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Phase equilibria in the partial system $LaPO_4$–K_3PO_4–$K_4P_2O_7$

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Abstract

The partial ternary system $LaPO_4$–K_3PO_4–$K_4P_2O_7$ has been investigated by differential thermal analysis and powder X-ray diffraction and its phase diagram deduced. Two systems $K_3La(PO_4)_2$–$K_4P_2O_7$ and $LaPO_4$–$K_4P_2O_7$ have been found to occur in this region. Their phase diagrams have also been determined.

INTRODUCTION

This paper presents the results of our investigations on lanthanum–potassium phosphates. They deal with that part of the ternary system La_2O_3–K_2O–P_2O_5 contained within the composition range of $LaPO_4$–K_3PO_4–$K_4P_2O_7$. This partial system was previously unknown. However, the phase diagrams of the two side systems, K_3PO_4–$K_4P_2O_7$ [1] and $LaPO_4$–K_3PO_4 [2] are known.

EXPERIMENTAL

The following starting materials were used: $K_3PO_4 \cdot 3H_2O$, analytical grade; K_2HPO_4, analytical grade, $La(NO_3)_3$, Fluka; H_3PO_4, 85%, analytical grade; K_2CO_3, analytical grade; and $NH_4H_2PO_4$, analytical grade. Lanthanum orthophosphate $LaPO_4$ was obtained from the following solution: 0.4 wt.% La_2O_3 (as $La(NO_3)_3$) and 15 wt.% P_2O_5 (as H_3PO_4) in 84.6 wt.% distilled water [3]. Potassium orthophosphate K_3PO_4 was prepared from $K_3PO_4 \cdot 3H_2O$ by heating at 900°C for 1 h. Potassium pyrophosphate $K_4P_2O_7$ was obtained from K_2HPO_4 by heating at 400°C for 1 h. The double orthophosphate $K_3La(PO_4)_2$ was prepared by sintering an equimolar mixture of $LaPO_4$ and K_3PO_4 at 1100°C for 20 h.

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The investigations were carried out using differential thermal analysis on heating and powder X-ray diffraction. A quenching technique was also used for phase determination. Samples were quenched in air or ice. The thermal analysis was performed using a derivatograph, type 3427 (MOM, Hungary) at a heating rate of 10°C min^{-1}, in a platinum cup under air atmosphere. High-purity Al_2O_3 was used as the standard material. Temperatures were read by means of a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of NaCl and K_2SO_4 and the polymorphic transition temperature of K_2SO_4 (583°C).

The phase purity of the reagents and the phase structure of the products were controlled and identified by powder X-ray diffraction on an HZG-4 diffractometer (Guinier camera) with a nickel filter and Cu Kα radiation.

RESULTS AND DISCUSSION

The phase equilibria occurring in that part of the ternary La_2O_3–K_2O–P_2O_5 system contained within the field limited by the compounds $LaPO_4$, K_3PO_4 and $K_4P_2O_7$ were examined. The studies began by determining the previously unknown phase diagram of the $LaPO_4$–$K_4P_2O_7$ system. Differential thermal analysis on heating and powder X-ray diffraction techniques were used during the examinations. The samples were prepared from the phosphates $LaPO_4$ and $K_4P_2O_7$. Heteromolar mixtures of these compounds were presynthesized by sintering them at 800°C for 20 h. The sinters obtained were analysed by differential thermal analysis on heating. The results of the thermal investigations showed that at higher temperatures, the reactions taking place between lanthanum orthophosphate $LaPO_4$ and potassium pyrophosphate are complex. Therefore, a description and discussion of these reactions are desirable.

A thermal effect occurs at approx. 980°C on the DTA curves of all the samples examined from the system under investigation and it is accompanied by the appearance of the liquid phase. This effect is strongest in samples rich in $K_4P_2O_7$ and proceeds without mass loss. In that part of the system poorer in $K_4P_2O_7$, i.e. in samples containing more than 20 wt.% $LaPO_4$, another thermal effect appears at approx. 1200°C on the DTA curves, accompanied by a very small mass loss. With the same sample mass, the size of this effect depends on the composition of the sample. This effect was found to be strongest within the composition range 40–70 wt.% $K_4P_2O_7$. Powder X-ray analysis was used to determine the reason for this effect and the processes proceeding at higher temperatures; thus the phases appearing could be identified. Both samples quenched from high temperatures and those cooled slowly down to room temperature were examined by X-ray diffraction after the thermal analysis on heating. Samples which were sintered and then quenched from different temperatures were also examined by X-ray diffraction.

