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The system $CePO_4$–KPO_3–$Ce(PO_3)_3$

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Abstract

In the ternary system Ce_2O_3–K_2O–P_2O_5 the partial system $CePO_4$–KPO_3–$Ce(PO_3)_3$ has been examined by differential thermal analysis, powder X-ray diffraction and infrared spectroscopy. Its phase diagram has been determined.

Keywords: Phase equilibria; Quasi-binary systems; Potassium–cerium phosphates

1. Introduction

Literature reports have shown that metaphosphate glasses will be a promising host material for optical components. Rare earth element doped tetra- and metaphosphate glasses have been widely applied mainly to miniature solid lasers and optical amplifiers. Investigations of Ln–M^I, Ln–M^{II} phosphates (M—alkali metal, M^{II}—alkaline earth metal, Ln—rare-earth metal) usually have concerned their chemical and physical properties, method of synthesis and possibilities of application [1–3]. Experimental results of phase equilibria of alkali metal/rare-earth element phosphates are less numerous [4–8].

In this paper, continuing previous studies of phase equilibria in the ternary system Ce_2O_3–K_2O–P_2O_5, the results of phase investigation of the system $CePO_4$–KPO_3–$Ce(PO_3)_3$ are presented. The phase diagram of the system of interest has not been reported earlier. This system is surrounded by the known binary side systems: $CePO_4$–$Ce(PO_3)_3$ [5], $CePO_4$–KPO_3 [8] and $Ce(PO_3)_3$–KPO_3 [6,7]. We have investigated the former two which are simple eutectic systems [5,8]. The reports [6,7] concerning the system $Ce(PO_3)_3$–KPO_3 show an essential discrepancy. According to Rzaigui et al. [6] two intermediate compounds occur, $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$ which incongruently melt at 880 and 741 °C, respectively. $KCe(PO_3)_4$ is isotypic with $KNd(PO_3)_4$ and it crystallizes in the monoclinic system ($P2_1$). For the $K_2Ce(PO_3)_5$ isotypic compounds were not found in the binary phosphates of alkali and rare-earth metals. According to Mardirosova et al. [7] only one intermediate compound, $KCe(PO_3)_4$, appears in this system. In view of this discrepancy we have re-examined the $Ce(PO_3)_3$–KPO_3 system and its phase diagram have verified.

2. Experimental

The samples for phase equilibria investigations in the ternary system were prepared from commercial regents (KH_2PO_4, K_2CO_3, $Ce(NO_3)_3{\cdot}6H_2O$, H_3PO_4, $NH_4H_2PO_4$, CeO_2, p.a. each) or from self-synthesized

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compounds: $CePO_4$, $Ce(PO_3)_3$, CeP_5O_{14} were obtained by the methods reported in [9]. Potassium metaphosphate, KPO_3, was obtained from KH_2PO_4 by dehydration at 350 °C for 2 h. $KCe(PO_3)_4$ was obtained from KPO_3 and $Ce(PO_3)_3$ by sintering a stoichiometric mixture of these compounds at 800 °C for 48 h. $K_2Ce(PO_3)_5$ was prepared from the mixture K_2CO_3 and CeP_5O_{14} in the molar ratio 1:1 by heating, at 400 °C for 12 h and at 720 °C for 48 h. The system $CePO_4$–KPO_3–$Ce(PO_3)_3$ was examined by differential thermal analysis (DTA on heating), powder X-ray diffraction, infrared (IR) spectroscopy and optical microscopy. The initial experiments have shown that the specimens of the system under investigation crystallize with difficulty and form glasses readily. Visual evaluation of the fusion temperature was employed in the case of samples whose melting point could not be determined from the DTA (because of the lack of thermal effects on the high temperature DTA curves). Examined samples for the visual evaluation were prepared as follows. The parent phosphates were weighed out in fixed amounts, mixed carefully and ground in an agate mortar, then pressed into pellets and presynthesized by the reaction in the solid phase at different temperatures (according to the composition of the sample). The visual observation consisted in taking notes of the temperature at which the specimen liquefied and the temperature at which it became transparent. Hence, the temperatures are treated as approximate. The DTA of heating was carried out by means of a derivatograph type 3427 (MOM, Hungary) within the temperature range 20–1300 °C with a heating rate of 10 °C min^{-1}, in platinum crucibles in an atmosphere of air. High purity Al_2O_3 was used as the standard substance. Temperatures were read with a Pt/Pt10Rh thermocouple, which was calibrated

