

Investigations of new binary phosphate $K_4Ce_2P_4O_{15}$

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Available online 5 March 2004

Abstract

The new potassium cerium(III) phosphate of formula $K_4Ce_2P_4O_{15}$ in the system $Ce_2O_3-K_2O-P_2O_5$ was prepared by solid state reactions and characterized by thermal analysis (DTA, TG, DSC), powder X-ray diffraction and IR spectroscopy. This compound exists only in the solid state (below 880 °C) and exhibits a polymorphic transition at 527 °C. The low-temperature form $\beta-K_4Ce_2P_4O_{15}$ of this compound crystallizes as a triclinic phase (space group P) with unit cell parameters: $a = 9.319(7)$, $b = 12.129(3)$, $c = 9.252(1)$ Å, $\alpha = 106.875$, $\beta = 100.086$, $\gamma = 107.202^\circ$, $V = 916.276$ Å³.

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Keywords: Potassium cerium(III) phosphate; Chemical synthesis; X-ray diffraction; Thermal analysis; IR spectroscopy

1. Introduction

The work on search for binary phosphates of lanthanide-alkali metal elements carried out in this laboratory, includes investigations of phase equilibria in ternary systems of $Ln_2O_3-M_2O-P_2O_5$ (where Ln stands for a lanthanide, and M for alkali metal). Those compounds are known from literature as materials suitable for luminophores and lasers [1–4]. This work concerns the author's study of a series of potassium and cerium(III) binary phosphates that appear in the ternary system $Ce_2O_3-K_2O-P_2O_5$, which was undertaken a few years ago in an attempt to elaborate its unknown phase diagram and attain a knowledge on the phosphates.

Cerium(III) phosphates such as $CePO_4$, $Ce(PO_3)_3$, CeP_5O_{14} [5–7] as well as those binary potassium and cerium(III) phosphates of $K_3Ce(PO_4)_2$, $KCe(PO_3)_4$, $K_2Ce(PO_3)_5$ [8,9] are known. Known are phase diagrams of some binary systems, i.e. $KPO_3-Ce(PO_3)_3$ [9,10] and $CePO_4-K_3PO_4$ [11] including also phase dependences in the partial ternary systems $CePO_4-KPO_3-Ce(PO_3)_3$ [12] and $Ce(PO_3)_3-KPO_3-P_2O_5$ [13].

The present paper concerns investigations of part of the ternary system that extends between the phosphates $CePO_4$, $K_3Ce(PO_4)_2$, $K_4P_2O_7$ and KPO_3 , i.e., in the P_2O_5 poor region. Attention is focused on the results which enable

identification of the new binary phosphate of the formula $K_4Ce_2P_4O_{15}$ and its thermal properties are described.

2. Experimental

The following initial reagents were used: CeO_2 (99.9 %) and H_3PO_4 (85%), KH_2PO_4 , K_2HPO_4 , K_2CO_3 , $(NH_4)_2HPO_4$, $Ce(NO_3)_3 \cdot 6H_2O$, $NH_4H_2PO_4$, all analytically pure.

Cerium orthophosphate $CePO_4$ was obtained from $Ce(NO_3)_3 \cdot 6H_2O$ and $NH_4H_2PO_4$ by the method given in reference [14]. Metaphosphate KPO_3 was obtained from KH_2PO_4 by heating at 350 °C for 2 h (by completely dehydrating). Pyrophosphate $K_4P_2O_7$ was prepared from K_2HPO_4 by heating at 300 °C for 2 h and at 500 °C for 5 h.

The investigations were performed by differential thermal analysis (DTA, TG, DTG) during heating and X-ray powder diffraction. The DTA-heating carried out with the TGDTA 92 thermoanalyzer (SETARAM), up to 1400 °C (heating rate: 10 K min⁻¹; reference material: α -alumina) under air. DSC option has been used too. The initial reagents were mixed in appropriate ratios, ground, pelletized, placed in platinum crucibles and sintered at 700–800 °C. The quenching techniques was also used for phase determination.

