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PHASE EQUILIBRIA IN THE Ce_2O_3–K_2O–P_2O_5 SYSTEM

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Ce_2O_3–K_2O–P_2O_5 ternary system has been investigated by thermoanalytical methods (DTA, DSC), powder X-ray diffraction, XPS and IR spectroscopy. The existence of three double potassium–cerium(III) phosphates has been confirmed and a new binary phosphate $K_4Ce_2P_4O_{15}$ has been found. Phase diagram and isothermal section at room temperature of the system Ce_2O_3–K_2O–P_2O_5 have been presented.

Keywords: *binary potassium–cerium(III) phosphates, phase diagram, phase equilibria, thermal properties*

Introduction

In recent years rare-earth phosphates have been extensively investigated due to their thermal stability in high temperature [1–5], catalytic activity [6–8] and interesting optical properties [9–20]. Alkali metal–lanthanide phosphates have been proposed for luminescent devices not only in the form of single crystals but also as powders or glasses [15–20]. A literature review indicates that the published reports are mainly concerned with the formation, crystal structure and spectroscopic characteristics of lanthanide and alkali metal–lanthanide double phosphates [9–21]. Phase diagrams play an important role in interpreting variations in properties with composition, but only some papers are devoted to phase investigations of ternary oxide systems of Ln_2O_3–M_2O–P_2O_5 [22-26].

In the previous work of our laboratory, much attention was paid on the elaboration of phase equilibria in ternary systems and the following phase diagrams of the systems have been examined: La_2O_3–Na_2O–P_2O_5, La_2O_3–K_2O–P_2O_5 [22, 26], Ce_2O_3–Na_2O–P_2O_5 [23], Y_2O_3–Na_2O–P_2O_5 and Y_2O_3–K_2O–P_2O_5 [24–25].

In this paper we present the results of investigation of the phase equilibria in the Ce_2O_3–K_2O–P_2O_5 ternary system within the $CePO_4$–K_3PO_4–KPO_3–$Ce(PO_3)_3$ composition range. The existence of four double potassium–cerium phosphates of formulas: $KCe(PO_3)_4$, $K_2Ce(PO_3)_5$ [27], $K_3Ce(PO_4)_2$ [28], $K_4Ce_2P_4O_{15}$ [29] has been determined in this ternary system. In order to better understand the phase equilibria occurring in the Ce_2O_3–K_2O–P_2O_5 ternary system, the presented diagram, in the P_2O_5-richest part is complemented by the results of the authors of [30]. We have also determined thermal characteristics, and optimum methods for the synthesis of phase-pure binary potassium–cerium phosphates which occur in the examined ternary system.

Experimental

Initial materials for the phase equilibria studies were of analytical grade: CeO_2 (ROTH Karlsruhe), $Ce(NO_3)_3\cdot 6H_2O$, H_3PO_4 (85%), $K_3PO_4\cdot 3H_2O$, K_2CO_3, KH_2PO_4, K_2HPO_4 and $NH_4H_2PO_4$ (all from POCh Gliwice). The cerium, potassium and double cerium–potassium phosphates were synthesized by the method described in [27, 28, 31, 32] from these commercial reagents. The initial reagents were mixed in appropriate ratios, ground, pelletized and placed in platinum crucibles and sintered at different temperatures, depending on composition of the examined samples.

DTA (both heating and cooling) experiments, DSC, X-ray powder diffraction, IR and XP spectroscopy were used to investigate the liquidus and solidus relations in Ce_2O_3–K_2O–P_2O_5 system.

The DTA–heating experiments were carried out with a derivatograph type 3427 (MOM, Hungary), up to 1350°C (heating rate: 10 K min^{-1}, reference material: α-alumina, platinum crucibles) under air. Thermal analysis of cooling was done in the range of 1300 to 20°C with a resistance furnace constructed with Pt30Rh winding (3 g mass samples were used). The thermoanalytical investigations were performed also by using Setsys^{TM} calorimeter (TG/DSC 1500; Setaram) in a temperature range 20–1300–20°C (scanning rate10 K min^{-1}, reference material: α-alumina, platinum crucibles) in argon atmosphere. Temperature was measured by means of a Pt/PtRh10 thermocouple. The enthalpy of double potassium–cerium(III) phosphates from Ce_2O_3–K_2O–P_2O_5 system was determined by using Setsys^{TM} calorimeter. The enthalpy of phase transitions of KNO_3, $AgSO_4$, and K_2SO_4 were used to calibrate the apparatus. The accuracy of value of enthalpy has been corrected. The high-temperature thermal studies above 1400°C were carried out in argon

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atmosphere in a horizontal resistance furnace with molybdenum winding. With the view to establish the nature of the effects recorded on the DTA/TG curves of the investigated phases, the quenching-in-ice technique was also used.

