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PHASE EQUILIBRIA IN THE SYSTEM YPO_4–K_3PO_4–$KMgPO_4$

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Abstract

The phase equilibria in the part of the ternary system YPO_4–K_3PO_4–$Mg_3(PO_4)_2$ over the composition range YPO_4–K_3PO_4–$KMgPO_4$ 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–K_3PO_4–$KMgPO_4$, thermal analysis

Introduction

The hitherto unknown phase diagram of the partial system YPO_4–K_3PO_4–$KMgPO_4$ 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–$KMgPO_4$, YPO_4–K_3PO_4 and K_3PO_4–$KMgPO_4$, which were previously investigated in our laboratory [1–3]. YPO_4 and $KMgPO_4$ form a simple eutectic system. The system YPO_4– K_3PO_4 contains one intermediate compound, $K_3Y(PO_4)_2$, melting peritectically at 1460°C. The system K_3PO_4–$KMgPO_4$ contains one intermediate compound, $K_4Mg(PO_4)_2$, which melts congruently at 1374°C. $K_4Mg(PO_4)_2$ and $KMgPO_4$ form a simple eutectic system. $K_4Mg(PO_4)_2$ and K_3PO_4 form continuous solid solutions.

Experimental

The following analytical grade materials were used: Y_2O_3 99.99%, H_3PO_4 85%, K_2CO_3, $K_3PO_4{\cdot}3H_2O$ and $MgHPO_4{\cdot}3H_2O$. YPO_4, $Mg_2P_2O_7$, K_3PO_4, $KMgPO_4$, $K_4Mg(PO_4)_2$ and $K_3Y(PO_4)_2$ were prepared in our laboratory.

YPO_4 was obtained from 0.4 mass% of Y_2O_3, 15 mass% of P_2O_5(as H_3PO_4) and 84.6 mass% of distilled water by the method given in [2]. $Mg_2P_2O_7$ was prepared from $MgHPO_4{\cdot}3H_2O$ by heating at 900°C for 1 h.

K_3PO_4 was prepared from $K_3PO_4{\cdot}3H_2O$ by heating at 900°C for 1 h.

$KMgPO_4$ was synthesized from $Mg_2P_2O_7$ and K_2CO_3 by the method given in [3].

$K_3Y(PO_4)_2$ was prepared by heating a 1:1 stoichiometric mixture of YPO_4 and K_3PO_4 at 1200°C for 4 h.

$K_4Mg(PO_4)_2$ was prepared from K_3PO_4 and $KMgPO_4$ by heating at 1200°C for 10 min [3]. The system YPO_4–K_3PO_4–$KMgPO_4$ was examined by DTA during heating,

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X-ray powder diffraction and microscopic analysis in reflected light. Samples for examination were prepared from the initial phosphates and treated preliminarily by sintering in the temperature interval 600–1250°C. The duration period and temperature of the synthesis was established from a series of tests, where the phase composition of the sinters obtained was each time checked by thermography and X-ray radiography. In this way the equilibrium state conditions were determined. Molten and sintered samples were used for thermal analysis. For DTA during heating, a 3427 derivatograph (MOM, Hungary) was used within the temperature range 20–1400°C; a high-purity Al_2O_3 was used as a standard substance. Temperatures were read by means of a Pt/Pt10Rh thermocouple that was calibrated *vs*. 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 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 that 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

Examination of the system YPO_4–K_3PO_4–$KMgPO_4$ showed that the mixed orthophosphate $K_3Y(PO_4)_2$ yields two previously unknown sections: $K_3Y(PO_4)_2$– $K_4Mg(PO_4)_2$ and $K_3Y(PO_4)_2$–$KMgPO_4$. These sections were determined over the full composition and temperature range by DTA during heating, X-ray diffractometry and microscopy.

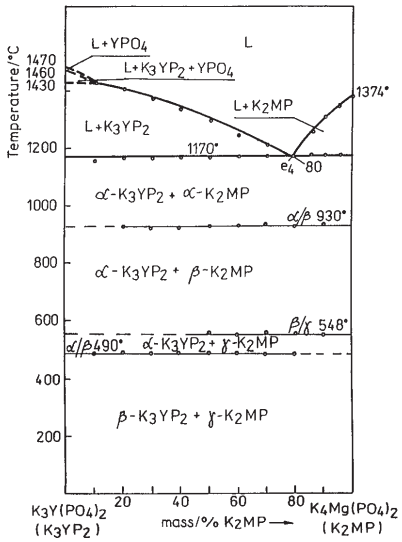

Fig. 1 Phase diagram of the system $K_3Y(PO_4)_2$–$K_4Mg(PO_4)_2$

Figure 1 presents the phase diagram of the system $K_3Y(PO_4)_2$–$K_4Mg(PO_4)_2$. $K_4Mg(PO_4)_2$ and $K_3Y(PO_4)_2$ form an eutectic e_4 at 80 mass% of $K_4Mg(PO_4)_2$ at 1170°C. The liquidus curve over the composition range 30–100 mass% of $K_4Mg(PO_4)_2$ was estimated on the basis of DTA. In the left part of the system, the melting points were read by means of an optical pyrometer. Compound $K_3Y(PO_4)_2$ is originated peritectically (in the side system YPO_4–K_3PO_4) according to the reaction: $YPO_4+L\rightarrow K_3Y(PO_4)_2$ (at 1460°C). Therefore, in the system $K_3Y(PO_4)_2$–$K_4Mg(PO_4)_2$ the peritectic reaction occurs within the composition range from 0 to approx. 10 mass% of $K_4Mg(PO_4)_2$. In this system two polymorphic transitions of $K_4Mg(PO_4)_2$ (α/β – 930°C, β/γ – 548°C) are reflected in the form of thermal effects on the DTA curves. The polymorphic transition of $K_3Y(PO_4)_2$, proceeding at 490°C, was observed as strong thermal effects on the DTA curves within the composition range 20–100 mass% of $K_3Y(PO_4)_2$.

