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# Phase equilibria in the system $YPO_4$-$Na_3PO_4$

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## Abstract

The phase diagram of the system $YPO_4$-$Na_3PO_4$ has been determined by differential, X-ray and microscopic methods. The system contains two intermediate compounds, $Na_3Y(PO_4)_2$ and $Na_3Y_2(PO_4)_3$. These double orthophosphates melt congruently at 1515 and 1635 ° C, respectively. Compound $Na_3Y(PO_4)_2$ shows a polymorphic transition at 850 ° C and $Na_3Y_2(PO_4)_3$ shows one at 470 ° C.

## INTRODUCTION

The research on calcium-yttrium phosphates, carried out in our laboratory over several years, has led to some interesting results. However, literature reports indicate that phosphates containing alkali metals and lanthanides are also of interest. Therefore, we have initiated an examination of sodium-yttrium phosphates. These compounds occur in the ternary system $Y_2O_3$-$Na_2O$-$P_2O_5$. The present paper presents the results of our investigations on double sodium-yttrium orthophosphates. Literature reports show that two types of double orthophosphates are known: $M^I_3Ln^{III}(PO_4)_2$, type **I**; and $M^I_3Ln^{III}_2(PO_4)_3$, type **II**, where $M^I$ = alkali metals, and $Ln^{III}$ = lanthanides, Sc, Y.

According to ref. 1, type **I** compounds containing Na and Y crystallise in the tetragonal system, the $\alpha$-form. The second type of structure, the $\beta$- or high-temperature form, was described by these authors for Na-Gd and Na-Y compounds. This "high" temperature form exhibits X-ray diffraction patterns only slightly different from the "low" temperature form [1].

Salmon et al. [2] prepared type **I** compounds containing Na and La, Pr, ... and Y and assigned them to the orthorhombic system.

After examining literature data, Bamberger et al. [3] concluded "...that many, if not all, of the preparations identified as having the stoichiometry $Na_3Ln_2(PO_4)_3$ (type **II**) consist mainly of $LnPO_4$ with minor amounts of $Na_3Ln(PO_4)_2$".

Double orthophosphates, $Na_3Ln(PO_4)_2$ and $Na_3Ln_2(PO_4)_3$, according to their composition, occur in the system $Ln^{III}PO_4$-$Na_3PO_4$.

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## EXPERIMENTAL

The following reagents were used: $Y_2O_3$, 99.99%; $H_3PO_4$, 85%, analytical grade; $NH_4H_2PO_4$, analytical grade; $Na_3PO_4 \cdot 12H_2O$, analytical grade; $Na_2CO_3$, analytical grade; and $NaH_2PO_4$, analytical grade. $YPO_4$, $Na_3PO_4$, $Y_2P_4O_{13}$ were synthesised in our laboratory. Yttrium orthophosphate, $YPO_4$, was obtained from solution by the method given in ref. 4. $Y_2P_4O_{13}$ phosphate was prepared from $Y_2O_3$ and $NH_4H_2PO_4$ according to ref. 5. Sodium orthophosphate, $Na_3PO_4$, was obtaining by slow dehydration of $Na_3PO_4 \cdot 12\ H_2O$ at 200, 300 and then at 600 ° C.

The binary system $YPO_4$–$Na_3PO_4$ was examined by differential thermal analysis, X-ray powder diffraction and microscopic examination in reflected light. Test samples were presynthesised by reaction in the solid phase. Molten and sintered samples were used for the investigations. Differential thermal analysis in heating mode was performed by means of a derivatograph type 3427 (MOM, Hungary) within the temperature range 20–1400 ° C (platinum cup, air atmosphere). High-purity alumina was used as the standard substance. In the thermal analysis, a furnace constructed in our laboratory was also used. Temperatures were read by means of a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of $Ca_2P_2O_7$, $K_2SO_4$, NaCl and the transition point of $K_2SO_4$ (583° C). The high-temperature thermal studies above 1400 ° C were performed in a horizontal resistance furnace with molybdenum winding, under argon. Test samples were presynthesised by reaction in the solid phase, pelletised, placed in a Pt30Rh boat and melted. Melting points were read by means of an optical pyrometer, which was calibrated against the melting points of $Na_3PO_4$ and $Ca_3(PO_4)_2$.

The quenching technique was also used for phase determination. The phases were identified by X-ray powder diffraction on an HZG-4 diffractometer (a Guinier camera) with Cu K$\alpha$ radiation.

