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Phase equilibria in the system YPO_4–$NaPO_3$

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Abstract

The phase diagram of the system YPO_4–$NaPO_3$ has been determined by differential thermal analysis, X-ray diffraction, infrared spectroscopy and microscopic methods. The system contains one intermediate compound, $Na_2YP_3O_{10}$. This double triphosphate melts incongruently at 640°C.

INTRODUCTION

Tripolyphosphates of rare earth elements and mixed tripolyphosphates of lanthanides and alkali metals are a relatively unknown group of compounds. There are only a few published works that report their existence and their methods of synthesis. Tripolyphosphates of the lanthanides La, Ce, Nd, Sm, Gd, Dy and Y have been obtained [1–8]. The authors have also managed to obtain mixed sodium–lanthanide tripolyphosphates of $NaLn_3(P_3O_{10})_2 \cdot H_2O$ type (where Ln = Pr, Tb, Ho, Eu, Yb, Lu). In the systems $M_5P_3O_{10}$–$Eu(NO_3)_3$–H_2O (where M = Cs, NH_4) [9], mixed europium tripolyphosphates were isolated. These compounds were obtained from solutions. There is no information in the literature on phase investigation of tripolyphosphates.

The previously unknown binary section YPO_4–$NaPO_3$ was determined during our phase investigations on the ternary system Y_2O_3–Na_2O–P_2O_5. It was discovered that sodium–yttrium tripolyphosphate with the formula $Na_2YP_3O_{10}$, is formed in this system. However, the compound $NaYP_2O_7$, which would correspond to the KYP_2O_7 identified in ref. 10, was not obtained.

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EXPERIMENTAL

The following starting reagents were used: Y_2O_3, 99.99%; H_3PO_4, 85%, analytical grade; NaH_2PO_4, analytical grade; Na_2HPO_4, analytical grade; $NH_4H_2PO_4$, analytical grade; and Na_2CO_3, analytical grade. YPO_4, $Y_2P_4O_{13}$, $Y(PO_3)_3$, $NaPO_3$ and $Na_4P_2O_7$ were synthesised in our laboratory. Yttrium orthophosphate YPO_4 was obtained by the method given in ref. 11. Yttrium phosphate $Y_2P_4O_{13}$ was prepared according to ref. 12. Yttrium metaphosphate $Y(PO_3)_3$ was prepared from Y_2O_3 and H_3PO_4 according to ref. 13. Sodium metaphosphate $NaPO_3$ was obtained from NaH_2PO_4 by heating at 500°C for 1 h. Sodium pyrophosphate $Na_4P_2O_7$ was prepared from Na_2HPO_4 by heating at 150°C for 1 h and at 500°C for 12 h.

The binary system YPO_4–$NaPO_3$ was examined by differential thermal analysis of heating, powder X-ray diffraction, infrared spectroscopy and microscopy in reflected light.

The differential thermal analysis of heating was performed by means of a derivatograph, type 3427 (MOM, Hungary) within the temperature range 20–1450°C (platinum cup, air atmosphere). High purity Al_2O_3 was used as the standard substance.

The phases were identified by X-ray powder diffraction on a HZG-4 diffractometer (Guinier camera) with Cu Kα radiation. In order to identify phases occurring in the system, infrared spectra were measured over the range 1400–400 cm^{-1} with an IR-75 Specord spectrophotometer. The samples were prepared in the form of pellets in KBr.

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

Figure 1 shows the phase diagram of the system YPO_4–$NaPO_3$. This system was investigated within the composition range 30–100 wt.% $NaPO_3$ and up to approx. 1500°C, by thermal analysis (heating), X-ray diffraction, microscopy and IR spectroscopy. It was discovered that the binary tripolyphosphate with the molar ratio $YPO_4 : NaPO_3 = 1:2$ is formed, and it was given the formula $Na_2YP_3O_{10}$. This compound melts peritectically at 640°C giving YPO_4 and a liquid rich in $NaPO_3$. It was characterised on the basis of thermal and X-ray examinations. Thermal analysis of the pure $Na_2YP_3O_{10}$ phase showed that there are two exothermal effects on the DTA heating curve: at 640°C and at approx. 1200°C. The first effect proceeds without mass loss whereas the second has a well marked mass loss on the TG curve. In order to interpret these effects, the $Na_2YP_3O_{10}$ sample was sintered at 700°C for 1 h and quenched. X-ray analysis of the obtained

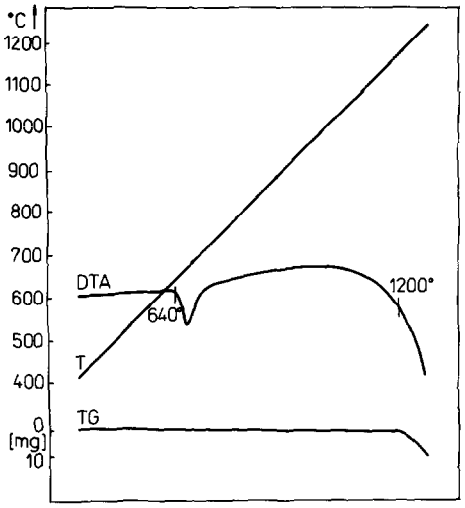

Fig. 1. T, DTA and TG curves of $Na_2YP_3O_{10}$, mass 330 mg, in air atmosphere.

product showed the presence of YPO_4. Examinations of isothermal mass losses were also carried out for $Na_2YP_3O_{10}$ (at 1200°C). To achieve this, pressed pellets of this compound were placed in a platinum crucible, sintered at 1200°C and weighed several times. It was discovered that, in these conditions, pure $Na_2YP_3O_{10}$ decomposes completely to YPO_4 after approx. 90 h. The results of the investigations indicate that $Na_2YP_3O_{10}$ decomposes incongruently (at 640°C) according to the reaction

$$Na_2YP_3O_{10}(cr) \rightarrow YPO_4(cr) + NaPO_3(am)$$

where cr = crystal form and am = amorphous form.