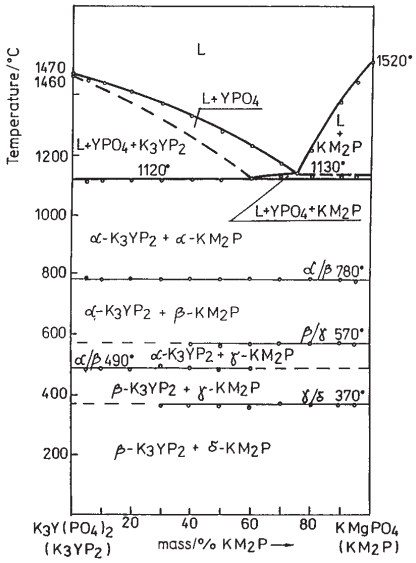

Fig. 2 Phase diagram of the system $K_3Y(PO_4)_2$–$KMgPO_4$

Figure 2 presents the phase diagram of the system $K_3Y(PO_4)_2$–$KMgPO_4$. This system is complex and is ternary in the upper part. There are four phases above 1120°C: liquid L, YPO_4, $K_3Y(PO_4)_2$ and $KMgPO_4$. During a peritectic reaction, L and YPO_4 were being used up to form crystals of $K_3Y(PO_4)_2$. Below 1120°C there are only two phases, $KMgPO_4$ and $K_3Y(PO_4)_2$, and the system is binary in nature. In this system three polymorphic transitions of $KMgPO_4$ (α/β –780°C, β/γ – 570°C, γ/δ – 370°C) and one transition of $K_3Y(PO_4)_2$ (α/β – 490°C) are reflected in the form of thermal effects on the DTA curves.

Figure 3 presents the phase diagram of the system YPO_4–K_3PO_4–$KMgPO_4$. Solidification isotherms are marked on the diagram. The primary crystallization fields of the compounds are separated by either eutectic or peritectic lines: e_1P line of binary eutectic

(YPO_4+$KMgPO_4$), p_1P line of binary peritectic, according to the reaction:

$$L_{p1P} + YPO_4 \rightarrow K_3Y(PO_4)_2,$$

PE line of binary eutectic ($K_3Y(PO_4)_2$+$KMgPO_4$), e_2E line of binary eutectic ($KMgPO_4$+$K_4Mg(PO_4)_2$), e_3e_4 line of binary eutectic (continuous solid solutions (K_3PO_4, $K_4Mg(PO_4)_2$)+$K_3Y(PO_4)_2$), e_4E line of binary eutectic ($K_3Y(PO_4)_2$+ $K_4Mg(PO_4)_2$).

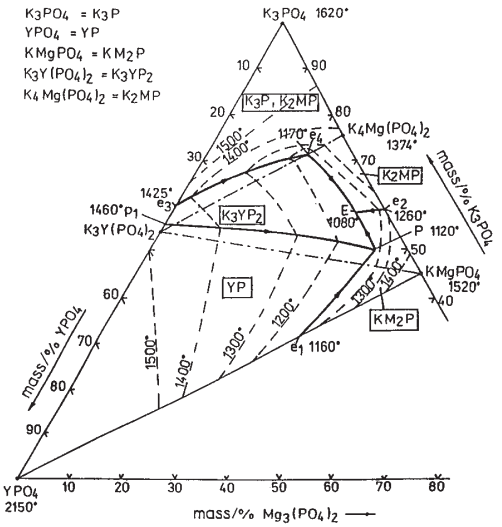

Fig. 3 Phase diagram of the system YPO_4–K_3PO_4–$KMgPO_4$

The primary crystallization field of YPO_4 occurs over the composition range YPp_1Pe_1, of $K_3Y(PO_4)_2$ over $p_1e_3e_4EP$, of $KMgPO_4$ over $e_1PEe_2KM_2P$, of $K_4Mg(PO_4)_2$ over $e_2Ee_4K_2MP$ and of solid solutions (K_3PO_4, $K_4Mg(PO_4)_2$) over $K_2MPe_4e_3K_3P$.

In the side-system YPO_4–K_3PO_4, a binary peritectic reaction occurs at 1460°C and, as a result of this reaction, $K_3Y(PO_4)_2$ is produced. This is reflected in the ternary system under investigation in the form of ternary peritectic P. In reaction of YPO_4 and the liquid of the composition corresponding to point P, $K_3Y(PO_4)_2$ and $KMgPO_4$ were being formed according to the ternary peritectic reaction:

$$L_p+YPO_4 \leftrightarrow K_3Y(PO_4)_2+KMgPO_4.$$

This peritectic reaction proceeds at the constant temperature of 1120°C. In the system under investigation, crystallization ends at point E, where the ternary eutectic evolves ($K_3Y(PO_4)_2$+$K_4Mg(PO_4)_2$+$KMgPO_4$) at the constant temperature of 1080°C.

References

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