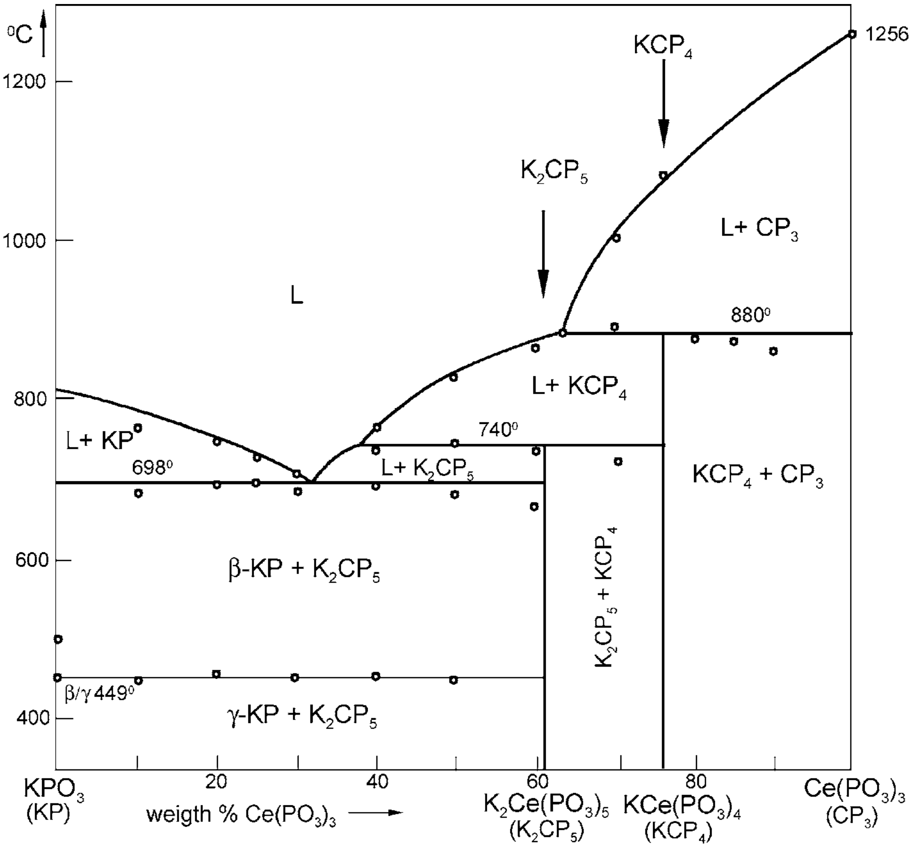

Fig. 1. Phase diagram of the system KPO_3–$Ce(PO_3)_3$.

by using the melting points of $Ca_2P_2O_7$, K_2SO_4 and NaCl.

A horizontal, resistance furnace with a molybdenum winding on a corundum tube was used for high temperature thermal investigation. Temperatures were read by means of an optical pyrometer which was calibrated against the melting points of $Ca_2P_2O_7$, Na_3PO_4 and $Ca_3(PO_4)_2$. The phase purity of reagents and obtained products was investigated by powder X-ray analysis on an HZG-4 diffractometer (Cu Kα radiation, Ni filter). 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

Investigation of the $CePO_4$–KPO_3–$Ce(PO_3)_3$ ternary system, in view of the mentioned discrepancy between the data [6,7], was started with examination of the quasi-binary system KPO_3–$Ce(PO_3)_3$. The system has been elaborated in the whole range of composition and temperature by DTA (on heating) and X-ray diffraction. Its phase diagram is presented in Fig. 1. Samples for the investigation were prepared from parent phosphates. Thermal examination was preceded by presynthesis which consisted in heating the samples at a temperature of 600 °C for 18 h. The DTA and X-ray investigations proved the existence of two binary metaphosphates. These are formed in a molar ratio of 1:1 and 2:1 of KPO_3 to $Ce(PO_3)_3$. Their corresponding formulae are $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$, respectively. Both phosphates melt peritectically at 880 and 740 °C, respectively. This result is in accordance with the data of [6]. The IRS of $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$ of the present work also is in agreement with that of the paper by Rzaigui et al. Moreover, the conditions under which synthesis of both mixed metaphosphates occurs have been investigated. It is found that the compounds are hardly produced (especially the $K_2Ce(PO_3)_5$) and a complicated thermal processing is necessary.