A comparison of the thermal effects that can be seen in Figs. 2 and 3 confirms these conclusions. Both figures show an analogous thermal effect on the TG curves at approx. 1200°C, which results from the mass loss caused by the decomposition (vaporisation) of $NaPO_3$ at 1200°C. Table 1 shows X-ray data for $Na_2YP_3O_{10}$ estimated by the powder method.

Numerous examinations carried out in our laboratory led to the formulation of three methods for the synthesis of pure $Na_2YP_3O_{10}$:

1. Sintering a 1:1 molar ratio mixture of Na_2CO_3 and $Y(PO_3)_3$ at 550°C for 24 h.

2. Sintering the mixture composed of 1 mole of $Na_4P_2O_7$ and 1 mole of $Y_2P_4O_{13}$ at 580°C for 48 h.

3. Sintering the mixture of $NH_4H_2PO_4$, Y_2O_3 and Na_2CO_3 (6:1:2 molar ratio) at 200, 300, 500 and 550°C for 12 h at each temperature.

It is worth mentioning that, although numerous attempts were made, pure $Na_2YP_3O_{10}$ could not be obtained from the stoichiometric mixture of YPO_4 and $NaPO_3$ by the solid phase reaction. This may result from the large differences in the melting points of the initial phosphates, YPO_4

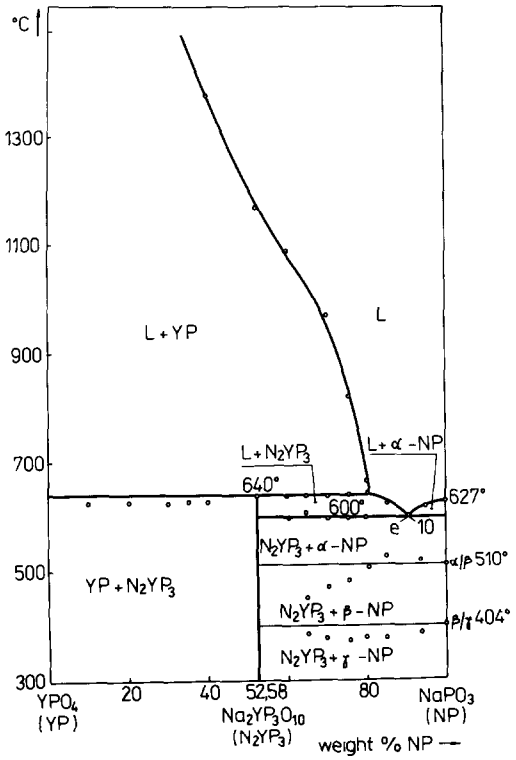

Fig. 2. Phase diagram of the system YPO_4–$NaPO_3$.

(2150°C) and $NaPO_3$ (627°C), and from the low temperature of the peritectic decomposition of $Na_2YP_3O_{10}$ (640°C). Because of these difficulties, samples for investigations of the system YPO_4–$NaPO_3$ were prepared from YPO_4 and $Na_2YP_3O_{10}$ to determine phase equilibria for that part of the

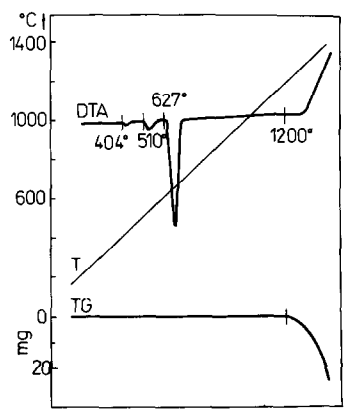

Fig. 3. T, DTA and TG curves of $NaPO_3$, mass 330 mg, in air atmosphere.

TABLE 1

X-ray data for $Na_2YP_3O_{10}$

2θ(exp)	d(exp)	I/I_0
11.04	8.015	12
13.14	6.739	5
13.41	6.605	7
14.19	6.242	15
14.67	6.040	5
17.47	5.075	4
17.74	4.999	6
19.70	4.506	4
20.63	4.305	15
21.40	4.153	100
25.03	3.558	10
25.93	3.436	45
26.20	3.402	45
27.14	3.286	7
29.23	3.055	10
29.44	3.034	14
30.52	2.929	84
31.03	2.882	35

system rich in yttrium orthophosphate; and from $Na_2YP_3O_{10}$ and $NaPO_3$ to determine the phase equilibria for that part of the system rich in sodium metaphosphate. The initial compounds, weighed in the correct amounts, were ground, pelletised and synthesised, initially by sintering at 550°C for 12 h.

Figure 1 shows the liquidus and solidus curves; the equilibria in the solid phase in the YPO_4–$NaPO_3$ system were determined by differential thermal analysis of heating. The peritectic reaction takes place up to 81 wt.% of $NaPO_3$. There is a eutectic in the system at 600°C, at 90 wt.% $NaPO_3$. Pure sodium metaphosphate shows two known polymorphic transitions ($\alpha \rightarrow \beta$ at 510°C and $\beta \rightarrow \gamma$ at 404°C). Both these transitions are reflected in lowered thermal effects in the YPO_4–$NaPO_3$ system.

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