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PHASE EQUILIBRIA IN THE P_2O_5-RICH PART OF THE SYSTEM Y_2O_3–Na_2O–P_2O_5

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Abstract

In the ternary system Y_2O_3–Na_2O–P_2O_5, the partial system $Y(PO_3)_3$–$NaPO_3$–P_2O_5 was examined by means of differential thermal analysis and X-ray powder diffraction; its phase diagram is given.

Keywords: phase equilibria, sodium–yttrium phosphates, system $Y(PO_3)_3$–$NaPO_3$–P_2O_5

Introduction

The aim of the present paper is to report a study of the phase equilibria in the system $Y(PO_3)_3$–$NaPO_3$–P_2O_5. This is in the P_2O_5-richest portion of the ternary system Y_2O_3–Na_2O–P_2O_5. Previous studies in our laboratory proved that serious experimental difficulties resulting from the thermal instability of the preparations at low temperatures and from their considerable liability to form glasses in partial systems of the type $Ln(PO_3)_3$–MPO_3–P_2O_5 (where Ln=La, Ce or Y, and M=Na or K) [1–4]. These phenomena make the examination of phase equilibria quite difficult.

The system $Y(PO_3)_3$–$NaPO_3$–P_2O_5 is limited by three side-systems: $Y(PO_3)_3$–P_2O_5 [5], $Y(PO_3)_3$–$NaPO_3$ [6] and $NaPO_3$–P_2O_5. The phase diagrams of the first two systems are known. In the side-system $Y(PO_3)_3$–$NaPO_3$, there is an intermediate compound $Na_2Y(PO_3)_5$, which melts incongruently at 670°C; in the system $Y(PO_3)_3$–P_2O_5, the compound YP_5O_{14} exists; it also melts incongruently, at 860°C.

Experimental

Samples for investigations of the system $Y(PO_3)_3$–$NaPO_3$–P_2O_5 were prepared from the following original compounds: Y_2O_3 (purity, 99.99%; ZOCh-

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Poland), H_3PO_4 85% p.a. (POCh-Poland), $NaH_2PO_4{\cdot}H_2O$ p.a. (POCh-Poland) and $NH_4H_2PO_4$ p.a. (POCh-Poland).

$Y(PO_3)_3$, YP_5O_{14}, $NaPO_3$ and $Na_2Y(PO_3)_5$ were prepared in our laboratory [6]. Yttrium metaphosphate, $Y(PO_3)_3$, was obtained from a stoichiometric mixture of Y_2O_3 and H_3PO_4, which was sintered in a platinum crucible at 200°C for 1 day, then at 300°C for 2 days and 900°C for 1 day. Yttrium ultraphosphate, YP_5O_{14}, was obtained from a mixture of Y_2O_3 and H_3PO_4 in an Y:P molar ratio of 1:6.5, which was sintered in a platinum crucible at 200, 300 and 750°C for 2 days each.

Sodium metaphosphate, $NaPO_3$, was obtained from $NaH_2PO_4{\cdot}H_2O$ by heating at 300°C for 1 h and 500°C for 1 h. Sodium–yttrium metaphosphate,