The phase purity of the reagents and phase structure of products were studied by powder X-ray diffraction at room temperature on a Simens D 5000 diffractometer with

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Co/Fe-radiation. The PDF-2 data base (ICDD) was searched to detect the phase present in the samples. IR spectra were measured over the range 1400–400 cm^{-1} (with KBr as diluent) with a Specord M-80 spectrophotometer (Carl Zeiss Jena).

3. Results and discussion

Experimental examination of the field limited by the compounds CePO_4 , $\text{K}_3\text{Ce}(\text{PO}_4)_2$, $\text{K}_4\text{P}_2\text{O}_7$ and KPO_3 (Fig. 1) were begun with thermal and X-ray powder diffraction tests. These consisted in annealing a number of the samples prepared in the field of interest at different temperatures for different heating times. The initial work resulted in finding extra reflections in some of the diffractograms—apart from the appearance of spots typical of the known phosphates that occurred in the area under investigation. These might be ascribed to a new phase, unknown so far. In order to identify it, at the first stage the samples comprising heteromolar mixtures of CePO_4 and $\text{K}_4\text{P}_2\text{O}_7$ phosphates were prepared. Analysis of the results showed the new extra reflections. It was admitted those might be originated of a new phase. Formula $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ was under consideration as related to the most probable stoichiometric composition of the phase because the reflections of interest in the diffractogram revealed the highest intensity for a sample of the mixture 2 mol CePO_4 and 1 mol $\text{K}_4\text{P}_2\text{O}_7$. Consequently, an attempt to obtain a phase-pure phosphate of $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ was made. It seemed this would be possible by means of the solid state reaction by taking the parent phosphates as a mixture in the CePO_4 : $\text{K}_4\text{P}_2\text{O}_7$ molar ratio of 2:1 but phosphate $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ is hardly produced and it is not a phase-pure. The next attempt was to employ other initial reagents and

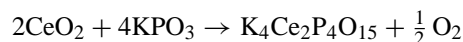
different thermal treatments for the synthesis the double phosphate $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$. The following mixtures of starting substances in appropriate stoichiometric amounts were used:

- (i) K_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
- (ii) K_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$ and CeO_2
- (iii) KH_2PO_4 and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
- (iv) KPO_3 and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
- (v) KPO_3 and CeO_2

The polycrystalline products of these reactions were washed with hot distilled water and dried at 300 °C in air to remove any remaining ammonium nitrate, ammonium phosphate, nitric acid, phosphoric acid and other impurities. The formation of multiphase products were observed in cases (i)–(iii). It proved that only in cases (iv) and (v) the phase-pure $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ could be synthesized. The phosphate was light yellow powder. The ICP analysis for samples synthesized by method (iv) and (v) showed 19.48 wt.% K, 34.82 wt.% Ce and 15.57 wt.% P (theoretical values: 19.54 wt.% K, 35.01 wt.% Ce and 15.48 wt.% P), which coincided with the composition $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ well.

In the case (iv), a pure $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ was obtained from mixture KPO_3 and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (molar ratio 4: 2) by heating at 200 ° for 5 h and at 750 °C for 48 h. However, double phosphate $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ is susceptible to hydrolysis. Treatment of sinters with hot water were yielded meaning dissolution of phosphate. ICP analysis shows that some of the cerium in $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ dissolves.

A phase-pure phosphate $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ is produced relatively easy by starting from a mixture of 2 mol CeO_2 and 4 mol KPO_3 upon heating at a temperature of 700–750 °C for 24 h (case (v)). During the course of the synthesis the observed mass decrement was constant and amounted to 1.90% of the initial mass of the substrates. Taking into account this decrement, one can assume the following reaction:



The observed mass decrement corresponds to the stoichiometry of the reaction proposed and it is nearly the same as the amount of the oxygen gas liberating ($m_{\text{theoretical}} = 1.96\%$).

In order to obtain information on the properties of the new phase, its thermal stability was first examined. Differential thermal analysis during heating was made in the range 20–1400 °C. Fig. 2 shows derivatogram of the $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ compound obtained in the way described above. In order to find what type of phase transition is to be attributed to the endothermic thermal effects in the DTA curve, the presynthesized sample of the stoichiometry $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ was annealed at different temperatures for different times, which was followed by freezing (in ice). It was found from the powder XRD-spectra of the samples frozen from temperatures below 879 °C that the reflections originated from $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ phosphate only; and the samples frozen from temperatures above 879 °C the reflections originated from CePO_4 , $\text{K}_4\text{P}_2\text{O}_7$, $\text{K}_3\text{Ce}(\text{PO}_4)_2$.