The phase purity of the reagents and the phase structure of the products were studied microscopically (microsections were examined in reflected light).

## RESULTS AND DISCUSSION

The double orthophosphates mentioned in the introduction can occur in the systems $Ln^{III}PO_4$–$M^I_3PO_4$, according to their composition. The present paper describes phase examinations of the $YPO_4$–$Na_3PO_4$ system. This system was previously unknown and has been investigated in our laboratory across the full composition range and within the temperature range 20–1700 ° C. Its phase diagram is presented in Fig. 1. This shows that samples melt above 1400 ° C in nearly the entire system. Therefore, the liquidus curve and some solidus curves as well, were drawn on the basis of observations

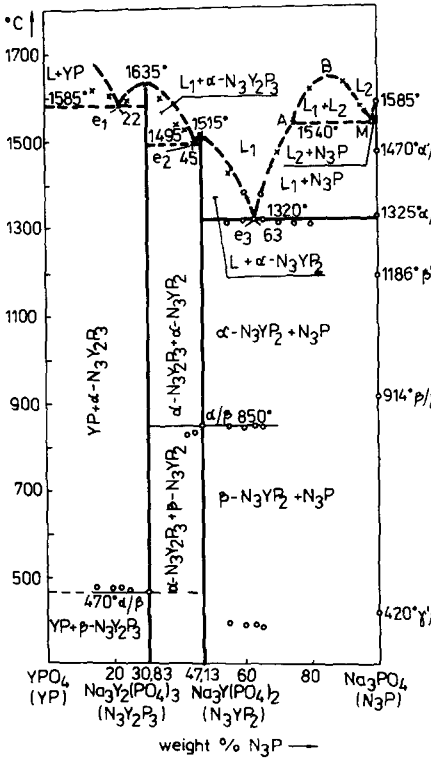

Fig. 1. Phase diagram of the system $YPO_4$–$Na_3PO_4$: o, thermal analysis (heating); ×, optical.

made with pelletised samples in a horizontal electric furnace. The temperatures were read by means of an optical pyrometer. Therefore the positions of the liquidus and solidus curves are approximate. Equilibria in the solid phase were determined on the basis of the thermal analysis during heating of both molten and sintered samples.

The investigations proved that two intermediate compounds occur in the $YPO_4$–$Na_3PO_4$ system. They are formed in 2 : 1 molar ratio $YPO_4$ : $Na_3PO_4$ (30.83 wt.% $Na_3PO_4$, 69.17 wt.%$YPO_4$) and in 1 : 1 molar ratio (47.13 wt.% $Na_3PO_4$, 52.87 wt.% $YPO_4$), i.e. $Na_3Y_2(PO_4)_3$ and $Na_3Y(PO_4)_2$, respectively. Phosphate $Na_3Y_2(PO_4)_3$ melts congruently at approx. 1635 °C and is stable down to room temperature. It was discovered that it shows a polymorphic transition at 470 °C (a strong thermal effect occurs at this temperature on the DTA curve of the sintered sample). The high-temperature modification ($\alpha$) cannot be stabilised at room temperature by quenching, either in air or in ice.

Phosphate $Na_3Y(PO_4)_2$ melts congruently at approximately 1515 °C and is stable down to room temperature. During differential thermal analysis of a sintered sample with the composition of this compound, a strong thermal effect occurs at 850 °C on the DTA curve. We conclude that it results from the polymorphic transition, $\alpha$-$Na_3Y(PO_4)_2 \rightarrow \beta$-$Na_3Y(PO_4)_2$. The examinations showed that the high-temperature modification ($\alpha$) can be stabilised at room temperature by rapid cooling in ice.

Several attempts were made to find the best method of synthesis for both these double orthophosphates in pure form. It was discovered that compound $Na_3Y(PO_4)_2$ is formed more easily. It can be obtained by means of several different reactions:

(1) $Na_3PO_4 + YPO_4 \rightarrow Na_3Y(PO_4)_2$ (900 °C for 15 h);

(2) $Y_2P_4O_{13} + 3Na_2CO_3 \rightarrow 2Na_3Y(PO_4)_2 + 3CO_2$ (850 °C for 24 h and then 900 °C for 15 h);

(3) $Y_2O_3 + 4NaH_2PO_4 + Na_2CO_3 \rightarrow 2Na_3Y(PO_4)_2 + CO_2 + H_2O$ (200, 300 and 500 °C for 24 h and then 900 °C for 15 h).