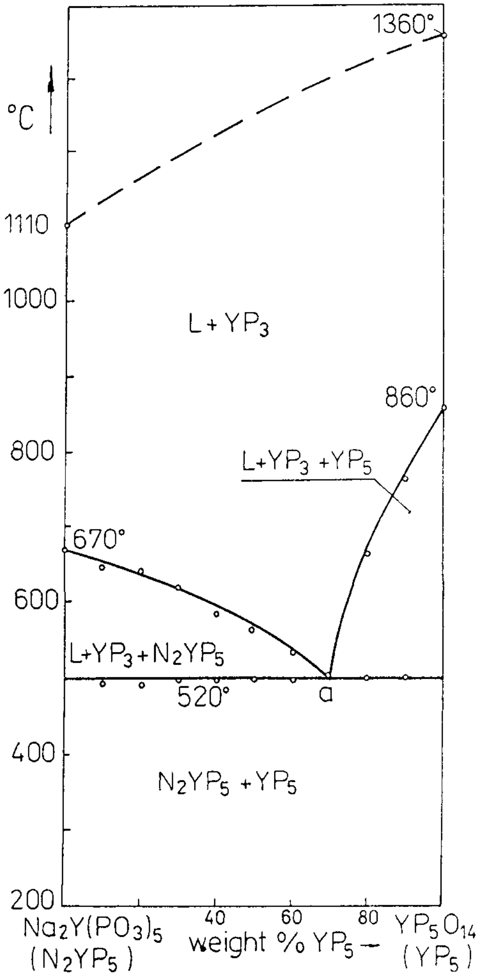

Fig. 1 Phase diagram of the system $Na_2Y(PO_3)_5$–YP_5O_{14}; ($Y(PO_3)_3$=YP_3; L=liquid phase)

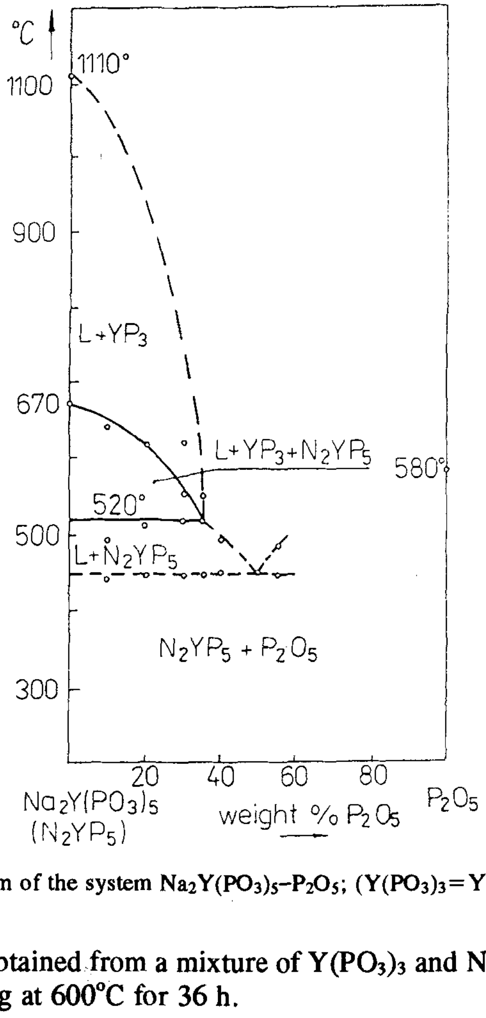

Fig. 2 Phase diagram of the system $Na_2Y(PO_3)_5$–P_2O_5; ($Y(PO_3)_3$=YP_3; L=liquid phase)

$Na_2Y(PO_3)_5$, was obtained from a mixture of $Y(PO_3)_3$ and $NaPO_3$ in a molar ratio of 1:2 by heating at 600°C for 36 h.

The investigations were performed by means of differential thermal (DTA) and X-ray analyses. Test samples were presynthesized by reactions in the solid phase. Initial substances, mixed in the desirable composition, were pressed into pellets and sintered at different temperatures for different times, depending on the composition. Platinum and porcelain crucibles were used.

The DTA was performed with a type 3427 derivatograph (MOM, Hungary) within the temperature range 20 to 1400°C. The operating conditions were as follows: sensitivity TG 500 mg, heating rate 10 deg·min^{-1}, platinum crucible. The standard substance used was Al_2O_3. The temperature was measured with a Pt/PtRh 10 thermocouple, which was standardized by using the melting points of NaCl (801°C) and K_2SO_4 (1073°C) and the polymorphic transition temperature of K_2SO_4 (583°C).

To define phase equilibria additionally, the quenching technique was also used; the samples were packed into platinum capsules, equilibrated in an electric furnace and then quenched in water. The phases obtained were identified by means of X-ray diffraction. The powder X-ray analysis at room temperature was performed in an HZG-4 diffractometer (CuK_α radiation, Ni filter).