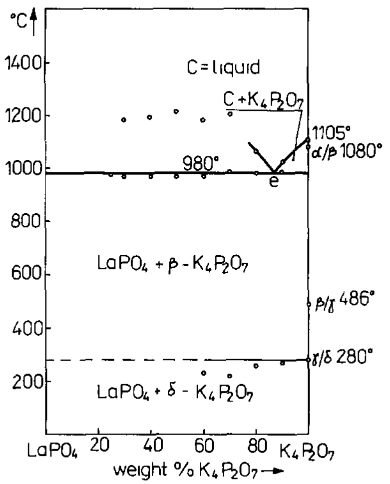

Fig. 1. Phase diagram of the system $LaPO_4$–$K_4P_2O_7$; o thermal analysis.

The X-ray analysis demonstrated that a mixture of phosphates $LaPO_4$ and $K_4P_2O_7$ is present below 1000°C, over the whole system. Both partly molten samples (at approx. 980°C) and those sintered and then quenched or cooled slowly from different temperatures below 980°C show this phase composition. However, X-ray analysis of samples quenched from high temperatures, above 1000°C, showed that they are a mixture of three phosphates: $LaPO_4$, $K_4P_2O_7$ and $K_3La(PO_4)_2$. Therefore, the thermal analysis on heating (heating rate approx. 5°C min^{-1}) indicates that complex processes proceed at high temperatures resulting in the formation of double orthophosphate $K_3La(PO_4)_2$. These processes start above 1000°C in the presence of the liquid phase. The thermal effect which can be seen on the DTA curves at approx. 1200°C comes from the $\alpha \rightarrow \beta$ polymorphic transition of $K_3La(PO_4)_2$. Our previous studies proved that $K_3La(PO_4)_2$ occurs in two polymorphic modifications, with the temperature of transition being 1215°C [2].

The distribution of high-temperature thermal effects on the DTA curves within the composition range 80–100 wt.% $K_4P_2O_7$ suggests that a eutectic occurs at the composition 87 wt.% $K_4P_2O_7$. The temperature of the eutectic is 980°C.

The suggested phase diagram of the system $LaPO_4$–$K_4P_2O_7$ was derived on the basis of the results described above and is presented in Fig. 1. The system is binary at lower temperatures; above 980°C, it is binary only in that part which is rich in potassium pyrophosphate (80–100 wt.% $K_4P_2O_7$) and polyphase in the rest of the composition range. Potassium pyrophosphate $K_4P_2O_7$ occurs in several known polymorphic modifications; the temperatures of its transitions are: $\alpha \rightarrow \beta$, 1080°C, $\beta \rightarrow \gamma$, 486°C, $\gamma \rightarrow \delta$ 280°C. Figure 1 shows that only the $\gamma \rightarrow \delta$ transition yields thermal effects

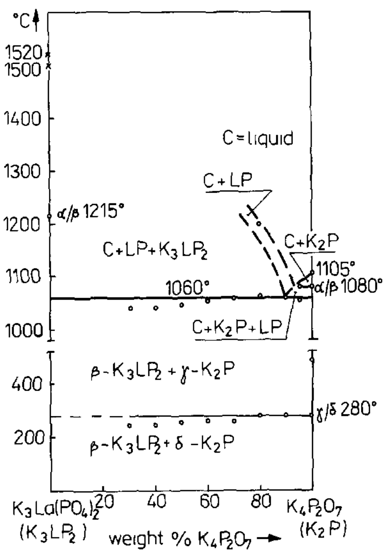

Fig. 2. Phase diagram of the system $K_3La(PO_4)_2$–$K_4P_2O_7$; o thermal analysis, LP = $LaPO_4$.

on the DTA heating curves, and only within the composition range 60–100 wt.% $K_4P_2O_7$.