The phase purity of the reagents and phase structure of products were identified by powder X-ray diffraction at room temperature on a Siemens D 5000 diffractometer (CuK$_\alpha$ or Co/Fe-radiation). The PDF-2 database (ICDD) [33] has been searched to detect the phases present in the samples.

The IRS and XPS were employed as complementary methods to verify the chemical composition and oxidation degree of cerium in phosphates under investigations.

Results and discussion

Phase equilibria in Ce_2O_3–K_2O–P_2O_5 ternary system

Phase diagram of the Ce_2O_3–K_2O–P_2O_5 ternary system within the composition range $CePO_4$–K_3PO_4–KPO_3–$Ce(PO_3)_3$ (Fig. 1) was investigated by polythermal cross-sections, and examining many samples. Remaining parts of the system were not investigated since any new chemical combinations had not been observed by the X-ray analysis of entirely or partially fused samples in this composition range. An additional reason for omitting those parts were considerable difficulties in experiments with preparations that have high melting points (above 1600°C) in the Ce_2O_3- and K_2O-rich part of the system as well as thermal decomposition of the samples in the P_2O_5-rich part of the system (due to release of P_2O_5). Other experimental difficulty was refractory crystallization of molten samples with their tendency for vitrification and hygroscopicity.

Figure 2 shows a phase diagram of the Ce_2O_3–K_2O–P_2O_5 system in the examined composition range, with partially drawn solidification isotherms. Seven binary and four ternary compounds occur in the Ce_2O_3–K_2O–P_2O_5 system. The binary phosphate $K_4Ce_2P_4O_{15}$ exists in solid phase only, and the remaining phosphates crystallize from liquid phase. Their primary crystallization fields are separated one another with eutectic and peritectic curves. Along the eutectic curves, at variable temperature, the binary eutectics crystallize and along the peritectic curves, also at varying temperature, the suitable phosphates are produced, e.g.: $Ce(PO_3)_3+L(p_2P_3)\rightarrow KCe(PO_3)_4$ or $KCe(PO_3)_4+L(p_3P_4)\rightarrow K_2Ce(PO_3)_5$. These fields are situated as follows:

CeP_5O_{14} in the range CP_5–e_2–P_1–P_2–E_1–;
$Ce(PO_3)_3$ in e_1–P_3–p_2–P_1–e_2–CP_3;
$CePO_4$ in
CP–K_3CP_2–p_4–P_6–f–e_7–h–P_5–E_3–e_6–E_2–P_4–P_3–e_1;
KPO_3 in KP–e_3–E_3–e_6–E_2–e_5–E_1–;
$K_5P_3O_{10}$ in p_1–e_3–E_3–P_5;
$K_4P_2O_7$ in e_4–K_2P–K_5P_3–p_1–P_5–e_7–P_6–E_4;
K_3PO_4 in K_3P–e_4–E_4–e_8;
$KCe(PO_3)_4$ in P_3–p_2–P_1–P_2–p_3–P_4;
$K_2Ce(PO_3)_5$ in P_2–E_1–e_5–E_2–P_4–p_3;
and $K_3Ce(PO_4)_2$ in p_4–e_8–E_4–P_6.

According to Fig. 2, the largest part of the system covers the primary crystallization field of the cerium orthophosphate $CePO_4$, whereas the primary crystallization fields of the remaining phosphates are much lower. The primary crystallization field of CeP_5O_{14} (in the P_2O_5-rich part of the system) has only been fixed partially because of experimental difficulties, i.e. glasses formation during cooling, decomposition of the samples with mass loss and change in phase composition. Four ternary eutectics and six ternary peritectics occur in the composition range under discussion. The onset of primary crystallization of compounds is spread over a wide temperature range, from about 600°C for P_2O_5-rich samples to about 2000°C for Ce_2O_3–rich ones.