Results and discussion

In order to determine the phase equilibria in the system $Y(PO_3)_3$–$NaPO_3$–P_2O_5, both in the solid phase and in the molten state, the samples were presynthesized by sintering at different temperatures. Table 1 shows the changes in the initial composition of three samples with different compositions after the following thermal treatment:

(a) samples were sintered at 300, 400 and 500°C for 10 h each and then quenched,

(b) samples were melted, and then cooled with grafting down to room temperature at a rate of 10 deg·min^{-1}.

Table 1 The composition changes of different initial samples due to thermal treatment

Initial composition of samples		Temperature treatment / °C	Phase composition of samples	
weight% of YP_5	weight% of NP		after thermal treatment*)	after thermal treatment**)
30	70	300	$NP+YP_5$	$NP+YP_3$
		400	$NP+YP_3$	
		500	$NP+N_2YP_3$	
50	50	300	YP_5+NP	YP_3+NP
		400	YP_3+NP	
		500	N_2YP_5	
70	30	300	YP_5+NP	N_2YP_5
		400	N_2YP_5	
		500	N_2YP_5	

$NaPO_3=NP$; $YP_5O_{14}=YP_5$; $Y(PO_3)_3=YP_3$

*) samples were sintered 10 h and then quenched

**) samples were melted and then cooled down to room temperature at the rate of 10 deg·min^{-1}.

The phase compositions of products obtained as a result of the described thermal treatment were determined in each case by powder X-ray analysis. It was discovered that the samples start to decompose as early as during sintering. The process was accompanied by the evaporation of P_2O_5, which resulted in a change in the initial compositions of the samples. For instance, a sample with the initial composition 30wt% $NaPO_3$+70wt% YP_5O_{14} forms $Na_2Y(PO_3)_5$ after sintering at 400°C.

The thermal and X-ray examinations proved that there are two subsystems in the system $Y(PO_3)_3$–$NaPO_3$–P_2O_5: (1) $Na_2Y(PO_3)_5$–YP_5O_{14}, and (2) $Na_2Y(PO_3)_5$–P_2O_5. An attempt was made to determine their diagrams; the results are presented in Figs 1 and 2.

Samples for examination of the system $Na_2Y(PO_3)_5$–YP_5O_{14} were synthesized from the initial phosphates by sintering them at 300°C for 12 h. Both yttrium ultraphosphate and sodium–yttrium metaphosphate, $Na_2Y(PO_3)_5$, are compounds which are formed peritectically from yttrium metaphosphate, $Y(PO_3)_3$, according to the reactions:

$$Y(PO_3)_3 + Lp_1 = YP_5O_{14}, \text{ and}$$

$$Y(PO_3)_3 + Lp_2 = Na_2Y(PO_3)_5$$

where Lp_1=liquid with the composition at point p_1, Lp_2=liquid with the composition at point p_2. Therefore, the section $Na_2Y(PO_3)_5$–YP_5O_{14} is polyphase in its upper part. Above 520°C, there are four phases: liquid L and the phosphates $Y(PO_3)_3$, $Na_2Y(PO_3)_5$ and YP_5O_{14}. As a result of peritectic reactions, liquid *L*

