Na_4P_2O_7$ was examined by differential thermal analysis (heating and cooling), powder X-ray diffraction and microscopy in reflected light.

The differential thermal analysis on heating and cooling in air was performed in a furnace constructed in our laboratory, with Pt30Rh winding; 3 g samples were used. In the thermal analysis, a derivatograph, type 3427 (MOM, Hungary) was also used. Operating conditions were as follows: sensitivity, TG, 500 mg; DTA, 1/10; DTG, 1/10; speed of heating, 10°C min^{-1}; platinum cup; air atmosphere. The standard used was high purity Al_2O_3. Temperatures were read by means of a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of $Ca_2P_2O_7$, K_2SO_4 and NaCl.

High temperature thermal studies above 1400°C were carried out under argon in a horizontal resistance furnace with molybdenum winding. The examined samples were pressed into pellets, placed in boats made from noble metal alloys, and fused. Temperatures were read by means of an optical pyrometer, which was calibrated against the melting points of $Ca_3(PO_4)_2$ and Na_3PO_4.

The accuracy of the temperature readings in the thermal analysis up to 800°C was ±1.5°C, and above 800°C, ±3°C; in the visual methods it was ±10°C and for an optical pyrometer ±20°C. The phase purity of the reagents and phase structure of the products were studied microscopically. Microsections were prepared from molten and crystallized samples and these were polished and examined in reflected light.

The initial components and the phases formed in the ternary system YPO_4–Na_3PO_4–$Na_4P_2O_7$ were identified by powder X-ray diffraction with an HZG-4 diffractometer (a Guinier camera) using Cu Kα radiation.

RESULTS AND DISCUSSION

The YPO_4–Na_3PO_4–$Na_4P_2O_7$ system has been examined using differential thermal analysis, X-ray diffractometry and microscopy in reflected

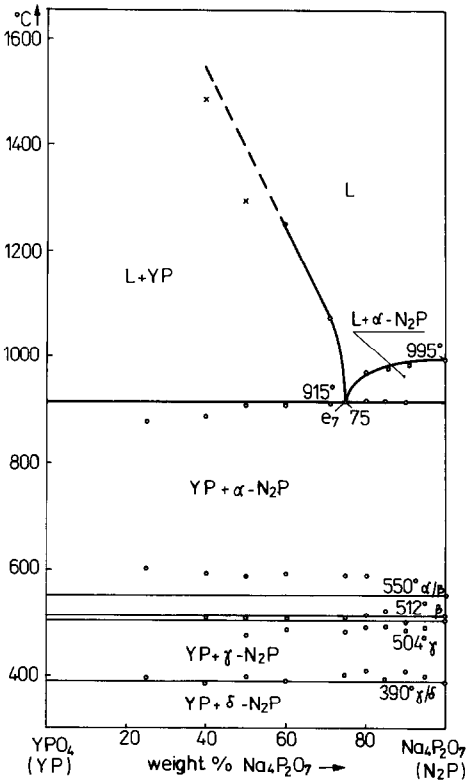

Fig. 1. Phase diagram of the system YPO_4–$Na_4P_2O_7$. ○, thermal analysis; ×, optical.

light. The first step was to determine the phase diagram of the binary side-system YPO_4–$Na_4P_2O_7$. This system was examined over the composition range 25–100 wt.% of $Na_4P_2O_7$, up to approximately 1500°C. Its phase diagram is presented in Fig. 1. The liquidus curve within the composition range 40–100 wt.% of $Na_4P_2O_7$ was drawn on the basis of thermal analysis of cooling. Samples richer in yttrium orthophosphate YPO_4 melt above 1400°C. To draw the liquidus curve in this part of the system, samples were first sintered at 900°C, then pressed into pellets and melted in a horizontal furnace with molybdenum winding (argon atmosphere). The melting points of the samples were measured with the use of an optical pyrometer. Because temperature measurements obtained in this way are lower than the real ones, the liquidus curves within the composition range 40–60 wt.% of $Na_4P_2O_7$ are hypothetical (broken line, Fig. 1).

