

INVESTIGATIONS OF POTASSIUM-CERIUM PHOSPHATES RICH IN P_2O_5

T. Znamierowska and J. Obremski

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF ENGINEERING AND ECONOMICS, ACADEMY OF ECONOMICS, 53345 WROCLAW, POLAND

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In the ternary system Ce_2O_3 - K_2O - P_2O_5 , the partial system $Ce(PO_3)_3$ - KPO_3 - P_2O_5 was examined by means of differential thermal analysis and powder X-ray diffraction. The phase compositions of the products obtained on various thermal treatments were investigated. The phase diagram of the system $Ce(PO_3)_3$ - KPO_3 - P_2O_5 is suggested.

As the literature shows, for the past several years there has been considerable interest in the rare earth elements and their compounds, alkali metal and lanthanide phosphates being of great importance among them. This results from the extensive applications of these substances.

For the past ten years, we have been carrying out studies on binary and ternary systems involving Y, La and Ce phosphates and alkali and alkaline earth metals. In this paper, the results of investigations on a portion of the ternary system Ce_2O_3 - K_2O - P_2O_5 rich in P_2O_5 , i.e. within the composition range $Ce(PO_3)_3$ - KPO_3 - P_2O_5 , are reported. This region has not been systematically studied before. There are two known binary systems: $Ce(PO_3)_3$ - KPO_3 and $Ce(PO_3)_3$ - CeP_5O_{14} . The former was determined by Rzaigui *et al.* [1], who reported the phase diagram of the system. The starting metaphosphates were found to form two intermediate compounds: $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$. These compounds melted incongruently at 880 and 741 $^{\circ}$, respectively. $KCe(PO_3)_4$, isotypic with $KNd(PO_3)_4$, has a monoclinic unit cell; its space group is $P2_1$. For $K_2Ce(PO_3)_5$, isotypic compounds were not found in double polyphosphates of rare earths and alkali metals [1]. The phase diagram of the system $Ce(PO_3)_3$ - CeP_5O_{14} has been determined in our laboratory [2]. It is a simple binary system of eutectic type.

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Akadémiai Kiadó, Budapest*

Experimental

The samples for investigation in the system $\text{Ce}(\text{PO}_3)_3\text{-KPO}_3\text{-P}_2\text{O}_5$ were obtained from the following original reagents: CeO_2 99.9 %, H_3PO_4 85% analytical grade, KH_2PO_4 analytical grade, $\text{NH}_4\text{H}_2\text{PO}_4$ analytical grade, and K_2CO_3 analytical grade.

KPO_3 , $\text{Ce}(\text{PO}_3)_3$, $\text{CeP}_5\text{O}_{14}$ and $\text{KCe}(\text{PO}_3)_4$ were prepared in our laboratory. KPO_3 was obtained by complete dehydration of KH_2PO_4 at 300° for 0.5 h and then at 500° for 2 h. $\text{Ce}(\text{PO}_3)_3$ was produced from CeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ by sintering stoichiometric quantities of these compounds, at 250 , 500 and 900° for 2, 5 and 15 h, respectively. $\text{CeP}_5\text{O}_{14}$ was obtained from CeO_2 and H_3PO_4 . A mixture of these compounds in the molar ratio $\text{P/Ce} = 10$ was placed in a porcelain crucible and vaporized slowly until a thick, transparent mass was obtained. The mass was then sintered in a gold crucible at 700° for 24 h. The hard product obtained was ground and washed several times with distilled water and dried at 200° . $\text{KCe}(\text{PO}_3)_4$ was prepared from KPO_3 and $\text{Ce}(\text{PO}_3)_3$ by sintering a stoichiometric mixture of these compounds at 840° for 20 h.

The investigations were carried out by means of differential thermal analysis (cooling and heating) and powder X-ray diffraction. Test samples were pre-synthesized by reaction in the solid phase. Initial substances, mixed in the desired composition, were pressed into pellets and sintered at 500° for 24 h. The thermal analysis during heating was performed with a derivatograph (Type 3427, MOM, Hungary) within the temperature range $20\text{-}1100^\circ$, at a heating rate of 10 deg/min, with a platinum cap, under air. As the standard substance, high-purity Al_2O_3 was used. Thermal analysis during cooling was carried out in a furnace constructed in our laboratory. The temperature was measured with a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of NaCl and K_2SO_4 . Additionally, the temperatures of melting were determined by visual observation of the samples during heating: the temperature when the first traces of liquid were seen, and the temperature at which the sample liquefied completely and became transparent, were noted.

