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PHASE EQUILIBRIA IN THE SYSTEM La_2O_3–K_2O–P_2O_5

W. Jungowska

Department of Inorganic Chemistry, Faculty of Engineering and Economics, University of Economics, 53345 Wrocław, Poland

Abstract

The ternary system La_2O_3–K_2O–P_2O_5 has been examined by thermal, X-ray, IR and microscopic methods. The existence of three double potassium-lanthanum phosphates, $K_3La(PO_4)_2$, $KLa(PO_3)_4$ and $K_2La(PO_3)_5$ has been confirmed, and the phase diagram of the ternary system La_2O_3–K_2O–P_2O_5 over the composition range $LaPO_4$–K_3PO_4–P_2O_5 has been determined.

Keywords: double potassium-lanthanum phosphates, phase diagram, phase equilibria

Introduction

A literature inspection indicates that phase examination of the ternary system La_2O_3–K_2O–P_2O_5 has not been carried out so far. However, the phase diagrams of the side systems La_2O_3–P_2O_5 [1] and K_2O–P_2O_5 [2, 3] are known as well as the binary section KPO_3–$La(PO_3)_3$ [4]. The existence of three double potassium–lanthanum phosphates of the formulas $KLa(PO_3)_4$ [4], $K_2La(PO_3)_5$ [4] and $K_3La(PO_4)_2$ [5] is also reported.

According to reference [1], an intermediate compound of formula $La_2P_4O_{13}$ occurs in the system $LaPO_4$–$La(PO_3)_3$. The authors of Ref. [6] do not confirm the existence of this compound.

The aim of the present work was to study the phase equilibria of the system La_2O_3–K_2O–P_2O_5 and to determine its phase diagram.

Experimental

The following parent materials of analytical grade were used: La_2O_3(99.99%), $La(NO_3)_3$ (Fluka), H_3PO_4 (85%), $K_3PO_4 3H_2O$, KH_2PO_4, K_2HPO_4, K_2CO_3, $NH_4H_2PO_4$. The methods of syntheses of lanthanum and potassium phosphates and also of double potassium-lanthanum phosphates are described in [6–10].The samples for investigations were prepared from adequate substances in assumed quantities, ground in an agate mortar, palletizes and sintered at different temperatures, depending on their composition.

Investigation was carried out by differential thermal analysis of heating and cooling, powder X-ray diffraction, infrared spectroscopy, and microscopy in reflected light. DTA of heating was performed by derivatograph type 3427 (MOM,

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Hungary). Thermal analysis during cooling was carried out in a furnace with platinum winding. A horizontal resistance furnace with molybdenum winding was used to melt samples within the temperature range 1400–1800°C under atmosphere of argon. Temperature was measured by means of an optical pyrometer. The phase purity of reagents and phase structure of products was controlled by powder X-ray diffraction in HZG-4 diffractometer (Guinier camera) with CuK_α radiation. A Specord IR-75 spectrophotometer was used for examination of phases in the system. The samples were prepared in the form of pellets in KBr. A quenching technique was also used for phase determination. Samples were quenched in air or ice.

Results and discussion

The ternary system La_2O_3–K_2O–P_2O_5 was investigated within the composition range $LaPO_4$–K_3PO_4–P_2O_5. Other parts of the system were not examined because of experimental difficulties. They were due to with a high temperature of melting of alloys in the La_2O_3- and K_2O-rich part of the ternary system, high hygroscopicity and reactivity in relation to platinum, high liability to forming glasses and also decomposition of the samples at high temperature in the P_2O_5-rich part of the system. Figure 1 presents the phase diagram of the system La_2O_3–K_2O–P_2O_5 within the composition range