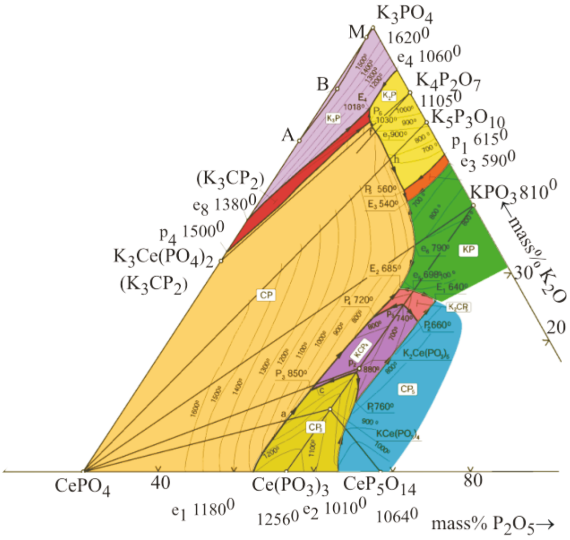

Fig. 2 Solidification isotherms in the system Ce_2O_3–K_2O–P_2O_5

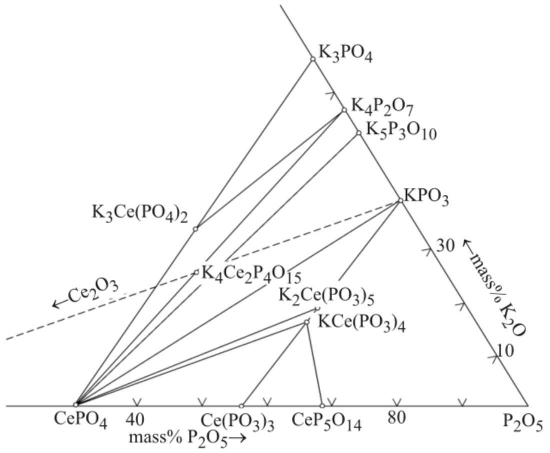

Fig. 1 The examined region in Ce_2O_3–K_2O–P_2O_5 ternary system

Investigations of polythermal cross-sections of the ternary system shown in Fig. 1 confirm that binary and ternary compounds form nine pseudo–binary systems. Their phase diagrams were established as a result of this work. The phase relations in three main systems (i.e. $Ce(PO_3)_3$–KPO_3 [27], $CePO_4$–K_3PO_4 [28], $CePO_4$–KPO_3 [32]) and the binary side systems (i.e. $CePO_4$–Ce_5PO_{14} and K_3PO_4–KPO_3) [34, 35] essentially affect the phase equilibria in the entire composition range in question.

Cerium orthophosphate $CePO_4$ yields the binary pseudo-sections with all binary and ternary compounds present in the system $CePO_4$–K_3PO_4–P_2O_5. Some of the sections, e.g. $CePO_4$–KPO_3, are simple binary eutectic systems within the whole temperature range. Most of them, e.g. $CePO_4$–$K_5P_3O_{10}$, $CePO_4$–$KCe(PO_3)_4$, $CePO_4$–$K_2Ce(PO_3)_5$, are complex and polyphase systems at high temperatures which result from the peritectic decomposition of $K_5P_3O_{10}$, $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$ compounds, respectively. In other words, they do not obey Gibbs' phase rule at high temperatures. At low temperature, the sections have a binary character. Therefore, such pseudo-binary phase diagrams may only be correctly interpreted if considered as part of ternary system.

The phase diagram of the Ce_2O_3–K_2O–P_2O_5 system with triple peritectic quadrangle, i.e. $Ce(PO_3)_3$–$KCe(PO_3)_4$–P_1–CeP_5O_{14}, $CePO_4$–P_3–$KCe(PO_3)_4$–$Ce(PO_3)_3$, $CePO_4$–P_4–$K_2Ce(PO_3)_5$–$KCe(PO_3)_4$, $CePO_4$–$K_4P_2O_7$–$K_5P_3O_{10}$–P_5, $CePO_4$–$K_3Ce(PO_4)_2$–P_6–$K_4P_2O_7$, is presented in Fig. 3, and some invariant points in the Ce_2O_3–K_2O–P_2O_5 ternary system are listed in Table 1.

Isothermal section of $CePO_4$–K_3PO_4–KPO_3 system at room temperature

The presence of the $K_4Ce_2P_4O_{15}$ phosphate which occurs in the solid phase only (below 880°C) affects phase equilibria existing in the $CePO_4$–K_3PO_4–KPO_3 system in the subsolidus region.

