Journal of Thermal Analysis, Vol. 45 (1995) 1037-1041

PHASE EQUILIBRIA IN THE SYSTEM YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$

Grażyna Czupińska

Department of Inorganic Chemistry, Faculty of Engineering and Economics,
Academy of Economics, 53354 Wroclaw, Poland

Abstract

The phase equilibria in that part of the ternary system YPO_4–K_3PO_4–$Mg_3(PO_4)_2$ which contains the composition range YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$ were examined and determined by differential thermal analysis, X-ray powder diffraction and microscopic analysis in reflected light.

Keywords: phase diagrams, phase equilibria, system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$

Introduction

The previously unknown phase diagram of the partial system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$ has been determined within our studies on the system YPO_4–K_3PO_4–$Mg_3(PO_4)_2$. The partial ternary system is surrounded by the binary side-systems YPO_4–$Mg_3(PO_4)_2$, $Mg_3(PO_4)_2$–$KMgPO_4$ and YPO_4–$KMgPO_4$. The phase diagrams of the first two systems are known [1, 2]. YPO_4 and $Mg_3(PO_4)_2$ form a simple eutectic system. The system $Mg_3(PO_4)_2$–$KMgPO_4$ contains one intermediate compound, $KMg_4(PO_4)_3$, which melts peritectically at 1175°C. The phase equilibria in the binary system YPO_4–$KMgPO_4$ are not known.

Experimental

The following analytical grade materials were used: Y_2O_3 99.99%, H_3PO_4 85%, MgO, K_2CO_3 and $MgHPO_4 \cdot 3H_2O$.

YPO_4, $Mg_2P_2O_7$, $Mg_3(PO_4)_2$, $KMgPO_4$ and $KMg_4(PO_4)_3$ were prepared in our laboratory.

YPO_4 was obtained from 0.4 wt% of Y_2O_3, 15 wt% of P_2O_5 (as H_3PO_4) and 84.6 wt% of distilled water by the method given in [3].

$Mg_2P_2O_7$ was prepared from $MgHPO_4 \cdot 3H_2O$ by heating at 900°C for 1 h.

$Mg_3(PO_4)_2$ was prepared from $Mg_2P_2O_7$ and MgO by heating at 1200°C for 20 minutes.

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

$KMgPO_4$ was synthesized from $Mg_2P_2O_7$ and K_2CO_3 by the method given in [2].

$KMg_4(PO_4)_3$ was prepared from $KMgPO_4$ and $Mg_3(PO_4)_2$ by heating at 1100°C for 1 h [2].

The system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$ was examined by DTA during heating, X-ray powder diffraction and microscopic analysis in reflected light. Samples for examination were prepared from the starting phosphates and treated preliminarily by sintering in the temperature interval 600–1100°C. Molten and sintered samples were used for thermal analysis. In the DTA during heating, a 3427 derivatograph (MOM, Hungary) was used within the temperature range 20–1400°C; high-purity Al_2O_3 was used as a standard substance. 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, and the transition point of K_2SO_4 (585°C). High-temperature thermal studies above 1400°C were performed in a vertical resistance furnace with molybdenum winding, under argon. Temperatures 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 phase purities of the reagents and the phase structures of the products were studied microscopically. Microsections were prepared from molten and crystallized samples, which were polished and examined in reflected light. The phases were identified by means of X-ray powder diffraction on an HZG-4 diffractometer (a Guinier camera) with CuK_α radiation.

Results and discussion

The system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$ was examined by using DTA, X-ray diffractometry and microscopy in reflected light. The first step was to determine the phase diagram of the binary side-system YPO_4–$KMgPO_4$. Samples for the investigations were synthesized from the starting orhophosphates and then subjected to complex thermal treatment. Sintering temperatures: 600–1100°C; duration of sintering: 30 min–7 days. The sintered samples were either cooled slowly down to room temperature or frozen in ice. The samples were also heated without preliminary synthesis up to 1000, 1100, 1160°C and then frozen in ice. Molten samples were cooled with grafting. X-ray photographs of the samples prepared in this way always showed a mixture of YPO_4 and $KMgPO_4$, which means that the starting phosphates did not form new compounds. Figure 1 presents the phase diagram of the system YPO_4–$KMgPO_4$.