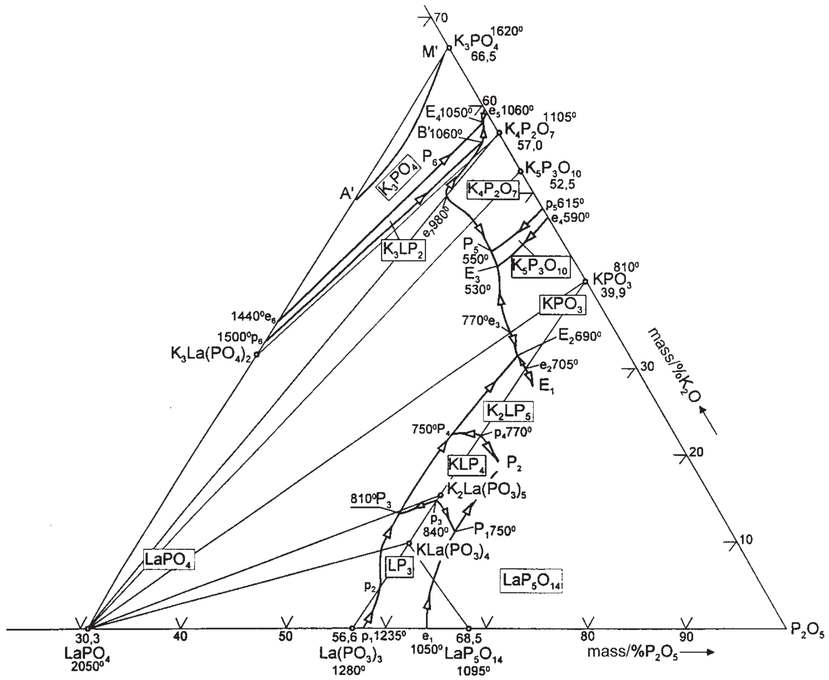

Fig. 1 Phase diagram of the system La_2O_3–K_2O–P_2O_5; $La(PO_3)_3$=LP_3, $K_3La(PO_4)_2$=K_3LP_2, $KLa(PO_3)_4$=KLP_4, $K_2La(PO_3)_5$=K_2LP_5

$LaPO_4$–K_3PO_4–P_2O_5, determined by DTA, X-ray diffraction and microscopy. Seven binary compounds and three ternary compounds occur in this area. All compounds crystallize from the liquid phase. The primary crystallization fields of these compounds are separated by eutectic or peritectic curves. The temperatures of primary crystallization of alloys cover a wide range, from approx. 700°C, for the samples P_2O_5-rich, to approx. 2000°C for those La_2O_3-rich. Six ternary peritectics and four ternary eutectics occur within the composition range $LaPO_4$–K_3PO_4–P_2O_5.

It was found that binary and ternary compounds form nine binary sections. Their phase diagrams were determined as a result of this work.

Lanthanum orthophosphate $LaPO_4$ appears to be of great importance for the phase equilibria in the system under investigation, especially in the area $LaPO_4$–K_3PO_4–KPO_3–$La(PO_3)_3$. The primary crystallization field of $LaPO_4$ covers a very wide composition range (Fig. 1). Moreover, $LaPO_4$ yields the binary sections with all binary and ternary compounds present in the system $LaPO_4$–K_3PO_4–P_2O_5. Most of this sections have a complex character. These are multiphase systems at high temperature, which result from the peritectic decomposition of $K_5P_3O_{10}$, $KLa(PO_3)_4$ and $K_2La(PO_3)_5$. At low temperature, the sections have a binary character. The most important is the binary system $LaPO_4$–K_3PO_4. Its phase diagram is shown in Fig. 2. The double phosphate of the formula $K_3La(PO_4)_2$ occurs in this system. It was found that $K_3La(PO_4)_2$ melts incongruently at approx. 1500°C, and at a temperature of 1215°C it shows a polymorphic transition. As a result of X-ray analysis it was found that the low-temperature modification, β-$K_3La(PO_4)_2$, has a monoclinic structure (lattice type P), and cell parameters: a=9.632(5), b=5.660(2), c=7.514(3) Å; α=90°, β=90.55(3)°, and γ=90°; V=409.62 Å^3. The high-temperature modification (α) cannot