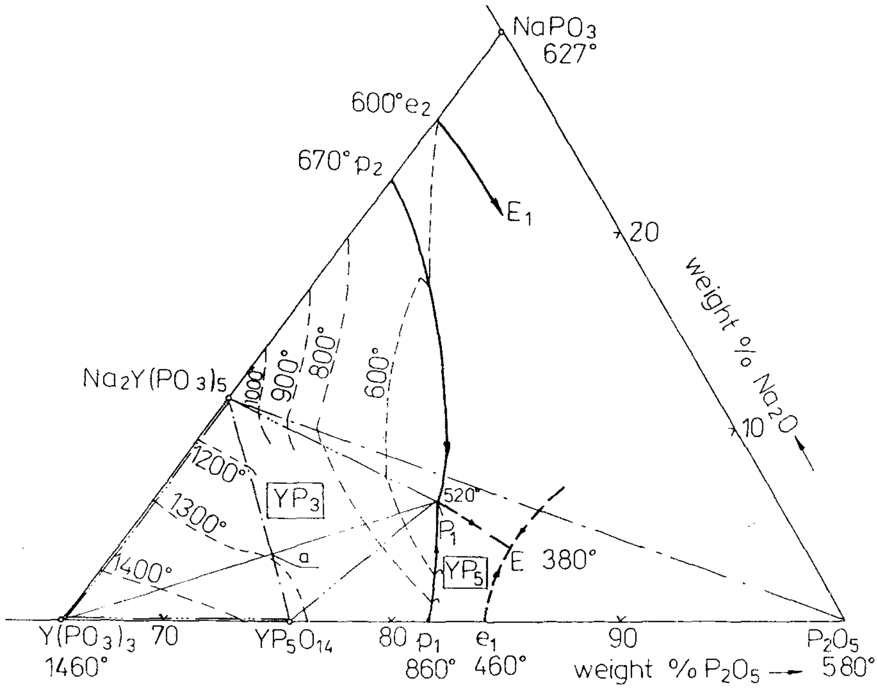

Fig. 3 The partial system $Y(PO_3)_3$–$NaPO_3$–P_2O_5; $Y(PO_3)_3$=YP_3, YP_5O_{14}=YP_5

and $Y(PO_3)_3$ are consumed to form the compounds $Na_2Y(PO_3)_5$ and YP_5O_{14}. Below 520°C, there are only these two phosphates. The liquidus curve in the phase diagram (Fig. 1) of the system under investigation is drawn with a broken line because it is hypothetical.

Samples for examination of the section $Na_2Y(PO_3)_5$–P_2O_5 were prepared from $Na_2Y(PO_3)_5$ and $NH_4H_2PO_4$. The initial compounds were mixed in different weight ratios and presintered at 200°C for 5 h and at 300°C for 2 h. Samples synthesized in this way were examined by measuring DTA heating curves. The results, together with those of X-ray analysis, yielded the phase equilibria in the composition range 0–55wt% P_2O_5. The volatility of P_2O_5 and its aggressive interaction with platinum increase together with the enrichment of the samples with P_2O_5. Therefore, it was impossible to perform measurements in the P_2O_5-richest part of the system. The suggested phase diagram of the system $Na_2Y(PO_3)_5$–P_2O_5 is presented in Fig. 2. The range of the ternary peritectic reaction extends up to 38wt% P_2O_5 at 62wt% $Na_2Y(PO_3)_5$. The eutectic temperature is 450°C; the composition of the eutectic is 50wt% P_2O_5 at 50wt% $Na_2Y(PO_3)_5$.

The phase diagram with liquidus isothermal lines for the system Y_2O_3–Na_2O–P_2O_5 in its P_2O_5-rich part, obtained from the present experiments, is shown in Fig. 3. During the solidification of alloys corresponding to the points of the field $Y(PO_3)_3$–$Na_2Y(PO_3)_5$–P_1–YP_5O_{14} (triple peritectic quadrangle), a triple peritectic reaction takes place:

$$Y(PO_3)_3 + Lp_1 \rightarrow Na_2Y(PO_3)_5 + YP_5O_{14}$$

at 520°C where Lp_1 is liquid with the composition at point P_1. This reaction proceeds at the constant temperature of 520°C.

References

1 I. Szczygieł and T. Znamierowska, J. Solid State Chem., 82 (1989) 181.
2 W. Jungowska, and T. Znamierowska, Mater. Chem. Phys., 24 (1990) 487.
3 G. Czupińska and T. Znamierowska, Prace Naukowe AE we Wrocławiu, 526 (1990) 233.
4 T. Znamierowska and J. Obremski, J. Thermal Anal., 37 (1991) 285.
5 W. Szuszkiewicz, Polish J. Chem., 67 (1993) 1539.
6 W. Szuszkiewicz, Mater. Chem. Phys., 38 (1994) 15.

Zusammenfassung — Im ternären System Y_2O_3–Na_2O–$_2O_5$ wurde mittels DTA und Röntgen-Pulverdiffraktion das Teilsystem $Y(PO_3)_3$–$NaPO_3$–P_2O_5 untersucht; das zugehörige Phasendiagramm wird angegeben.