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Phase equilibria in the system Y_2O_3–K_3PO_4–$K_3Y(PO_4)_2$

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Abstract

The phase diagram of the partial ternary system Y_2O_3–K_3PO_4–$K_3Y(PO_4)_2$ has been determined during research on potassium–yttrium phosphates. One ternary peritectic and one ternary eutectic occur in this system.

INTRODUCTION

The literature on rare earth elements and their compounds with other chemical elements is abundant. Double condensed phosphates of rare earths and alkali metals are of fundamental importance because of their wide range of application (laser and luminescent materials). Literature reports usually deal with the methods of their synthesis, their X-ray crystallographic analyses and their possible uses. Studies presenting the results of research into their phase equilibria are less widespread.

Investigations of yttrium–potassium phosphates have been performed in our laboratory for several years [1–5]. This paper presents the results of fundamental phase research on the system Y_2O_3–K_3PO_4–$K_3Y(PO_4)_2$. It is surrounded by three side-systems: Y_2O_3–K_3PO_4, K_3PO_4–$K_3Y(PO_4)_2$ and Y_2O_3–$K_3Y(PO_4)_2$. The system K_3PO_4–$K_3Y(PO_4)_2$ has been studied before [5], but phase equilibria in the systems Y_2O_3–K_3PO_4 and Y_2O_3–$K_3Y(PO_4)_2$ were previously unknown.

EXPERIMENTAL

The following starting materials were used: Y_2O_3 (99.99%), H_3PO_4 (85%) (analytical grade) and $K_3PO_4 \cdot 3H_2O$ (analytical grade).

Potassium orthophosphate K_3PO_4 was prepared from $K_3PO_4 \cdot 3H_2O$ by heating at 900°C for 1 h. Yttrium orthophosphate YPO_4 was obtained from

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the following solution: 0.4 wt.% Y_2O_3, 15 wt.% P_2O_5 (as H_3PO_4) and 84.6 wt.% distilled water, according to ref. 3. The double orthophosphate $K_3Y(PO_4)_2$ was prepared by heating a 1:1 stoichiometric ratio of YPO_4 and K_3PO_4 at 1200°C for 4 h.

The investigations were carried out by differential thermal analysis, powder X-ray diffraction and microscopy in reflected light. Molten and sintered samples were used for thermal analysis. The high temperature thermal studies were performed under argon in a vertical resistance furnace with a molybdenum winding. 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 DTA was performed by means of a derivatograph, type 3427 (MOM, Hungary).

The phase purity of the reagents and the phase structure of the products were studied microscopically. Microsections were prepared from molten and crystallized samples, which were polished and examined in reflected light. Phase identification was made with Cu Kα radiation using an HZG-4 diffractometer.

RESULTS AND DISCUSSION

The Y_2O_3–K_3PO_4 system was examined over the full composition range and over the temperature range 20–1800°C using differential thermal anylysis, microscopy and X-ray diffractometry. Samples for investigations were pre-synthesized from the starting components by sintering at 1000°C for 12 h and at 1200°C for 4 h. The studies proved that the initial components do not form new compounds but a eutectic system. Figure 1

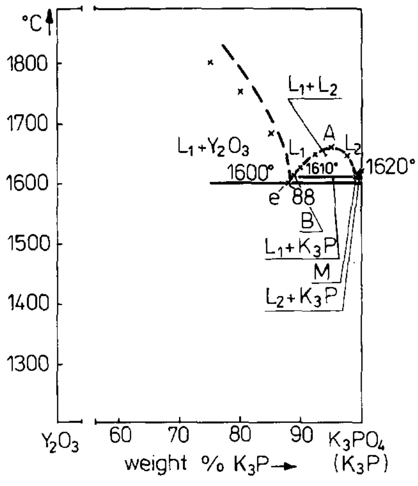

Fig. 1. Phase diagram of the system Y_2O_3–K_3PO_4: ×, optical.

presents the phase diagram of the system Y_2O_3–K_3PO_4. The melting points of the samples were measured using an optical pyrometer. Potassium orthophosphate melts at 1620°C. According to ref. 6, K_3PO_4 has two polymorphic transitions: during cooling, α/β at 1066–1051°C and β/γ at 545°C; during heating, the α/β transition is in the temperature range 1060–1150°C. In the Y_2O_3–K_3PO_4 system under investigation, no effects resulting from the transitions of K_3PO_4 were observed on the DTA curves of either the melted or sintered samples. This may be caused by the existence of a miscibility gap in the liquid phase over the composition range 89–100 wt.% K_3PO_4. Over this composition range, at high temperatures above 1600°C, the liquid is divided into two liquid solutions, L_1 and L_2 (Fig. 1). Above point A, there is the stability field of liquid solutions which have complete miscibility of components. In the BAM field, the mixture of liquid solutions $L_1 + L_2$ is stable. On the left, above the liquidus curve, there is a monophase field of the stability of the liquid solution L_1, and on the right there is a monophase field of the liquid solution L_2. Between the solidus and liquidus curves, there are diphase fields. At point M, which is called monotectic, at the constant temperature of 1610°C (monotectic temperature), a monotectic transition proceeds according to the reaction $L_{2M} \rightarrow K_3PO_4 + L_{1B}$ (where L_{2M} = liquid L_2 with the composition of point M, L_{1B} = liquid L_1 with the composition of point B). In the system under investigation, a eutectic occurs at the composition 88 wt.% K_3PO_4, at 1600°C.