The previously unknown section $K_3La(PO_4)_2$–$K_4P_2O_7$ was found to occur in the partial system $LaPO_4$–K_3PO_4–$K_4P_2O_7$. Figure 2 shows its phase diagram based on the thermal analysis and X-ray diffraction results. Samples for investigations were prepared from the initial phosphates and presynthesized at 900°C for 18 h. The course of the liquidus curve is proposed only, because the thermal effects resulting from melting are very weak, even unnoticeable, on the DTA heating curves. The system $K_3La(PO_4)_2$–$K_4P_2O_7$ is ternary in its upper part. Above 1060°C, four phases occur, i.e. liquid C and the compounds $K_4P_2O_7$, $K_3La(PO_4)_2$ and $LaPO_4$. As a result of the peritectic reaction, liquid C reacts with orthophosphate $LaPO_4$ forming double orthophosphate $K_3La(PO_4)_2$. Below 1060°C the system is binary and only two phases, $K_3La(PO_4)_2$ and $K_4P_2O_7$, coexist. Figure 2 proves that only the $\gamma \rightarrow \delta$ transition of $K_4P_2O_7$ gives thermal effects on the DTA curves. They occur within the composition range 30–100 wt.% $K_4P_2O_7$.

Figure 3 presents the phase diagram of the system $LaPO_4$–K_3PO_4–$K_4P_2O_7$. The primary crystallization fields of the binary and ternary compounds are separated by the eutectic and peritectic curves. In the side system $LaPO_4$–K_3PO_4, there is a limited solubility of components in the liquid state, within the composition range 75–100 wt.% K_3PO_4 above 1600°C [2]. This phenomenon is reflected in the ternary system in the form of limited solubility of liquid components in the field AB′M. In the system $LaPO_4$–K_3PO_4–$K_4P_2O_7$, one ternary eutectic E_4 occurs at 1050°C. Along

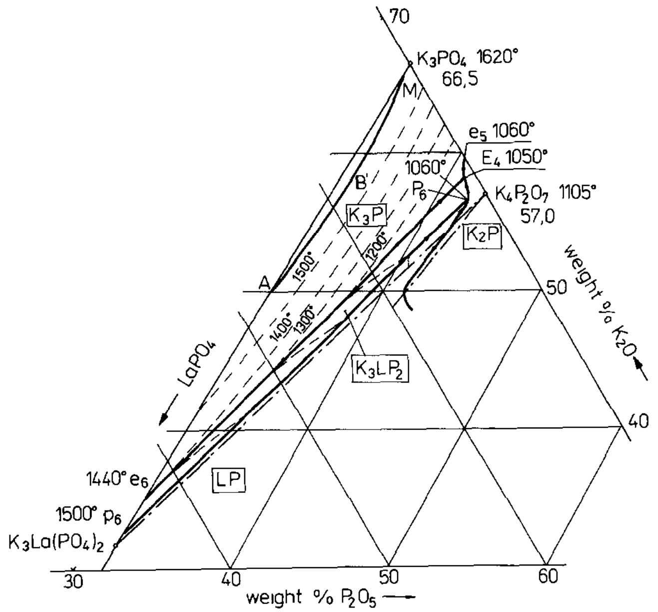

Fig. 3. Phase diagram of the system $LaPO_4$–K_3PO_4–$K_4P_2O_7$; $K_3P = K_3PO_4$, $K_2P = K_4P_2O_7$, $K_3LP_2 = K_3La(PO_4)_2$, LP = $LaPO_4$.

the p_6P_6 curve, a binary peritectic reaction proceeds according to the equation $C(p_6P_6) + LaPO_4 \rightarrow K_3La(PO_4)_2$. During the solidification of alloys from the field $LaPO_4$–$K_3La(PO_4)_2$–P_6–$K_4P_2O_7$ (triple peritectic quadrangle), the ternary peritectic reaction $C(P_6) + LaPO_4 \rightarrow K_3La(PO_4)_2 + K_4P_2O_7$ takes place ($C(P_6)$ denotes liquid with the composition of point P_6). This reaction proceeds at the constant temperature of 1060°C.

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