Both mixed metaphosphates, in the composition range under consideration give the two sections, unknown ever before: (1) $KCe(PO_3)_4$–$CePO_4$ and (2) $K_2Ce(PO_3)_5$–$CePO_4$.

The determined phase diagram of the quasi-binary system $CePO_4$–$KCe(PO_3)_4$ is presented in Fig. 2.

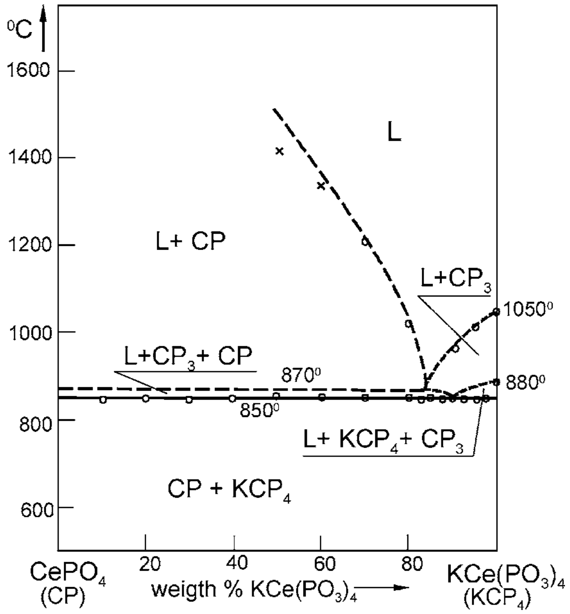

Fig. 2. Phase diagram of the system $CePO_4$–$KCe(PO_3)_4$. $Ce(PO_3)_3 = CP_3$.

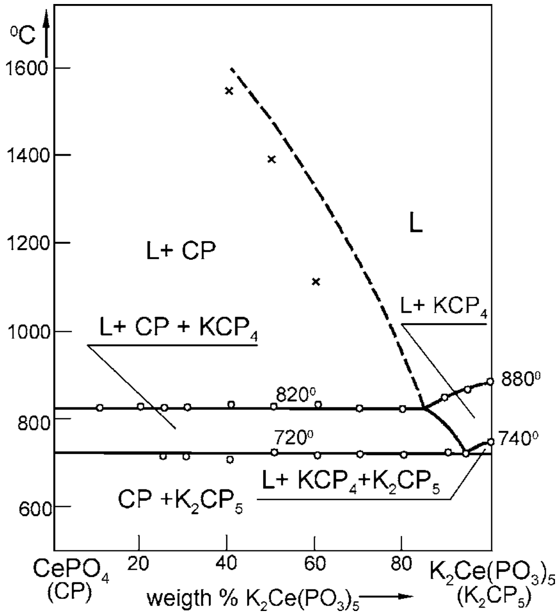

Fig. 3. Phase diagram of the system $CePO_4$–$K_2Ce(PO_3)_5$. $KCe(PO_3)_4 = KCP_4$.

Samples for this investigation were synthesized from the parent phosphates by means of sintering at a temperature of 750 °C for 10 h. DTA curves in the whole range of composition reveal a strong thermal effect in the temperature range 850–870 °C. On the other hand, the effects which originate from melting are very weak and sometimes imperceptible. Therefore the liquidus curve in the composition range 60–100 wt.% $KCe(PO_3)_4$ is drawn based on visual observation of the samples. The section $CePO_4$–$KCe(PO_3)_4$ above 850 °C has a multiphase character with its four phases: liquid L, and $CePO_4$, $Ce(PO_3)_3$, $KCe(PO_3)_4$. This is a result of a peritectic reaction in which the liquid L and cerium metaphosphate $Ce(PO_3)_3$ are used up for the formation of $KCe(PO_3)_4$ crystals. According to the Gibbs' phase rule this reaction proceeds at a constant temperature of 850 °C. Below the temperature only two phases, $CePO_4$ and $KCe(PO_3)_4$, exist and the system has a binary character only in the subsolidus region.