The quenching technique was also used for phase determination. The phases were identified by means of powder X-ray diffraction on an HZG-4 diffractometer with $\text{CuK}\alpha$ radiation.

Results and discussion

Potassium-cerium phosphates rich in P_2O_5 occur in the ternary system Ce_2O_3 - K_2O - P_2O_5 within the composition range $Ce(PO_3)_3$ - KPO_3 - P_2O_5 . Preliminary thermal and X-ray investigations revealed that complex phase transitions occur in this interval. It was discovered above all that most samples decompose at relatively low temperatures. The process is often accompanied by a larger or smaller mass loss, which can be observed in the DTG curves, and by a change in phase composition. Further, molten samples are liable to form glasses during cooling. The described phenomena considerably limited the possibility of using thermal analysis during cooling, since there were no thermal effects in the DTA curves, or they were hardly perceptible. Moreover, they appeared unsystematically, at different temperatures, which made their interpretation difficult. Therefore, it was assumed that thermal analysis during heating would be more advisable for determination of the phase equilibria in the system $Ce(PO_3)_3$ - KPO_3 - P_2O_5 . For example, Fig. 1 shows the distribution of the thermal effects perceptible in the DTA curves of samples of mixtures of the phosphates KPO_3 and CeP_5O_{14} , at different weights.

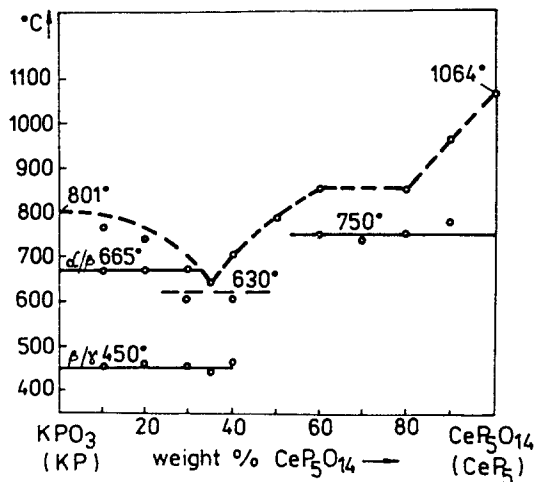


Fig. 1 DTA heating data on precalcined compositions containing the phosphates KPO_3 and CeP_5O_{14}

Figure 2 shows how the initial phase composition of these samples changes according to the thermal treatment used. The open circles indicate the in-

initial compositions of the samples. Figure 2(A) and (B) present the changes in phase composition that occur in the samples as a result of sintering at 600-700°, followed by (A) slow cooling down to room temperature, (B) quenching from these temperatures. Figure 2(C) and (D) show the changes in phase composition that occur in molten samples, which are then cooled slowly with grafting (C) down to room temperature, (D) to 600-800° and