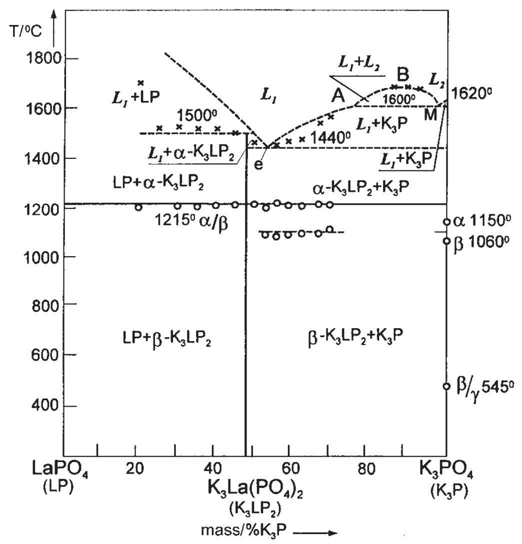

Fig. 2 Phase diagram of the system $LaPO_4$–K_3PO_4; o – thermal analysis; x – optical; L=liquid

be stabilized at room temperature by quenching in air or ice. The appearance of a limited solubility of the components in the liquid state above approx. 1600°C is worth noting in the system $LaPO_4$–KPO_4, within the composition range from 75 to approx. 100 mass% K_3PO_4. It is manifested by the separation of the liquid into two liquid solutions, L_1 and L_2, in the ABM field.

Another binary system of great importance, found in composition area of interest, is the system $La(PO_3)_3$–KPO_3. It essentially affects the formation of phase equilibria in the P_2O_5-rich part of the system $LaPO_4$–K_3PO_4–P_2O_5. The phase diagram of the system $La(PO_3)_3$–KPO_3 is shown in Fig. 3. Evidence for the occurrence of two double metaphosphates, $KLa(PO_3)_4$ and $K_2La(PO_3)_5$, in this system has been found. Both these compounds melt incongruently: $KLa(PO_3)_4$ at 840°C (acc. to [4] at 880°C), $K_2La(PO_3)_5$ at 770°C. They are stable up to room temperature and do not show any polymorphic transitions. The phase diagram of the system $La(PO_3)_3$–KPO_3 is verified in the $La(PO_3)_3$-rich part of it. It was found that $LaPO_4$ occurs as a result of peritectic decomposition of $La(PO_3)_3$ into $LaPO_4$ and a liquid, within the composition range 88–100 mass% $La(PO_3)_3$, which proceeded above 1190°C.

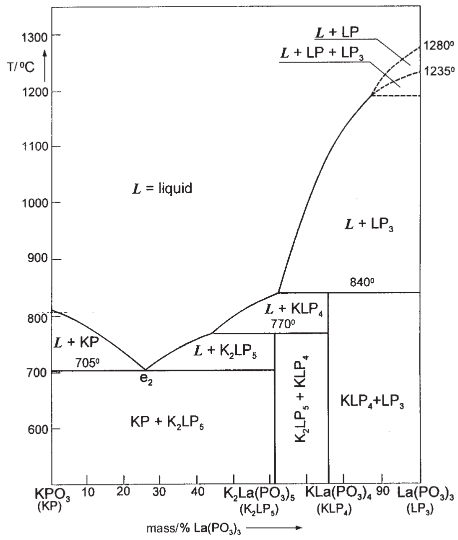

Fig. 3 Phase diagram of the system $La(PO_3)_3$–KPO_3; $LaPO_4$=LP

On the basis of various thermal treatment (sintering and cooling to room temperature or quenching from different temperatures, and also DTA) it was found that temperatures of peritectic decompositions of $KLa(PO_3)_4$ and $K_2La(PO_3)_5$, in P_2O_5-rich ternary samples, are lowered by approx. 100 and 150–250°C respectively, in comparison to the decomposition temperature of the pure compounds (i.e. 840 and 770°C). It also appears that $KLa(PO_3)_4$ is a more stable compound than $K_2La(PO_3)_5$, in the more P_2O_5-enriched samples.

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