PACS number(s): 81.30.Dz

PHASE EQUILIBRIA IN THE SYSTEM $CePO_4 - K_4P_2O_7 - KPO_3$

I. Szczygieł

Department of Inorganic Chemistry, Faculty of Engineering and Economics, Wrocław
University of Economics, ul. Komandorska 118/120, 53-345 Wrocław, Poland
e-mail: irena.szczygiel@ae.wroc.pl

The $CePO_4 - K_4P_2O_7 - KPO_3$ portion of the $Ce_2O_3 - K_2O - P_2O_5$ ternary system has been investigated using thermoanalytical methods (DTA, DSC), powder X–ray diffraction, IR spectroscopy and photoelectron spectroscopy (XPS). Two systems: $CePO_4 - K_4P_2O_7$ and $CePO_4 - K_5P_3O_{10}$, which are binary only in subsolidus region, have been found.

Key words: ternary systems, X–ray diffraction, phase diagram, thermoanalytical methods, IR spectroscopy and photoelectron spectroscopy.

There are many literature reports on alkali metal-lanthanide phosphates, where $Ln = La$, Nd, Sm, Gd, and some on the connections of cerium phosphate with alkali metals. The published data usually deal with the methods of their synthesis, crystal and spectroscopic characteristic. Studies on phase equilibria are less popular.

The investigations of cerium-potassium phosphates have been carried out in our laboratory for over ten years [1–8]. Earlier we studied double phosphates in partial systems: $Ce(PO_3)_3 - KPO_3 - P_2O_5$ [6], $CePO_4 - KPO_3 - Ce(PO_3)_3$ [7], $CePO_4 - K_3PO_4 - K_4P_2O_7$ [8]. It was found that these systems contain four double phosphates: $KCe(PO_3)_4$, $K_2Ce(PO_3)_5$, $K_3Ce(PO_4)_2$ and $K_4Ce_2P_4O_{15}$. $K_4Ce_2P_4O_{15}$ exists only in the solid phase [8] and the remaining phosphates crystallize from the liquid phase. The present paper is a next part of the investigations on the potassium-cerium phosphates in the $Ce_2O_3 - K_2O - P_2O_5$ ternary system within the $CePO_4 - K_4P_2O_7 - KPO_3$ composition range.

Initial materials for the phase equilibria studies were analytical grade: KH_2PO_4, K_2HPO_4, $Ce(NO_3)_3 \cdot 6H_2O$, $NH_4H_2PO_4$ and CeO_2. From these commercial reagents the phosphates $CePO_4$, $K_4P_2O_7$, $K_5P_3O_{10}$, KPO_3, $K_4Ce_2P_4O_{15}$. were synthesized. Cerium orthophosphate $CePO_4$ was synthesized by the method provided in [9]. Potassium diphosphate $K_4P_2O_7$ was prepared from K_2HPO_4 by heating at 300 °C for 2 h and at 500 °C for 5 h. Potassium tripolyphosphate $K_5P_3O_{10}$ was obtained by sintering the mixture of KH_2PO_4 and K_2HPO_4 in the molar ratio 1 : 2 at 200 °C for 1 h and at 550 ºC for 5 h. Metaphosphate KPO_3 was obtained from KH_2PO_4 by heating at 350 °C for 2 h. The binary phosphate $K_4Ce_2P_4O_{15}$ was produced by solid state reaction of cerium oxide (IV) CeO_2 with potassium phosphate KPO_3.

The samples were investigated using differential thermal analysis, both heating and cooling, X–ray powder diffraction, IRS and XPS. The DTA–heating was carried out with a derivatograph type 3 427 (MOM, Hungary), up to 1 350 °C (heating rate: 10 ºK·min^{-1}, reference material: α–alumina, platinum crucibles) under air. Thermal

analysis during cooling was done through the range 1 300 to 20 °C with a resistance furnace constructed with Pt30Rh winding (3 g mass samples were used). Also, the thermoanalytical investigations were performed by using Setsys^{TM} calorimeter (TG–DSC 1 500; SETARAM) in a temperature range 20–1 300–20 °C (scanning rate 10 K·min^{-1}, reference material: α–alumina, platinum crucibles) in argon atmosphere. Temperature was measured by means of a Pt/PtRh10 thermocouple. The initial reagents were mixed in appropriate ratios, ground, pelletized, placed in platinum crucibles and sintered at 500–900 °C. The quenching techniques was also used for phase determinations.