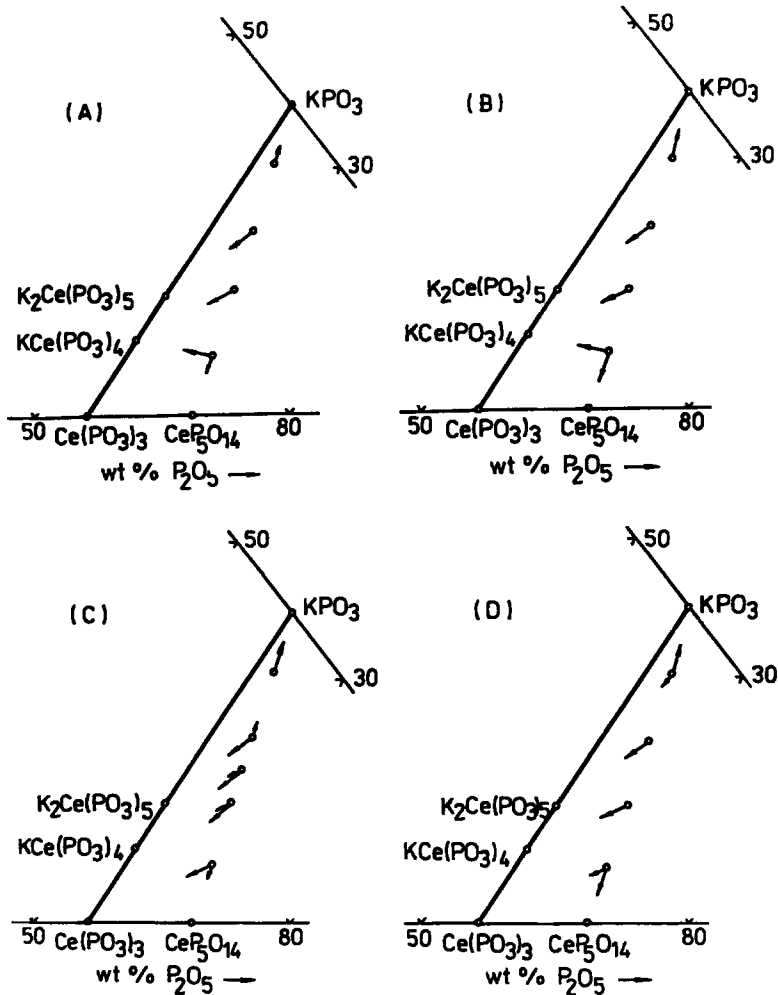


Fig. 2 Condition of samples: o - initial composition. Data are shown for (A) samples sintered (600-700°C) and cooled to room temperature; (B) samples sintered (600-700°C) and quenched; (C) samples melted and cooled to room temperature; (D) samples melted, sintered (600-700°C) and quenched

quenched from these temperatures. The phases occurring in the products were in each case identified via X-ray powder diffraction.

It is clear from Fig. 2 that the phase composition of the products depends not only on the initial composition of the sample, but also on the thermal treatment used. For example, in the sample of composition 80 wt% of $\text{CeP}_5\text{O}_{14}$ + 20 wt% of KPO_3 , sintered at 700° (not molten), $\text{CeP}_5\text{O}_{14}$ and $\text{KCe}(\text{PO}_3)_4$ were found to occur (Fig. 2(A) and (B)). However, after being melted and then either cooled down to room temperature (Fig. 2(C)) or quenched from 700° (Fig. 2(D)), this sample proved to be a mixture of the phosphates $\text{CeP}_5\text{O}_{14}$ and $\text{Ce}(\text{PO}_3)_3$.

On the basis of these investigations, the following interpretation of the thermal effects to be seen in Fig. 1 was suggested:

- (a) the effect at approximately 630° results from the ternary eutectic (E_1) which occurs in the part of the system $\text{Ce}(\text{PO}_3)_3$ - KPO_3 - P_2O_5 rich in KPO_3 ;
- (b) the effect at approximately 750° is connected with the peritectic decomposition of $\text{K}_2\text{Ce}(\text{PO}_3)_5$;
- (c) the effects at 450 and 665° are connected with polymorphic transitions of KPO_3 .

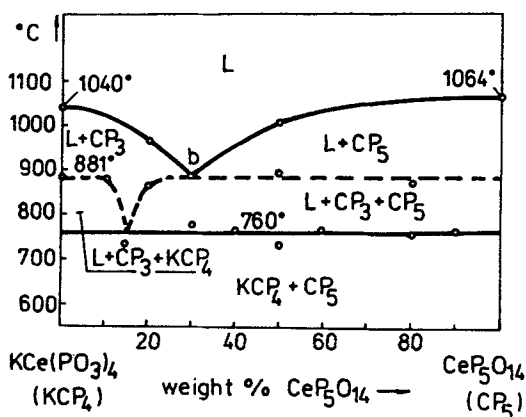


Fig. 3 Phase diagram of the system $\text{KCe}(\text{PO}_3)_4$ - $\text{CeP}_5\text{O}_{14}$; $\text{Ce}(\text{PO}_3)_3 = \text{CP}_3$, $\text{KCe}(\text{PO}_3)_4 = \text{KCP}_4$, $\text{CeP}_5\text{O}_{14} = \text{CP}_5$

It was also discovered that in the composition range under investigation, the previously unknown system $\text{KCe}(\text{PO}_3)_4$ - $\text{CeP}_5\text{O}_{14}$ occurs. This system is complex since in its upper part, above 760° , there are four phases: liquid L and the phosphates $\text{Ce}(\text{PO}_3)_3$, $\text{CeP}_5\text{O}_{14}$ and $\text{KCe}(\text{PO}_3)_4$. As a result of the

peritectic reaction, liquid L reacts with $\text{Ce}(\text{PO}_3)_3$ to give the phosphate $\text{KCe}(\text{PO}_3)_4$. In consequence of this, below 760° , there are only two phases: $\text{KCe}(\text{PO}_3)_4$ and $\text{CeP}_5\text{O}_{14}$. Therefore, above 760° , the system is ternary, while below this temperature it is binary. Figure 3 presents the phase diagram of the system $\text{KCe}(\text{PO}_3)_4$ - $\text{CeP}_5\text{O}_{14}$ as determined in our laboratory.