The phase diagram of the system $CePO_4$–$K_2Ce(PO_3)_5$ is shown in Fig. 3. The samples were presynthesized by sintering the parent phosphates at 600 °C for 10 h. In the whole composition range under discussion two strong thermal effects occur on the DTA curves at temperatures about 720 and 820 °C. Any effect connected with melting is not present and the liquidus curve has been determined based on the visual observations. At higher temperatures the system has a multiphase character. Above 720 °C four phases occur: liquid L, and the compounds $CePO_4$, $KCe(PO_3)_4$ and $K_2Ce(PO_3)_5$. Via peritectic reaction the liquid L and phosphate $KCe(PO_3)_4$ are used up to form crystals of $K_2Ce(PO_3)_5$. Below 720 °C only two phases, $CePO_4$ and $K_2Ce(PO_3)_5$, occur, hence the system has a binary character in the subsolidus region only.

Fig. 4 shows the phase diagram of the system $CePO_4$–KPO_3–$Ce(PO_3)_3$ with solidification isotherms. There are five fields of primary crystallization in the composition range of interest. These are

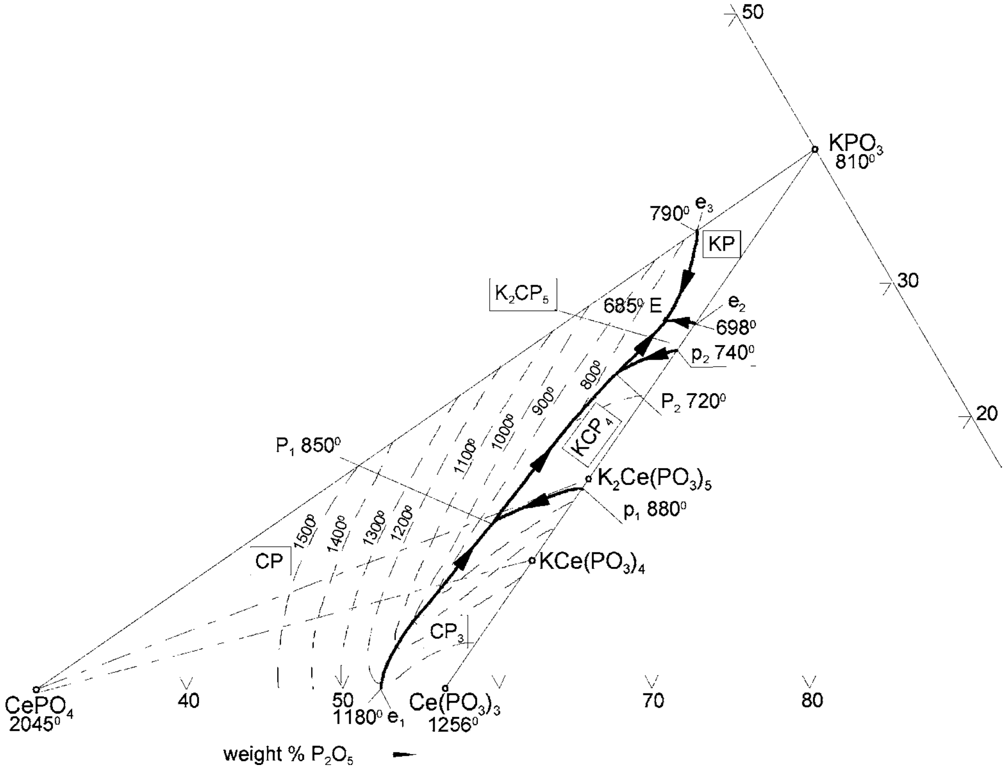

Fig. 4. Phase diagram of the system $CePO_4$–KPO_3–$Ce(PO_3)_3$ including solidification isotherms. $CePO_4$ = CP; $Ce(PO_3)_3$ = CP_3; KPO_3 = KP; $KCe(PO_3)_4$ = KCP_4; $K_2Ce(PO_3)_5$ = K_2CP_5.