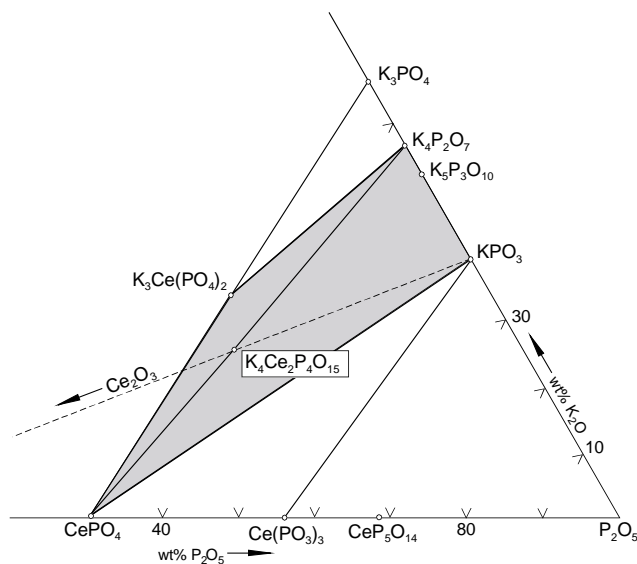


Fig. 1. The coexistence region of $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$, $\text{K}_3\text{Ce}(\text{PO}_4)_2$, potassium phosphates and cerium(III) phosphate in the system Ce_2O_3 – K_2O – P_2O_5 .

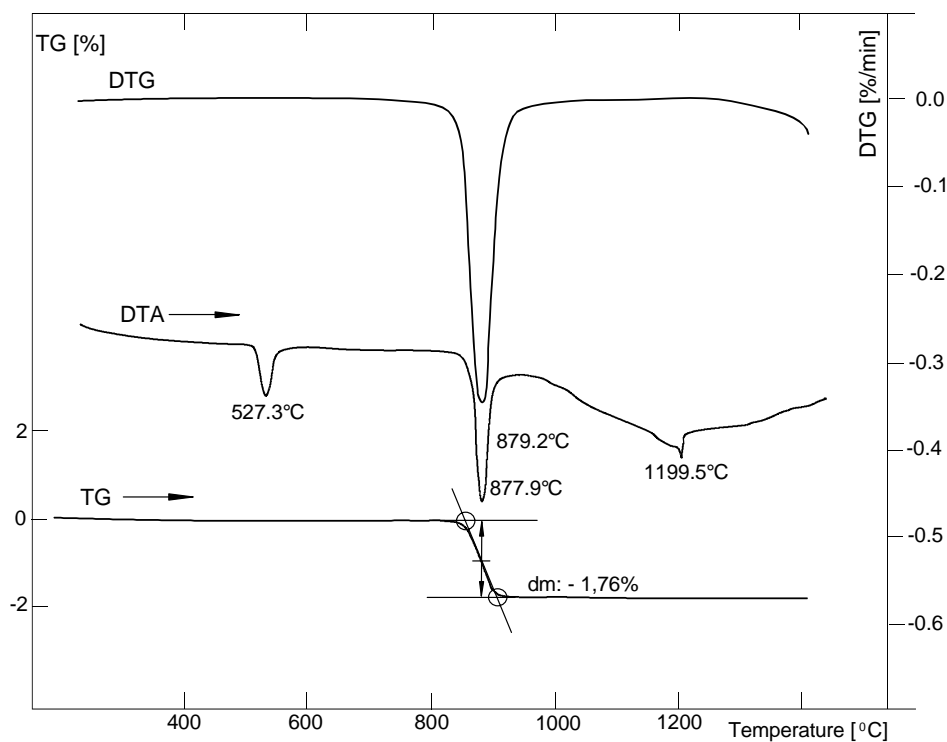


Fig. 2. DTA, TG and DTG curves of $K_4Ce_2P_4O_{15}$, $m = 92.57$ mg, air atmosphere.