Attempts to synthesise phosphate $Na_3Y_2(PO_4)_3$ proved that: (1) if the mixture of 2:1 stoichiometric ratio of $YPO_4$ and $Na_3PO_4$ is sintered or melted, a mixture of $Na_3Y(PO_4)_2$ and $Na_3Y_2(PO_4)_3$ is obtained in the reaction products; and (2) if the mixture of one mole of $Y_2O_3$ and three moles of $NaPO_3$ is sintered at 800 °C, $YPO_4$ and $Na_3Y(PO_4)_2$ are obtained. However, as a result of sintering at 1000 °C for 15 h, pure phosphate phase, $Na_3Y_2(PO_4)_3$, is obtained.

Difficulties in obtaining phosphate $Na_3Y_2(PO_4)_3$ complicated the research on the $YPO_4$–$Na_3PO_4$ system. The determination of its phase diagram was preceded by different thermal examinations and the phase compositions of the products obtained were identified each time by X-ray diffractometry. It was discovered, for example, that if samples from the $YPO_4$–$Na_3PO_4$ system are synthesised from initial orthophosphates, these compounds together with $Na_3Y(PO_4)_2$ are usually present in the reaction products (in both sintered and molten samples).

Finally, the phase diagram presented in Fig. 1 was determined on the basis of the following procedure. It was assumed that the $YPO_4$–$Na_3PO_4$ system is composed of three partial binary systems: (1) $YPO_4$–$Na_3Y_2(PO_4)_3$; (2) $Na_3Y_2(PO_4)_3$–$Na_3Y(PO_4)_2$; and (3) $Na_3Y(PO_4)_2$–$Na_3PO_4$. Each of these systems was examined separately, i.e.:

- samples from the first system were synthesised from $YPO_4$ and $Na_3Y_2(PO_4)_3$ by sintering at 1100 °C for 3 h and then melting;
- samples from the second system were synthesised from $Na_3Y_2(PO_4)_3$ and $Na_3Y(PO_4)_2$ by sintering at 1000 °C for 3 h and then melting;
- samples from the third system were synthesised from $Na_3Y(PO_4)_2$ and $Na_3PO_4$ by sintering at 900 °C for 3 h and then melting.

During this, it was discovered that each of these partial systems is eutectic. To summarise, in the $YPO_4$–$Na_3PO_4$ system, there are three eutectics: $e_1$ at 1585 °C containing approx. 22 wt.% $Na_3PO_4$, $e_2$ at 1495 °C containing approx. 45 wt.% $Na_3PO_4$ and $e_3$ at 1320 °C containing 63 wt.% $Na_3PO_4$.

According to literature data, sodium orthophosphate, $Na_3PO_4$, shows many polymorphic transitions. During our experiments, we detected only four of them, namely: $\alpha \rightarrow \beta'$ (1325 °C); $\beta' \rightarrow \beta$ (1186 °C); $\beta \rightarrow \gamma'$ (914 °C); and $\gamma' \rightarrow \gamma$ (420 °C). In the partial system $Na_3Y(PO_4)_2$–$Na_3PO_4$, on the DTA curve, within the approximate composition range 55–65 wt.% $Na_3PO_4$, a very strong thermal effect occurs at around 400 °C. It results (probably) from the $\gamma' \rightarrow \gamma$-$Na_3PO_4$ polymorphic transition. This effect does not appear in that part of the system rich in $Na_3PO_4$; nor are the effects connected with another polymorphic transition of $Na_3PO_4$ observed. This may result from the fact that there is a limited solubility of components in the liquid state, within the approximate composition range 75–100 wt.% $Na_3PO_4$ at high temperatures (around 1540 °C). Therefore the liquid is divided into two liquid solutions: $L_1$ and $L_2$. There is a field of stability of liquid solutions with unlimited mutual phase solubility above point B (Fig. 1), over the liquidus curve. In the ABM field, the mixture of liquid solutions, $L_1 + L_2$, is stable. To the left of this field, over the liquidus curve, there is a monophase field of stability of liquid solution $L_1$; and on the right, there is a monophase field of stability of liquid solution $L_2$. Between the liquidus curve and the solidus curve, there are two-phase fields. At point M (a monotectic point), at the constant temperature of approx. 1540 °C (monotectic temperature), a monotectic transition proceeds according to the reaction: $L_{2M} \rightarrow Na_3PO_4 + L_{1A}$ (where $L_{2M}$ is liquid $L_2$ with the composition of point M, and $L_{1A}$ is the liquid $L_1$ with composition corresponding to point A).

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