The phase purity of the reagents and phase structure of products were controlled and identified by powder X–ray diffraction at room temperature on a Siemens D 5000 diffractometer with Co/Fe–radiation. IR spectra were measured in the range 1400–400 cm^{-1} with a Specord M–80 spectrophotometer (Carl Zeiss Jena). XPS were used to study the chemical state of cerium in cerium phosphates and cerium–potassium phosphates.

The part of the $Ce_2O_3 – K_2O – P_2O_5$ ternary system contained within the area limited by phosphates $CePO_4$, $K_4P_2O_7$ and KPO_3 (Fig. 1) has been examined using thermoanalytical methods (DTA, DSC), powder X–ray diffraction, IR spectroscopy and photoelectron spectroscopy (XPS). Phase relations within ternary systems are inherently related in nature of phase equilibra in the surrounding subsystems. It was found that the $CePO_4 – K_4P_2O_7$ system, shown in Fig. 2, is quasi–binary only in the subsolidus region, i.e. below 900 °C. Above 900 °C it is only binary in the composition range 87–100 wt.% $K_4P_2O_7$. In the other part of the composition range it is a polyphase. The system $CePO_4 – K_4P_2O_7$ contains one binary phosphate: $K_4Ce_2P_4O_{15}$ (molar ratio $CePO_4 : K_4P_2O_7 = 2:1$). This compound exists only in the solid state. $K_4Ce_2P_4O_{15}$ decomposes irreversibly at 879 °C [8, 10]. It exhibits a polymorphic transition at 527 °C. Cerium orthophosphate $CePO_4$ occurs in two polymorphic modifications with a transition temperature of α/β–620 °C, whereas $K_4P_2O_7$ is known to appear in a four polymorphic modifications with transition temperatures of α/β–1080 °C; β/γ–486 °C; γ/δ–280 °C [11]. It results from the figure that only the γ/δ transformation of $K_4P_2O_7$ exhibits weak thermal effects present on the DTA curves, but only in the composition range 60–100 wt % $K_4P_2O_7$.

The other subsystem, $K_4P_2O_7 – KPO_3$, contains intermediate compound $K_5P_3O_{10}$. This phosphate melts incongruently at 615 °C according to the scheme: $K_5P_3O_{10} \rightarrow K_4P_2O_7 +$ liquid (rich in KPO_3), and occurs in two polymorphic modifications [11]. Its transformation point is 452 °C.

In the last subsystem $CePO_4 – KPO_3$ no intermediate compounds are formed; it is a simple eutectic system with the eutectic composition 85 wt.% KPO_3 (15 wt.% $CePO_4$) at 790 °C. Phase diagram of the system $CePO_4 – KPO_3$ is given in Fig. 3.

Phase equilibria in three subsystems that surround the $CePO_4 – K_4P_2O_7 – KPO_3$ system (i.e. $CePO_4 – K_4P_2O_7$, $K_4P_2O_7 – KPO_3$, and $CePO_4 – KPO_3$) place constraints on the ternary equilibria. Invariant points in these subsystems are given in Table. Polythermal cross section of ternary system in Fig. 1 shows another system, built of two real compounds: $CePO_4$ and $K_5P_3O_{10}$.

The diagram of the $CePO_4 – K_5P_3O_{10}$ system given in Fig. 4. $CePO_4 – K_5P_3O_{10}$ section does not have all the features of the real equilibrium system. In other words it does not obey the Gibbs phase rule. The result is one of components of the system is an incongruently melting compound ($K_5P_3O_{10}$). Therefore, this phase diagram may only be correctly interpreted if considered as a part of the $CePO_4 – K_4P_2O_7 – KPO_3$ ternary system. Above the temperature of 560 °C it has a polyphase character with its four phases: a liquid L, $CePO_4$, $K_4P_2O_7$, and $K_5P_3O_{10}$. As a result of a peritectic reaction the

liquid L and the phosphate $K_4P_2O_7$ undergo consumption to produce $K_5P_3O_{10}$ crystals. Below 560 °C only two compounds exist, which are $CePO_4$ and $K_5P_3O_{10}$. The section has a quasi-binary character in the subsolidus region only – phase rule is obeyed.