Figure 4 shows the isothermal section of this system at room temperature. It was elaborated based on the above discussed sections and the results of DTA and X-ray analysis applied to presynthesized samples of heteromolar mixtures of the phosphates $CePO_4$, $K_3Ce(PO_4)_2$, K_3PO_4, $K_4P_2O_7$, $K_4Ce_2P_4O_{15}$, $K_5P_3O_{10}$, KPO_3 and CeO_2. On this basis it was established that the following sections occur in the subsolidus region: $K_3Ce(PO_4)_2$–$K_4Ce_2P_4O_{15}$, $K_3Ce(PO_4)_2$–$K_4P_2O_7$, $K_4Ce_2P_4O_{15}$–$K_5P_3O_{10}$ and $K_4Ce_2P_4O_{15}$–KPO_3. They divide the composition

Table 1 Some invariant points in the ternary system Ce_2O_3–K_2O–P_2O_5

Reactions	Reaction temperature/°C	Type
$L \rightarrow CePO_4+Ce(PO_3)_3$	1180	eutectic(e_1)
$L \rightarrow Ce(PO_3)_3+CeP_5O_{14}$	1010	eutectic(e_2)
$L \rightarrow K_5P_3O_{10}+KPO_3$	590	eutectic(e_3)
$L \rightarrow K_3PO_4+K_4P_2O_7$	1060	eutectic(e_4)
$K_5P_3O_{10} \rightarrow L+K_4P_2O_7$	615	peritectic(p_1)
$L \rightarrow Ce(PO_3)_3+KPO_3$	698	eutectic(e_5)
$KCe(PO_3)_4 \rightarrow L+Ce(PO_3)_3$	880	peritectic(p_2)
$K_2Ce(PO_3)_5 \rightarrow L+KCe(PO_3)_4$	740	peritectic(p_3)
$L \rightarrow CePO_4+K_4P_2O_7$	900	eutectic(e_7)
$L \rightarrow K_3Ce(PO_4)_2+K_3PO_4$	1380	eutectic(e_8)
$K_3Ce(PO_4)_2 \rightarrow L+CePO_4$	1500	peritectic(p_4)
$L(E_1) \rightarrow KPO_3+K_2Ce(PO_3)_5+CeP_5O_{14}$	640	ternary eutectic
$L(P_1)+Ce(PO_3)_3 \rightarrow KCe(PO_3)_4+CeP_5O_{14}$	760	ternary peritectic
$L(P_3)+Ce(PO_3)_3 \rightarrow CePO_4+KCe(PO_3)_4$	850	ternary peritectic
$L(P_4)+KCe(PO_3)_4 \rightarrow CePO_4+K_2Ce(PO_3)_5$	720	ternary peritectic
$L(E_2) \rightarrow KPO_3+K_2Ce(PO_3)_5+CePO_4$	685	ternary eutectic
$L(E_3) \rightarrow CePO_4+K_5P_3O_{10}+KPO_3$	540	ternary eutectic
$L(P_5)+K_4P_2O_7 \leftrightarrow CePO_4+K_5P_3O_{10}$	560	ternary peritectic
$L(E_4) \rightarrow K_3PO_4+K_4P_2O_7+K_3Ce(PO_4)_2$	1018	ternary eutectic
$L(P_6)+CePO_4 \leftrightarrow K_3Ce(PO_4)_2+K_4P_2O_7$	1030	ternary peritectic
$K_4Ce_2P_4O_{15} \rightarrow CePO_4+K_4P_2O_7$	879	peritectoid reaction