The system Y_2O_3–$K_3Y(PO_4)_2$ was also examined over the full composition range and over the temperature range 20–1800°C. Synthesized sam-

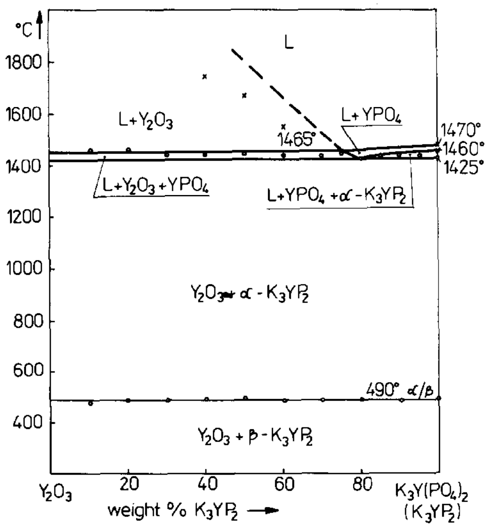

Fig. 2. Phase diagram of the system Y_2O_3–$K_3Y(PO_4)_2$: o, thermal analysis; ×, optical.

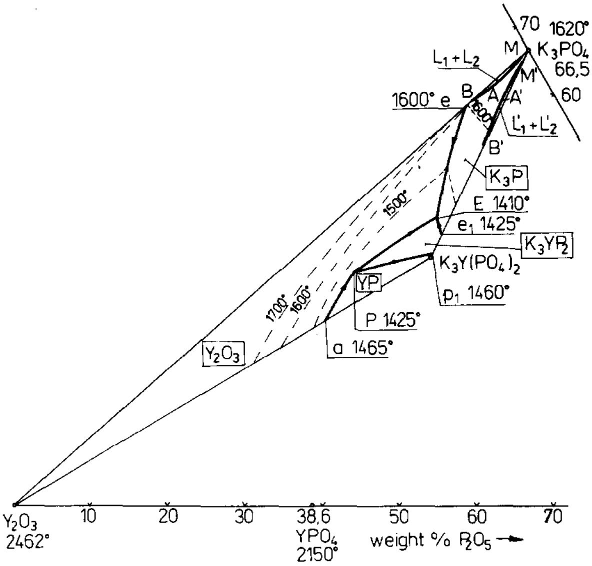

Fig. 3. Phase diagram of the system Y_2O_3–K_3PO_4–$K_3Y(PO_4)_2$: $K_3PO_4 = K_3P$; $K_3Y(PO_4)_2 = K_3YP_2$; $YPO_4 = YP$.

ples (sinters from 1000 and 1200°C, time of sintering 4 h) and molten samples were used for the investigations. Figure 2 presents the phase diagram of the system Y_2O_3–$K_3Y(PO_4)_2$. Y_2O_3 melts congruently at 2439°C, according to ref. 7; $K_3Y(PO_4)_2$ melts incongruently at 1460°C [5]. At high temperatures, the system Y_2O_3–$K_3Y(PO_4)_2$ is multiphase. Above 1425°C, there are four phases: liquid L, and compounds Y_2O_3, YPO_4 and $K_3Y(PO_4)_2$. As a result of the peritectic reaction, liquid L and yttrium orthophosphate, YPO_4, react forming crystals of $K_3Y(PO_4)_2$. Below 1425°C, the system is binary and only Y_2O_3 and $K_3Y(PO_4)_2$ exist. The polymorphic transition of $K_3Y(PO_4)_2$ proceeding at 490°C [5] was observed over the whole Y_2O_3–$K_3Y(PO_4)_2$ system as strong thermal effects on the DTA curves.

For examinations of the system Y_2O_3–K_3PO_4–$K_3Y(PO_4)_2$, samples which were first sintered at different temperatures (1000–1400°C) and molten samples were used. Figure 3 shows the phase diagram of the system under investigation with solidification isotherms. Primary crystallization fields of the compounds are separated by eutectic and peritectic curves. In the side systems Y_2O_3–K_3PO_4 and YPO_4–K_3PO_4, there are miscibility gaps of components in the liquid phase (about 1600°C). This is reflected in the ternary system and is marked by fields BAM and B'A'M' in Fig. 3. In the system Y_2O_3–K_3PO_4–$K_3Y(PO_4)_2$, there is one ternary peritectic P. The triple peritectic reaction proceeds at the constant temperature of 1425°C according to the equation $L(P) + YPO_4 \rightarrow K_3Y(PO_4)_2 + Y_2O_3$ where $L(P)$ = liquid with the composition corresponding to point P. In the system under investigation, crystallization is complete at point E, where the ternary eutectic ($Y_2O_3 + K_3Y(PO_4)_2 + K_3PO_4$) is evolved at the constant temperature of 1410°C.

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