Table

Some invariant points in the bounding binary subsystems

| Reactions	Reaction temperature [°C]	type
$K_4P_2O_7 – KPO_3$ subsystem [11]		
$L \leftrightarrow KPO_3$	810	melting
$L \leftrightarrow K_4P_2O_7$	1105	melting
$L \leftrightarrow K_5P_3O_{10} + KPO_3$	590	eutectic
$K_5P_3O_{10} \leftrightarrow L + K_4P_2O_7$	615	peritectic
$\beta–K_5P_3O_{10} \leftrightarrow \alpha–K_5P_3O_{10}$	452	transition
Quasi-binary $CePO_4 – KPO_3$ system [7]		
$L \leftrightarrow KPO_3$	810	melting
$L \leftrightarrow CePO_4$	2045	melting
$L \leftrightarrow CePO_4 + KPO_3$	790	eutectic
$\beta–CePO_4 \leftrightarrow \alpha–CePO_4$	620	transition
$\beta–KPO_3 \leftrightarrow \alpha–KPO_3$	665	transition
$\beta–KPO_3 \leftrightarrow \gamma–KPO_3$	449	transition
Quasi-binary $CePO_4 – K_4P_2O_7$ system [8]		
$L \leftrightarrow CePO_4$	2045	melting
$L \leftrightarrow K_4P_2O_7$	1105	melting
$L \leftrightarrow CePO_4 + K_4P_2O_7$	900	eutectic
$\delta–K_4P_2O_7 \rightarrow \gamma–K_4P_2O_7$	280	transition
$\beta–K_4Ce_2P_4O_{15} \rightarrow \alpha–K_4Ce_2P_4O_{15}$	527	transition