With $KMgPO_4$, YPO_4 forms a eutectic e_1 at 70 wt% of $KMgPO_4$ at 1160°C. The liquidus curve over the composition range 50–100 wt% of $KMgPO_4$ was estimated on the basis of DTA. In the other part of the system, the melting points were read by means of an optical pyrometer. $KMgPO_4$ has several polymorphic modifications [2]. In the system YPO_4–$KMgPO_4$ under investigation

three polymorphic transitions of $KMgPO_4$ are reflected in the form of thermal effects in the DTA curves. The transitions α/β (780°C) and β/γ (570°C) can be observed within the composition range 20–100 wt% of $KMgPO_4$, while the effect of the γ/δ transition can be detected only within the composition range 60–100 wt% of $KMgPO_4$.

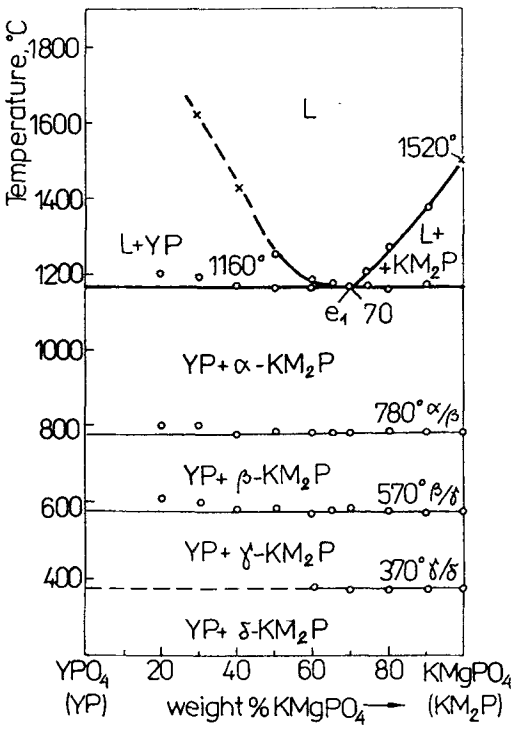

Fig. 1 Phase diagram of the system YPO_4–$KMgPO_4$; o - thermal analysis, x - optical

Examinations of the system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$ showed that the mixed orthophosphate $KMg_4(PO_4)_3$ forms a previously unknown section with YPO_4.

Figure 2 presents the phase diagram of the system YPO_4–$KMg_4(PO_4)_3$ which was determined by DTA during heating, X-ray diffractometry and microscopy.

This system is complex and is ternary in the upper part. Above 1100°C there are four phases: liquid *L*, YPO_4, $KMg_4(PO_4)_3$ and $Mg_3(PO_4)_2$. As a result of a peritectic reaction, *L* and $Mg_3(PO_4)_2$ are used up to form crystals of $KMg_4(PO_4)_3$. Below 1100°C there are only two phases, YPO_4 and $KMg_4(PO_4)_3$, and the system is binary in nature. $KMg_4(PO_4)_3$ has several polymorphic modifications [2]. In the system YPO_4–$KMg_4(PO_4)_3$ under investigation, only one transition, α/β (980°C), causes thermal effects within the composition range 30–100 wt% of $KMg_4(PO_4)_3$.

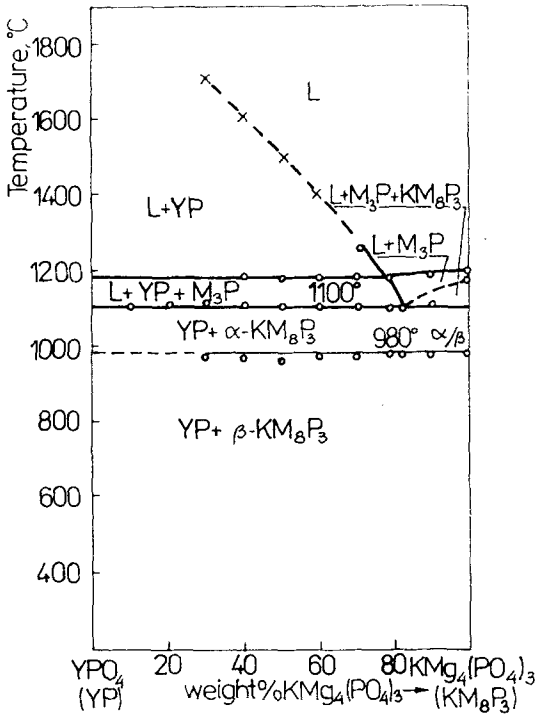

Fig. 2 Phase diagram of the system YPO_4–$KMg_4(PO_4)_3$; $Mg_3(PO_4)_2$=M_3P, o - thermal analysis, x - optical

Figure 3 presents the phase diagram of the system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$.