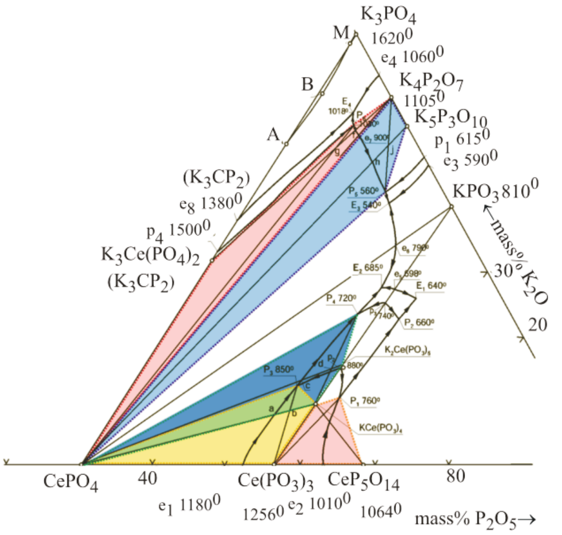

Fig. 3 Phase diagram of the $Ce_2O_3–K_2O–P_2O_5$

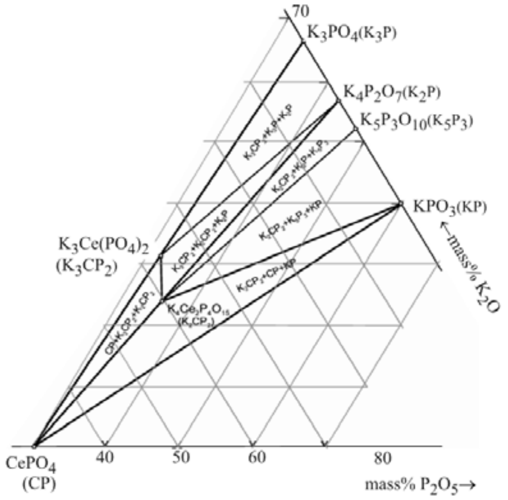

Fig. 4 Isothermal section of the system $CePO_4–K_3PO_4–KPO_3$ at room temperature

range under discussion into six partial ternary systems (i.e. six fields of the coexisting phases):

1) $CePO_4–K_3Ce(PO_4)_2–K_4Ce_2P_4O_{15}$;
2) $K_3Ce(PO_4)_2–K_3PO_4–K_4P_2O_7$;
3) $K_3Ce(PO_4)_2–K_4Ce_2P_4O_{15}–K_4P_2O_7$;
4) $K_4Ce_2P_4O_{15}–K_4P_2O_7–K_5P_3O_{10}$;
5) $K_4Ce_2P_4O_{15}–K_5P_3O_{10}–KPO_3$;
6) $CePO_4–K_4Ce_2P_4O_{15}–KPO_3$.

Binary phosphates in the $Ce_2O_3–K_2O–P_2O_5$ ternary system

Cerium(III) is quite easily oxidized to Ce(IV) and often gives non-stoichiometric oxides (of mixed valence) CeO_x, where $1.5<x<2$. A number of authors think, however, that there is rather no problem of mixed valence of cerium (Ce(III)/Ce(IV) in condensed phosphates, since stable phosphates are produced by both cerium(III) and cerium(IV) [36–40]. In the solid phase, cerium(IV) phosphates precipitated from aqueous solutions are stable, but only at lower temperatures. At higher temperatures (>800°C) cerium(IV), in phosphates, undergoes a reduction to cerium(III) with a liberation of equivalent amount of oxygen [37–39]. In the solid phase, cerium(III) gives stable phosphates [31, 36, 38–40].

Our own results are in agreement with those data reports and confirm that cerium has oxidation degree +3 in the phosphates under investigation [27–29, 41, 42]. Examinations by thermal methods (DSC, DTA), XRD, XPS and IR spectroscopy of the ternary system within the composition range $CePO_4–K_3PO_4–P_2O_5$ enabled to characterize the binary phosphates: $K_3Ce(PO_4)_2$, $K_4Ce_2P_4O_{15}$, $KCe(PO_3)_4$, $K_2Ce(PO_3)_5$. These are intermediate compounds formed on the polythermal sections $CePO_4–K_3PO_4$, $CePO_4–K_4P_2O_7$ and $Ce(PO_3)_3–KPO_3$, respectively. The sections $CePO_4–K_3PO_4$ and $Ce(PO_3)_3–KPO_3$ show features of quasi–binary systems in the entire composition and temperature range [27, 28], whereas the $CePO_4–K_4P_2O_7$ system is quasi-binary in the subsolidus region below 900°C, while above 900°C is such only in the $K_4P_2O_7$-richest part, i.e. in the composition range 87–100 mass% of $K_4P_2O_7$ [29]. $K_3Ce(PO_4)_2$, $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$ phosphates occur also in particular composition ranges of the ternary system $Ce_2O_3–K_2O–P_2O_5$ (Fig. 2).