The above results permit to state that $K_4Ce_2P_4O_{15}$ phosphate exists only in the solid state. At the temperature $879^\circ C$ its decomposition begins. The thermal effects visible on the DTA curves of heating of $K_4Ce_2P_4O_{15}$ phosphate are interpreted as follows:

- the effect at $527^\circ C$ is connected with the polymorphic transition $\alpha/\beta-K_4Ce_2P_4O_{15}$;
- the effect at $879^\circ C$ is ascribed to the reaction of decomposition of $K_4Ce_2P_4O_{15}$ to $CePO_4$, $K_4P_2O_7$ and $K_3Ce(PO_4)_2$;

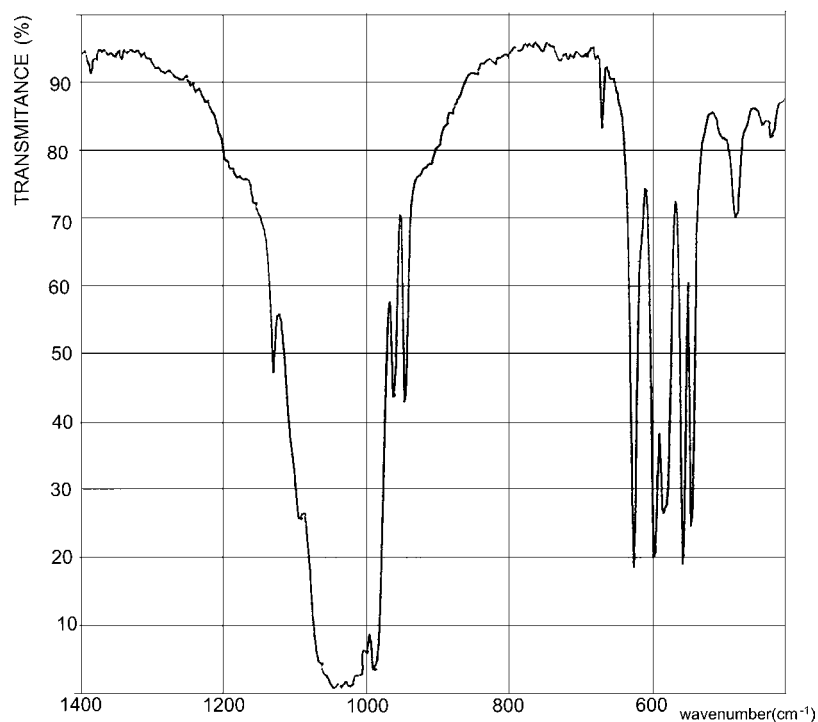
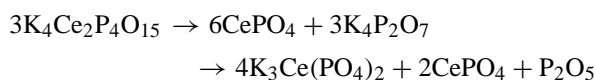


Fig. 3. IR spectrum of $\beta-K_4Ce_2P_4O_{15}$.

- the effect at 1198 °C is connected with the polymorphic transition $\alpha/\beta\text{-K}_3\text{Ce}(\text{PO}_4)_2$.

It seemed to be reasonable to make an attempt to collect some knowledge on the kinetics of $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ decomposition. Consequently, a presynthesized sample with such a composition was annealed at a temperature of 880 °C for half an hour, which was followed by freezing. Diffraction spectrum of this sinter revealed the presence of reflections typical of CePO_4 and $\text{K}_4\text{P}_2\text{O}_7$. Then the sample was additionally annealed at 910 °C for half an hour, again followed by freezing. Diffraction spectrum of this sinter showed the presence of reflections typical of CePO_4 and $\text{K}_3\text{Ce}(\text{PO}_4)_2$. In order to determine the origin of gradual weight loss, thermal analysis combined with mass spectrometry of gas phase was employed. A sample of the $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ phosphate, heated at 880 °C for 5 h, resulted in mass loss of 2.0%. The accompanying analysis of the gas phase was given evidence of P_2O_5 . Based on this result the decomposition mechanism of the phosphate could be proposed as follows:



In favour of this network we can refer to the fact that a small, mentioned above, mass decrement (1.76%), connected with the release of P_2O_5 , was noted in the TG curve. N.B.: we undertook an attempt to determine the magnitude of mass decrement due to an isothermal heating at 910 °C of the sample with the composition $\text{K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$. It was found that the decrement was constant of about 4.8% upon two hundred hours of heating ($m_{\text{theoretical}} = 5.91\%$ of P_2O_5) and the obtained sinter was a mixture of CePO_4 and $\text{K}_3\text{Ce}(\text{PO}_4)_2$.