$K_4Ce_2P_4O_{15} \rightarrow CePO_4 + K_4P_2O_7$ reaction	879	peritectoid
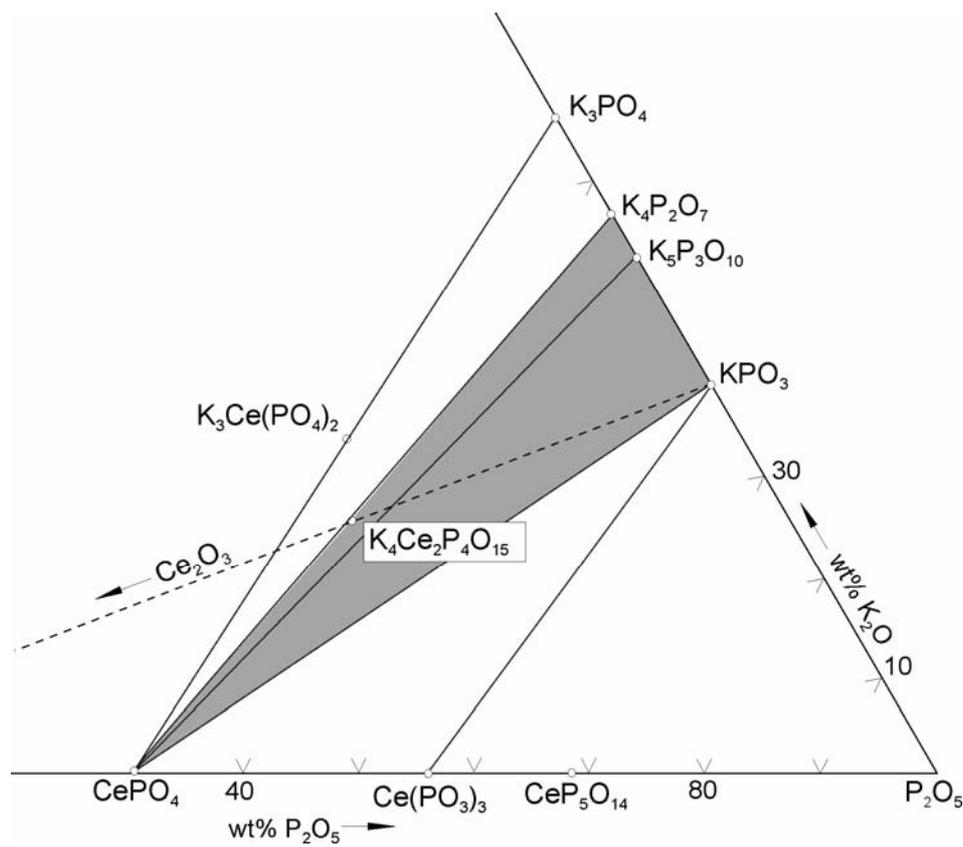
Fig. 1. The examined region in the $Ce_2O_3 - K_2O - P_2O_5$ ternary system
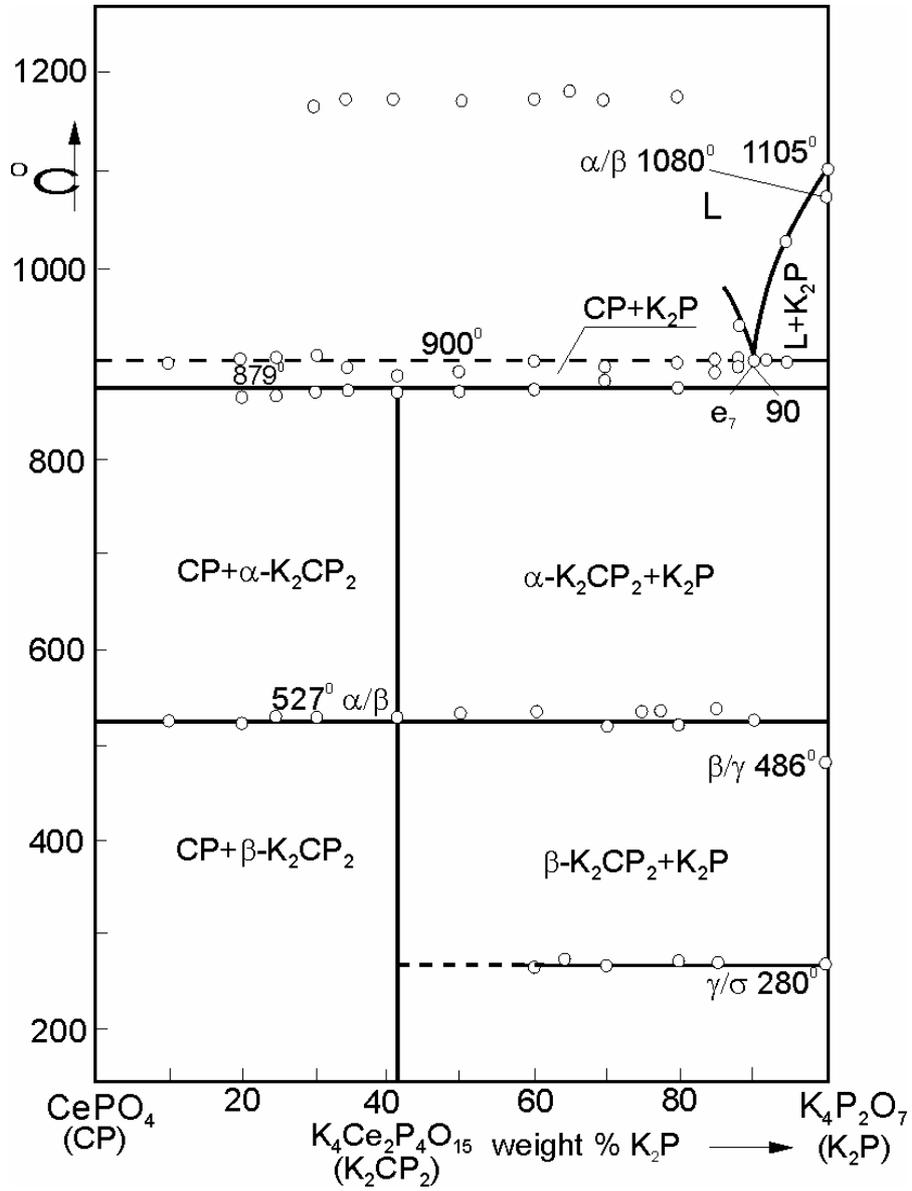
Fig. 2. Phase diagram of the system $CePO_4 - K_4P_2O_7$
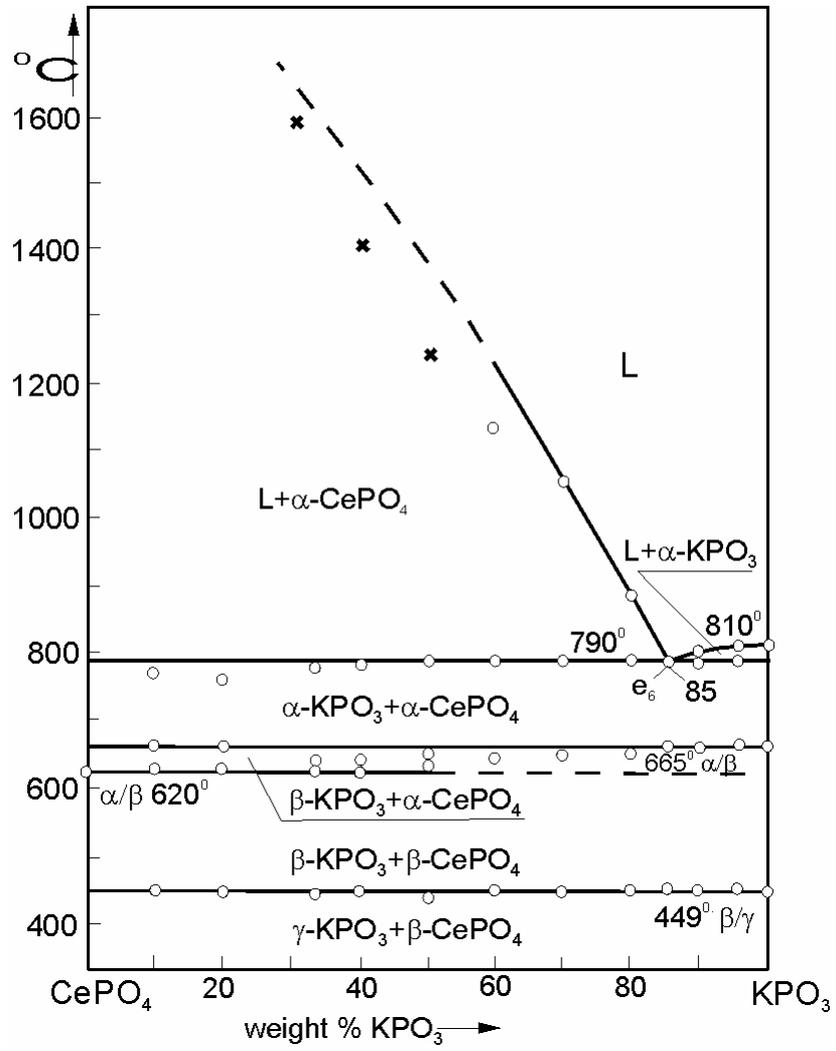
Fig. 3. Phase diagram of the system $CePO_4 - KPO_3$
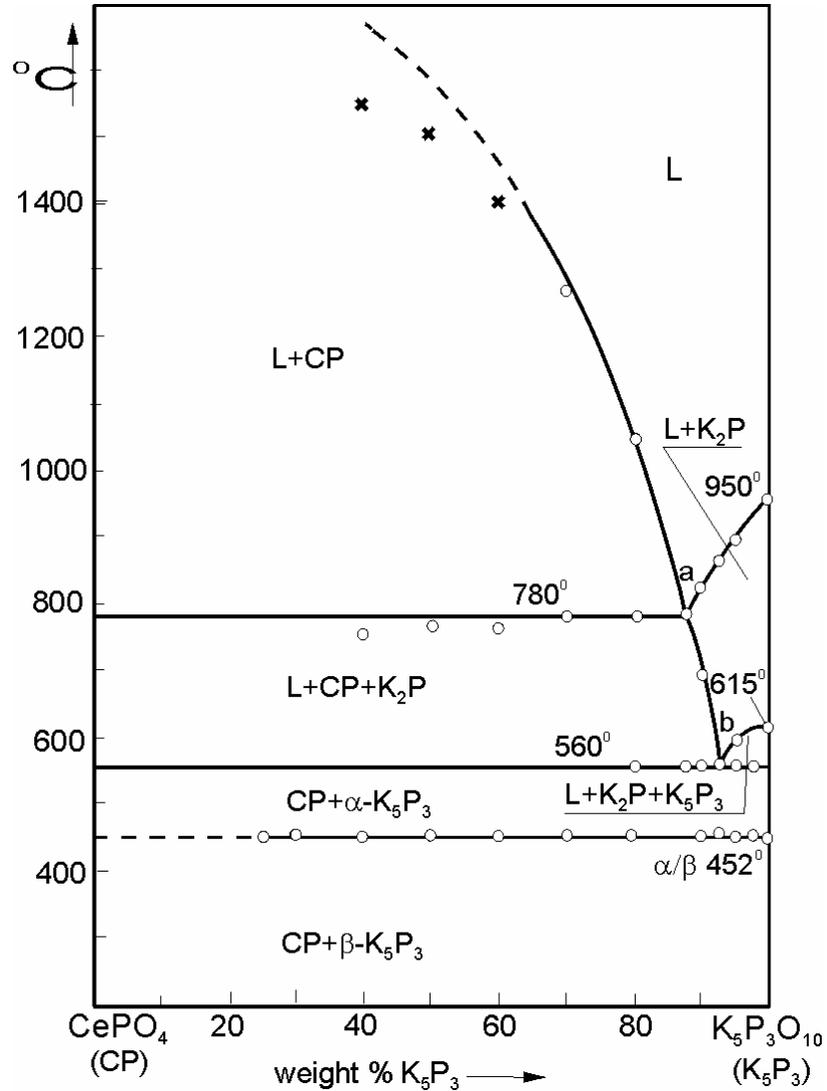
Fig. 4. Phase diagram of the cross section $CePO_4 - K_5P_3O_{10}$