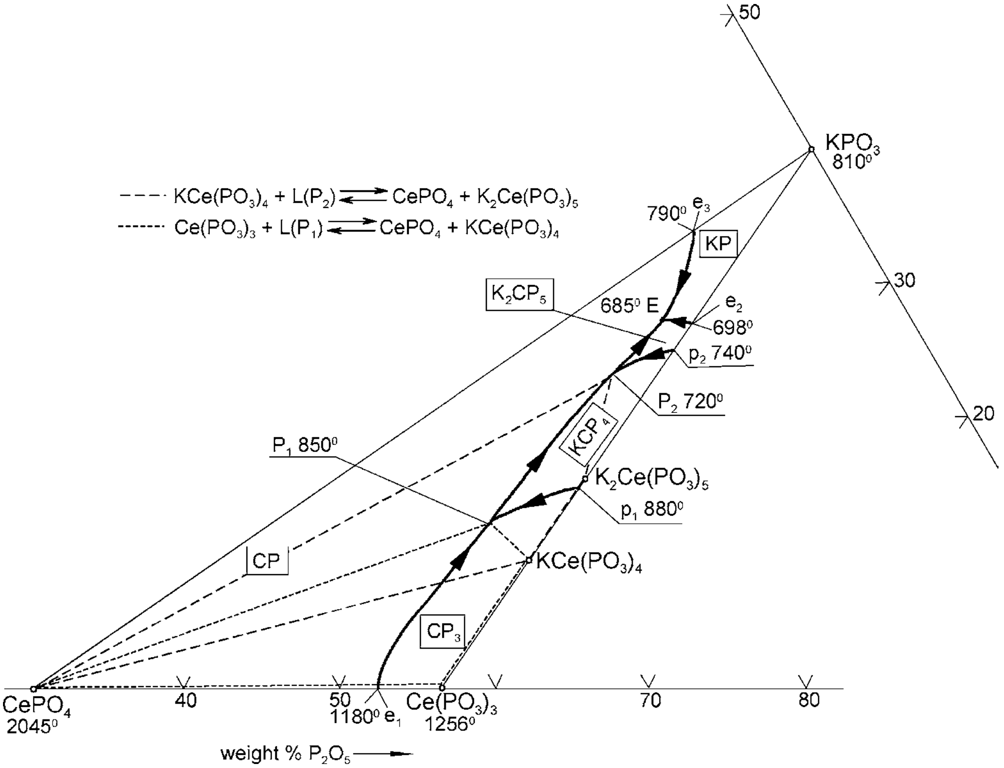

Fig. 5. Phase diagram of the system $CePO_4$–KPO_3–$Ce(PO_3)_3$ with triple peritectic quadrangle. $CePO_4$ = CP; $Ce(PO_3)_3$ = CP_3; KPO_3 = KP; $KCe(PO_3)_4$ = KCP_4; $K_2Ce(PO_3)_5$ = K_2CP_5.

bounded each other by the curves of binary eutectic: e_3E (KPO_3+CePO_4), e_2E ($KPO_3+K_2Ce(PO_3)_5$), P_2E ($CePO_4 + K_2Ce(PO_3)_5$), e_1P_1 ($Ce(PO_3)_3 + CePO_4$), P_1P_2 ($KCe(PO_3)_4+CePO_4$), with the compounds that crystallize along them and the ones of binary peritectic for which curve p_1P_1 corresponds to the reaction: $Ce(PO_3)_3 + L(p_1P_1) \rightarrow KCe(PO_3)_4$; curve p_2P_2 to the reaction: $KCe(PO_3)_4 + L(p_2P_2) \rightarrow K_2Ce(PO_3)_5$.

The phase diagram of the $CePO_4$–KPO_3–$Ce(PO_3)_3$ system is presented in Fig. 5, where the ternary peritectics are marked by quadrangles. During solidification of the alloys that are located in the area $CePO_4$–P_1–$KCe(PO_3)_4$–$Ce(PO_3)_3$ (ternary peritectic quadrangle) a ternary peritectic reaction proceeds according to the equation: $Ce(PO_3)_3 + L(P_1) \rightarrow CePO_4 + KCe(PO_3)_4$, where $L(P_1)$ denotes a liquid with its composition corresponding to the point P_1. The reaction proceeds at a constant temperature of 850 °C.

Likewise, during solidification of the alloys occurred in the quadrangle of the ternary peritectic $CePO_4$–P_2–$K_2Ce(PO_3)_5$–$KCe(PO_3)_4$ another ternary peritectic reaction proceeds, viz. $KCe(PO_3)_4 + L(P_2) \rightarrow CePO_4+K_2Ce(PO_3)_5$ (where $L(P_2)$ denotes liquid of the composition corresponding to the point P_2). The above reaction, according to the Gibbs phase rule, takes place at a constant temperature of 720 °C.

The crystallization of the alloys in the system in question: $CePO_4$–KPO_3–$Ce(PO_3)_3$ ends in the point E, where the ternary eutectic of $KPO_3+K_2Ce(PO_3)_5+CePO_4$ occurs which melts at a constant temperature of about 685 °C.

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