Phase equilibria in the solid phase were examined by thermal analysis of heating and cooling. From these experiments, it was found that YPO_4 and $Na_4P_2O_7$ form a simple eutectic system: eutectic temperature, 915°C; composition, 75 wt.% $Na_4P_2O_7$ and 25 wt.% YPO_4. Sodium pyrophosphate has several polymorphic modifications [4]. The temperatures of transitions

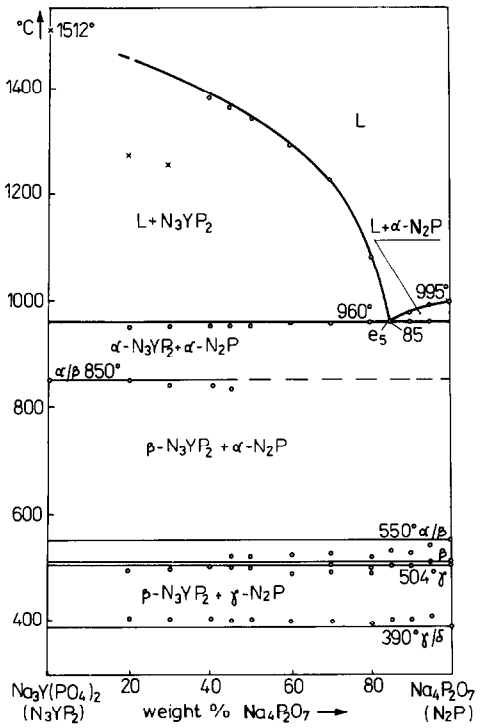

Fig. 2. Phase diagram of the system $Na_3Y(PO_4)_2$–$Na_4P_2O_7$: ○, thermal analysis; ×, optical.

in pure $Na_4P_2O_7$ are α/β, 550°C; β/γ, 512–504°C; and γ/δ, 390°C. In the binary system all polymorphic transitions of $Na_4P_2O_7$ are reflected in the form of thermal effects on the DTA curves. The α/β transition of $Na_4P_2O_7$ in the binary system under investigation proceeds at a higher temperature, 600°C.

The examinations carried out in this laboratory demonstrated that $Na_3Y(PO_4)_2$ forms a section with the pyrophosphate, $Na_4P_2O_7$. Figure 2 shows the phase diagram of this system determined by differential thermal analysis of heating and powder X-ray diffraction. The initial components form a simple eutectic system: eutectic temperature e_5, 960°C; composition, 85 wt.% $Na_4P_2O_7$ and 15 wt.% $Na_3Y(PO_4)_2$. The high temperature polymorphic α/β and β/γ transitions of $Na_4P_2O_7$ are reflected over the entire composition range examined, usually in the form of two strong thermal effects on the DTA curves. Similarly, the γ/δ transition of $Na_4P_2O_7$ is also accompanied by a strong thermal effect. The polymorphic transition of $Na_3Y(PO_4)_2$, which occurs at 850°C in the pure compound, is lowered a little in the system, and forms a visible thermal effect only in the composition range 0–50 wt.% of $Na_4P_2O_7$.

It was discovered that the double orthophosphate $Na_3Y_2(PO_4)_3$ also forms a binary section with the pyrophosphate, $Na_4P_2O_7$. Figure 3 shows

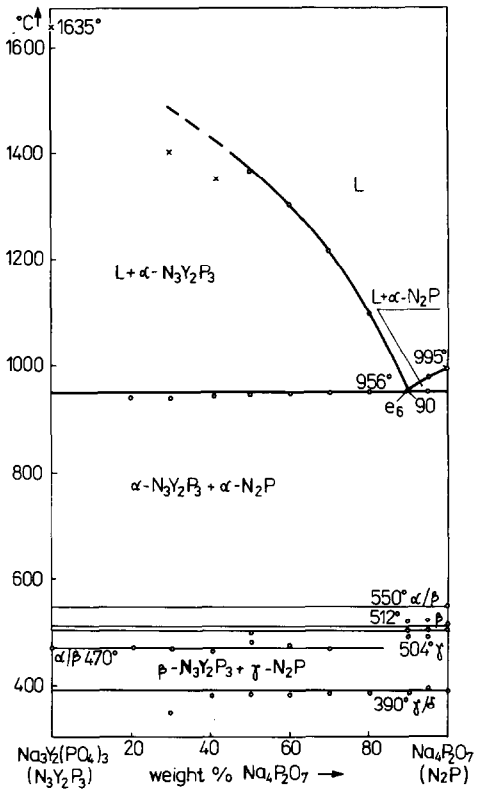

Fig. 3. Phase diagram of the system $Na_3Y_2(PO_4)_3$–$Na_4P_2O_7$: ○, thermal analysis; ×, optical.