The X-ray structural data of the double cerium phosphates which occur in $Ce_2O_3–K_2O–P_2O_5$ ternary system are presented in Table 2. The experimental XRD patterns of $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$ have been given in [45]. Experimental X-ray powder diffraction patterns of $K_3Ce(PO_4)_2$ and $K_4Ce_2P_4O_{15}$, produced by ourselves, were presented in original papers [28, 41].

Table 2 The structural data of potassium–cerium phosphates

Compound	Structure	Lattice parameters
$KCe(PO_3)_4$ [45]	monoclinic $P2_1/m$ (C^2_{2h})	a=7.278, b=8.478, c=8.037 Å; β=92.04°; Z=2
$K_2Ce(PO_3)_5$ [45]	unknown	
β-$K_3Ce(PO_4)_2$ [28]	monoclinic $P2_1/m$ (C^2_{2h})	a=9.579, b=5.634, c=7.468 Å; β=90.81°; Z=2
β-$K_4Ce_2P_4O_{15}$ [41]	triclinic P-1 (C^1_i)	a=9.319, b=12.129, c=9.252 Å; α=106.854, β=100.086, γ=107.20°

The infrared and Raman spectroscopic characteristics of these phosphates were reported earlier [14, 15].

Reliability of phase investigations is affected by the purity of compounds under investigation, therefore much time was devoted to study their thermal stability and to elaborate the most favourable synthesis methods of phase-pure cerium and potassium–cerium binary phosphates (to match the relevant parent substances, synthesis temperature and period of synthesis).

Thermal stability of all these binary phosphates was investigated from room temperature up to their melting points.

It has been found that $K_3Ce(PO_4)_2$ is stable from room temperature up to 1500°C. At 1500°C it melts incongruently (reversibly) according to the following reaction:

$$K_3Ce(PO_4)_2 \leftrightarrows CePO_4 + \text{a liquid } K_3PO_4\text{-rich}$$

This compound exhibits a reversible polymorphic transition α/β-$K_3Ce(PO_4)_2$ at 1180°C. The value of enthalpy of the polymorphic transition, as determined by the DSC method from the heating curve, is ΔH=77.1 J g^{-1} (34.5 kJ mol^{-1}). Because transition α/β-$K_3Ce(PO_4)_2$ is reversible, therefore ΔG=0 at phase-transition onset temperature (1180°C) and calculation of transition entropy shows that ΔS value for double potassium–cerium orthophosphate is about 29 J mol^{-1} K^{-1}. According to [43] ΔS for potassium–lanthanide double phosphates is in the range 21 to 31 J mol^{-1} K^{-1}. The high temperature modification α-$K_3Ce(PO_4)_2$ cannot be room temperature stabilized by freezing. This may be due to close structural similarity between the low- and high-temperature forms of $K_3Ce(PO_4)_2$. Ushakov *et al.* [43] report about affinity between the high temperature modifications $K_3Ln(PO_4)_2$ of hexagonal structure $P\bar{3}m1$ (of ideal glaserite, $K_3Na(SO_4)_2$) or $P\bar{3}$ (of distorted glaserite) and the low–temperature modifications of monoclinic structure $P2_1/m$ (arcanite-like form, β-K_2SO_4). Their high temperature X-ray diffraction studies on $K_3Y(PO_4)_2$ and $K_3Gd(PO_4)_2$ confirm this prediction.

$K_3Ce(PO_4)_2$ phosphate can be obtained in the phase pure form *via* solid state reaction as a result of sintering an equimolar mixture of parent phosphates at a temperature of 900°C for 20 h. It is formed also as a result of slowly cooling a melted equimolar mixture of $CePO_4$ and K_3PO_4.

$K_3Ce(PO_4)_2$ phosphate can be prepared in high-temperature solution using of stoichiometric amounts of CeO_2 and K_2HPO_4. Mixture was very slowly heated to 1150°C in a platinum crucible in air, held at this temperature for 6 h. Then the sample was cooled to 900°C at 2°C h^{-1} and then rapidly quenched in ice, washed in water and dried. The obtained, well-crystallized product was phase-pure.