It has been found that a ternary peritectic and ternary eutectic occur in the $CePO_4 -$ $K_4P_2O_7 - KPO_3$ system. The peritectic reaction proceeds according to the equation: $L(P)$ + $K_4P_2O_7 \leftrightarrows CePO_4 + K_5P_3O_{10}$ at 560 °C ($L(P)$ stands for a liquid of the composition corresponding to point P). Ternary eutectic ($CePO_4 + K_5P_3O_{10} + KPO_3$) is yielded at a constant temperature of 540 °C.

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ФАЗОВА РІВНОВАГА В СИСТЕМІ $CePO_4 - K_4P_2O_7 - KPO_3$

І. Щигел

Відділ неорганічної хімії, інженерний і економічний факультет, Вроцлав Економічний університет, вул. Командорська 118/120, 53-345 Вроцлав, Республіка Польща

Калориметричними методами, методами рентгенівської дифракції, інфрачервоної та фотоелектронної спектроскопії досліджено систему $CePO_4 - K_4P_2O_7 - KPO_3$, яка є складовою частиною потрійної сполуки $Ce_2O_3 - K_2O - P_2O_5$. В ділянці нижче від лінії солідусу виявлено дві бінарні системи $CePO_4 - K_4P_2O_7$ та $CePO_4 - K_5P_3O_{10}$.

Ключові слова: потрійні системи, рентгенівська дифракція, фазова діаграма, калориметричні методи, інфрачервона спектроскопія, фотоелектронна спектро-скопія.