Solidification isotherms are marked in the diagram. In the composition under investigation, there are two binary compounds: YPO_4 and $Mg_3(PO_4)_2$, and two ternary compounds: $KMgPO_4$ and $KMg_4(PO_4)_3$, which crystallize from the liquid phase. The primary crystallization fields of these phosphates are separated by either eutectic or peritectic curves:

e_1E of binary eutectic (YPO_4+$KMgPO_4$),

e_3E of binary eutectic ($KMgPO_4$+$KMg_4(PO_4)_3$),

p_1P of binary peritectic, according to the reaction:

$$L_{p1}P + Mg_3(PO_4)_2 \rightarrow KMg_4(PO_4)_3,$$

e_2P of binary eutectic (YPO_4+$Mg_3(PO_4)_2$),

PE of binary eutectic (YPO_4–$KMg_4(PO_4)_3$).

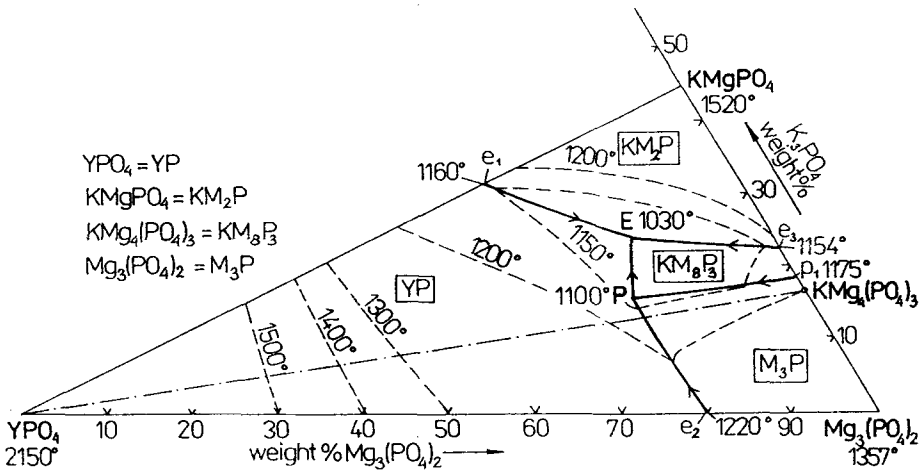

Fig. 3 Phase diagram of the system YPO_4–$KMgPO_4$–$Mg_3(PO_4)_2$

In the side-system $KMgPO_4$–$Mg_3(PO_4)_2$, a binary peritectic reaction occurs at 1175°C and, as a result of this reaction, $KMg_4(PO_4)_3$ is produced. This is reflected in the ternary system under investigation in the form of ternary peritectic *P*. As a result of the reaction of $Mg_3(PO_4)_2$ and the liquid with composition corresponding to point *P*, YPO_4 and $KMg_4(PO_4)_3$ are formed according to the ternary peritectic reaction:

$$L_P + Mg_3(PO_4)_2 \rightarrow YPO_4 + KMg_4(PO_4)_3$$

This peritectic reaction proceeds at the constant temperature of 1100°C. In the system under investigation, crystallization ends at point *E*, where the ternary eutectic evolves (YPO_4+$KMgPO_4$+$KMg_4(PO_4)_3$) at the constant temperature of 1030°C.

References

1 G. Czupińska, J. Thermal Anal., 38 (1992) 2343.
2 J. Berak and T. Podhajska-Kaźmierczak, Polish J. Chem., 65 (1991) 1137.
3 G. Czupińska and T,. Znamierowska, J. Thermal Anal., 39 (1993) 539.

Zusammenfassung — Im ternären System YPO_4-K_3PO_4-$Mg_3(PO_4)_2$ wurde das Phasengleichgewicht des Teiles mit dem Kompositionsintervall YPO_4-$KMgPO_4$-$Mg_3(PO_4)_2$ untersucht und mittels Differentialthermoanalyse, Röntgenpulverdiffraktion und Auflichtmikroskopie bestimmt.