Binary phosphate $K_4Ce_2P_4O_{15}$ exists only in the solid state, below 880°C. At temperature of 879°C it decomposes to $CePO_4$, $K_4P_2O_7$, $K_3Ce(PO_4)_2$. Based on DTA and powder X-ray diffraction analysis the decomposition process of the $K_4Ce_2P_4O_{15}$ phosphate is proposed as follows:

$$3K_4Ce_2P_4O_{15} \rightarrow 6CePO_4 + 3K_4P_2O_7 \rightarrow$$
$$\rightarrow 4K_3Ce(PO_4)_2 + 2CePO_4 + P_2O_5$$

DSC analysis (of heating) showed a phase transition to occur in the $K_4Ce_2P_4O_{15}$ phosphate at a temperature of 527°C, of which the enthalpy of polymorphic transformation amounts to 57.7 J g^{-1} (46.2 kJ mol^{-1}). High temperature form α-$K_4Ce_2P_4O_{15}$ cannot be room temperature stabilized by fast cooling or freezing in ice. Though, any inverse transition was not observed. Probably it proceeds too slowly under the conditions of experiment used.

It has been established that the most favourable conditions to obtain a phase pure compound of $K_4Ce_2P_4O_{15}$ are the following:

- Heating the mixture KPO_3 and $Ce(NO_3)_3 \cdot 6H_2O$ in the molar ratio 4:2 at a temperature of 200°C for 5 h and at 750°C for 48 h, then washing the product with hot water to remove contaminants;
- Sintering a mixture of 2 moles CeO_2 and 4 moles KPO_3 at a temperature of 700–750°C for 24 h;
- Low-temperature synthesis from $Ce(NO_3)_3 \cdot 6H_2O$, KNO_3 and $NH_4H_2PO_4$ (the method is subject to Patent Application [44]).

Large enthalpy values of the α/β–$K_3Ce(PO_4)_2$ (34.5 kJ mol^{-1}) and α/β–$K_4Ce_2P_4O_{15}$ (46.2 kJ mol^{-1}) phase transitions suggest a first–order mechanism.

Literature reports [45, 46] concerning the $Ce(PO_3)_3$–KPO_3 system show essential discrepancy. According to [45] two intermediate phosphates occur, $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$. According to Mardirosova *et al.* [46] only one phosphate appears in this system. We re-examined the $Ce(PO_3)$–KPO_3 system and our results have confirmed the data of Rzaigui *et al.* [45] concerning the phosphates $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$. Both phosphates incongruently melt at temperatures 880 and 740°C, respectively, according to the following reactions:

$$KCe(PO_3)_4 \leftrightarrows Ce(PO_3)_3 + \text{a liquid } KPO_3\text{-rich}$$

$$K_2Ce(PO_3)_5 \leftrightarrows KCe(PO_3)_4 + \text{a liquid } KPO_3\text{-rich}$$

None of them shows a polymorphic transition. Synthesis conditions of both mixed polyphosphates were investigated. It is found that these are difficult to obtain (particularly the $K_2Ce(PO_3)_5$), and need a complicated thermal treatment.

It has been established that the most favourable synthesis method of $KCe(PO_3)_4$ is solid-state sintering an equimolar mixture of KPO_3 and $Ce(PO_3)_3$ at a temperature of 800°C for 48 h. So obtained $KCe(PO_3)_4$ metaphosphate is of phase purity; i.e. it doesn't contain of impurities. However, the method failed to give a pure $K_2Ce(PO_3)_5$. This may be due to a great difference in melting point between the parent phosphates $Ce(PO_3)_3$ (1256°C) and KPO_3 (810°C) as well as the low peritectic decomposition point of $K_2Ce(PO_3)_5$ (740°C). This compound in the phase pure form can, however, be obtained from equimolar mixture of CeP_5O_{14} and K_2CO_3 via heating at a temperature of 400 and 720°C for 12 and 48 h, respectively.

Conclusions

The phase diagram with liquidus isotherms and isothermal section at room temperature of the oxide system Ce_2O_3–K_2O–P_2O_5 have been examined. The system contains seven binary and four ternary compounds: $CePO_4$, $Ce(PO_3)_3$, CeP_5O_{14}, KPO_3, $K_5P_3O_{10}$, $K_4P_2O_7$, K_3PO_4, $KCe(PO_3)_4$, $K_2Ce(PO_3)_5$, $K_4Ce_2P_4O_{15}$ and $K_3Ce(PO_4)_2$. The $K_4Ce_2P_4O_{15}$ phosphate exists only in solid phase, the remaining phosphates crystallize from the liquid phase. Their primary crystallization fields, which are separated one another with eutectic and peritectic curves, are established.

We have also determined thermal characteristics and optimal methods for the synthesis of phase-pure potassium–cerium binary phosphates which occur in the examined ternary system.

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