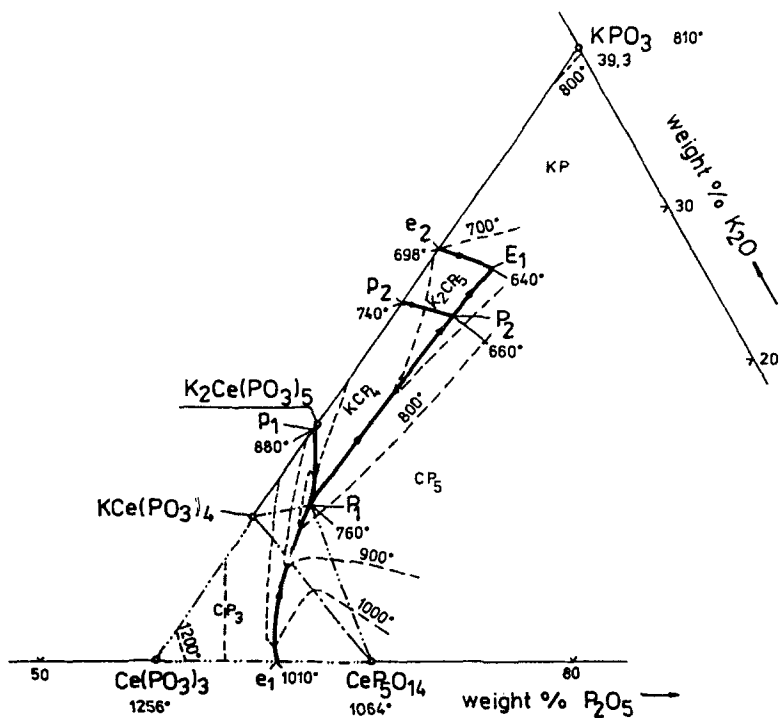


Fig. 4 Phase diagram of the system $\text{Ce}(\text{PO}_3)_3$ - KPO_3 - P_2O_5 ; $\text{KPO}_3 = \text{KP}$, $\text{Ce}(\text{PO}_3)_3 = \text{CP}_3$, $\text{CeP}_5\text{O}_{14} = \text{CP}_5$, $\text{KCe}(\text{PO}_3)_4 = \text{KCP}_4$, $\text{K}_2\text{Ce}(\text{PO}_3)_5 = \text{K}_2\text{CP}_5$

On the basis of the thermal and X-ray investigations, the phase diagram of the system $\text{Ce}(\text{PO}_3)_3$ - KPO_3 - P_2O_5 was suggested. It is presented in Fig. 4. In the composition range under investigation, there are five primary crystallization fields of binary and ternary compounds. These fields are separated by the eutectic or peritectic curves. The curve p_1P_1 corresponds to solidification of a double peritectic point according to the reaction: $L_{p,p} + \text{Ce}(\text{PO}_3)_3 \rightarrow \text{KCe}(\text{PO}_3)_4$. During solidification of the melts, corresponding to the points of the $\text{Ce}(\text{PO}_3)_3$ - $\text{KCe}(\text{PO}_3)_4$ - P_1 - $\text{CeP}_5\text{O}_{14}$ field (triple

peritectic quadrangle), a triple peritectic reaction takes place: $L_P + \text{Ce}(\text{PO}_3)_3 \rightarrow \text{KCe}(\text{PO}_3)_4 + \text{CeP}_5\text{O}_{14}$ at 760° (L_P = the liquid whose composition corresponds to point P_1). Moreover, in the part of the system richer in KPO_3 , the ternary peritectic point P_2 occurs at approximately 660° and the ternary eutectic point E_1 at approximately 640° .

References

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- 2 I. Szczygiel and T. Znamierowska, *J. Solid State Chem.*, 82 (1989) 181.

Zusammenfassung — Mittels DTA und Röntgendiffraktion wurde im ternären System $\text{Ce}_2\text{O}_3\text{-K}_2\text{O-P}_2\text{O}_5$ das Teilsystem $\text{Ce}(\text{PO}_3)_3\text{-KPO}_3\text{-P}_2\text{O}_5$ untersucht. Die Phasenzusammensetzungen der durch verschiedene Erhitzungsvorgänge erhaltenen Produkte wurden untersucht und ein Phasendiagramm für das System $\text{Ce}(\text{PO}_3)_3\text{-KPO}_3\text{-P}_2\text{O}_5$ erstellt.