DSC measurements have revealed one high-temperature endothermic irreversible phase transition at 527 °C, whose enthalpy amounts to 57.685 J g^{-1} (46.2 kJ mol^{-1}), suggesting a first-order mechanism.

The high-temperature polymorphic modification $\alpha\text{-K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ is not susceptible to room temperature stabilization by means of fast freezing or cooling in ice. In order to determine crystallographic structure of the low-temperature modification $\beta\text{-K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$, measurements were made by powder X-ray diffraction on a Siemens D-5000 diffractometer, employing the stepwise method with the radiation Co/Fe. Computation was made by using the program Win-Index version 3.03 Siemens Analytical X-Ray System (indexing method: ITO). The XRD data, indexed as a triclinic material (lattice type *P*), are listed in Table 1. The lattice parameters were optimized by LSQ refinement, resulting in refined values of $a = 9.319(7)$, $b = 12.129(3)$, $c = 9.252(1) \text{ \AA}$, $\alpha = 106.87(5)$; $\beta = 100.08(6)$; $\gamma = 107.20(2)$ and $V = 916.276 \text{ \AA}^3$.

The IR spectrum of $\beta\text{-K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$ within the range $1400\text{--}400 \text{ cm}^{-1}$, is given in Fig. 3.

Table 1
X-ray analysis data for modification $\beta\text{-K}_4\text{Ce}_2\text{P}_4\text{O}_{15}$

Number	<i>hkl</i>	Intensities	d_{obs} (Å)	d_{calc} (Å)
1	$\bar{1}\bar{1}1$	40.2	5.93417	5.93723
2	011	57.1	5.73819	5.73375
3	020	10.7	539396	5.39648
4	$0\bar{1}2$	20.0	4.55362	4.55223
5	$\bar{1}\bar{1}2$	14.3	4.29131	4.29518
6	002	13.4	4.24114	4.24268
7	111	10.3	4.07959	4.08149
8	120	10.0	3.95453	3.95127
9	210	9.3	3.54690	3.54643
10	102	10.2	3.42823	3.42867
11	$\bar{2}12$	9.5	3.38239	3.38163
12	$\bar{1}31$	17.9	3.21183	3.21309
13	$\bar{2}\bar{2}1$	100.0	3.10851	3.10887
14	$\bar{1}\bar{1}3$	29.0	3.04283	3.04542
15	$2\bar{2}2$	9.5	2.97866	2.97932
16	$\bar{1}\bar{2}3$	27.4	2.91506	2.91442
17	040	27.5	2.69908	2.69827
18	$\bar{2}\bar{2}3$	10.1	2.57115	2.57121
19	$\bar{1}42$	9.6	2.50425	2.50563
20	$\bar{1}42$	11.1	2.46117	2.46101
21	$\bar{2}\bar{3}3$	12.9	2.31716	2.31663
22	$0\bar{3}4$	10.9	2.21411	2.21315
23	$3\bar{5}1$	13.9	2.15052	2.15052
24	141	16.5	2.05586	2.05590
25	$\bar{3}\bar{3}3$	11.7	1.97889	1.97906
26	$2\bar{6}2$	10.1	1.96218	1.96154
27	$3\bar{4}3$	11.2	1.94006	1.93974
28	$4\bar{2}2$	13.3	1.90072	1.89975
29	205	13.9	1.75948	1.75870
30	331	12.8	1.73066	1.72991
31	223	9.2	1.71140	1.71191
32	$\bar{1}55$	10.9	1.62720	1.62757
33	$\bar{1}55$	10.1	1.55519	1.55553
34	403	9.2	1.50816	1.50856
35	572	9.1	1.32177	1.32185

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