the phase diagram of this system as determined by differential thermal analysis of heating and powder X-ray diffraction. The initial phosphates form a simple eutectic system: eutectic temperature e_6, 956°C; composition, 90 wt.% $Na_4P_2O_7$. The high temperature α/β and β/γ transitions of $Na_4P_2O_7$, within the composition range 90–100 wt.% of $Na_4P_2O_7$, form three strong thermal effects on the DTA curves. In the other part of the system, they are reflected in the form of one big effect probably together with the α/β transition of $Na_3Y_2(PO_4)_3$, which proceeds at 470°C in pure $Na_3Y_2(PO_4)_3$. The γ/δ transition of $Na_4P_2O_7$ is also accompanied by a strong thermal effect.

Figure 4 shows the phase diagram of the system YPO_4–Na_3PO_4–$Na_4P_2O_7$ with solidification isotherms.

The binary systems mentioned above divide the entire ternary system into three partial systems which are shown in Fig. 4. A ternary eutectic occurs in each of them, namely E_1 (930°C), E_2 (940°C) and E_3 (900°C). In the composition range under consideration, five primary crystallization fields of binary and ternary compounds appear. These fields are sepa-

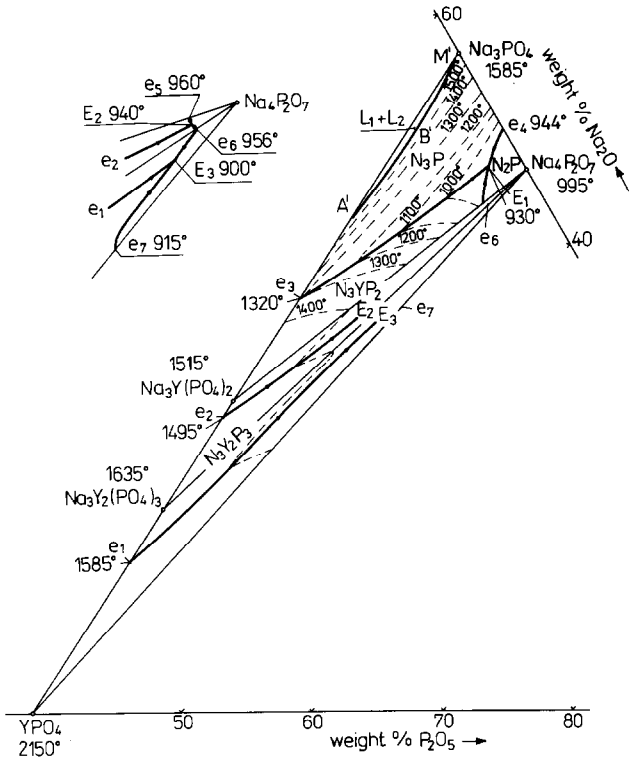

Fig. 4. Phase diagram of the system YPO_4–Na_3PO_4–$Na_4P_2O_7$: $N_3Y_2P_3 = Na_3Y_2(PO_4)$; $N_3YP_2 = Na_3Y(PO_4)_2$; $N_3P = Na_3PO_4$; $Na_4P_2O_7 = N_2P$.

rated by eutectic curves, e_4E_1 ($Na_3PO_4 + Na_4P_2O_7$), e_3E_1 ($Na_3PO_4 + Na_3Y(PO_4)_2$), $E_1e_5E_2$ ($Na_3Y(PO_4)_2 + Na_4P_2O_7$), $E_2e_6E_3$ ($Na_3Y_2(PO_4)_3 + Na_4P_2O_7$), e_1E_3 ($Na_3Y_2(PO_4)_3 + YPO_4$) and E_3e_7 ($YPO_4 + Na_4P_2O_7$), with the compounds that crystallize along them.

In the side system YPO_4–Na_3PO_4 there is a field of limited solubility of the components in the liquid state within the composition range 75–99 wt.% of Na_3PO_4 (above 1630°C) [1]. This limited solubility is also present in the same ternary melts within the A'B'M' field.

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