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PHASE EQUILIBRIA IN THE PARTIAL SYSTEM $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$

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Abstract

The ternary system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$ was investigated by differential thermal analysis, powder X-ray diffraction and microscopy in reflected light. Two double phosphates, $NaCeP_2O_7$ and $NaCe(PO_3)_4$, occur in this system. Both $NaCeP_2O_7$ and $NaCe(PO_3)_4$ melt incongruently, at 800 and 865°C, respectively. Two systems, $NaCeP_2O_7$–$NaCe(PO_3)_4$ and $CePO_4$–$NaCe(PO_3)_4$, were found to occur in this region. Their phase diagrams are presented.

Keywords: phase diagram, system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$

Introduction

The present study is the last part of our phase investigations on sodium cerium(III) phosphates. These investigations result from the great interest in lanthanide compounds as materials with luminophore and laser properties. It therefore seemed interesting to identify and determine physicochemical properties of all sodium-cerium(III) phosphates in the molten salts, to determine the conditions of their syntheses and to determine the phase diagram of the ternary system Ce_2O_3–Na_2O–P_2O_5. A literature review demonstrates that the crystallochemical structure, physicochemical properties and conditions of synthesis of the cerium(III) phosphates $CePO_4$, $Ce(PO_3)_3$ and CeP_5O_{14} are known [1–3]. However, information on mixed sodium cerium(III) phosphates is sparse and often incoherent. Reference has been made to the following compounds: $Na_3Ce(PO_4)_2$, $Na_3Ce_2(PO_4)_3$, $NaCeP_2O_7$ and $NaCe(PO_3)_4$ [4–6].

Up till now, the phase equilibria in that part of the system Ce_2O_3–Na_2O–P_2O_5 which is rich in P_2O_5 [7], and in that which is rich in Ce_2O_3 [8–10], have been investigated in our laboratory. This paper reports our studies on the phase equilibria in the partial ternary system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$. Its phase diagram has not been described so far. It is surrounded by three side-systems:

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$CePO_4$–$NaPO_3$, $NaPO_3$–$Ce(PO_3)_3$ and $CePO_4$–$Ce(PO_3)_3$. The former system was examined in our laboratory [11]. The investigations showed that the starting phosphates form the compound with formula $NaCeP_2O_7$ by reacting at 1:1 molar ratio. The compound melts peritectically at 800°C and occurs in two polymorphic modifications. The temperature of transition is 595°C. The high-temperature modification, α-$NaCeP_2O_7$, cannot be stabilized at room temperature by quenching in air or ice. The low-temperature modification, β-$NaCeP_2O_7$, crystallizes in the orthorhombic system (a=5.28, b=12.65, c=4.31 Å, α=β=γ=90°, V=288.1 Å^3). In the second system, which was determined by Rzaigui *et al.* [12], the compound $NaCe(PO_3)_4$ occurs. It melts peritectically at 865°C and crystallizes in the monoclinic system (space group C_2/c). The phase diagram of the system $CePO_4$–$Ce(PO_3)_3$ is not known.

Experimental

Cerium(III) phosphates and double sodium cerium(III) phosphates were prepared from the following ready-made compounds: $NaH_2PO_4 \cdot H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $NH_4H_2PO_4$ and H_3PO_4 85%, all anal. grade, and CeO_2 of 99.9% purity.

$CePO_4$, $Ce(PO_3)_3$, $NaPO_3$, $NaCeP_2O_7$ and $NaCe(PO_3)_4$ were obtained in our laboratory by the methods reported in [7, 10].

The experiments on the discussed system were performed by differential thermal analysis (DTA), X-ray powder diffraction and microscopic analysis in reflected light. Samples for thermal analysis were presynthesized by reaction in the solid phase. In thermal analysis (DTA) during heating, a type 3427 derivatograph (MOM, Hungary) was used. Thermal analysis on cooling was performed by means of a resistance furnace with a Pt30Rh winding, constructed in our laboratory. Temperatures were measured by a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of NaCl and K_2SO_4 and the polymorphic transition point of K_2SO_4 (583°C). The phases were identified by powder X-ray diffraction. A HZG-4 diffractometer (a Guinier camera) with CuK_α radiation was used. The purity of the reagents and the phase structures of the products were controlled microscopically.

Results and discussion

The partial ternary system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$ was examined by DTA, X-ray powder diffraction and microscopy. Thermal analysis during heating up to approx. 1400°C was mainly used. Many literature data report that $CePO_4$ and $Ce(PO_3)_3$ are unstable at higher temperatures. Their decompositions are accompanied by the evaporation of P_2O_5 and by changes in the compositions of the initial samples. The thermal instability of both these phosphates was also observed in our laboratory. Another reason for not using thermal analysis on cooling was the tendency to glass-formation during the crystallization of alloys richer in $NaPO_3$.

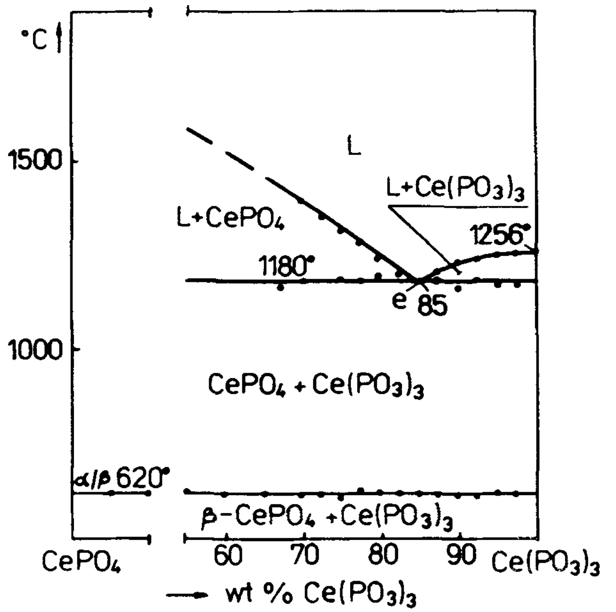

Fig. 1 Phase diagram of the system $CePO_4$–$Ce(PO_3)_3$

The examinations of the phase equilibria in the partial ternary system under investigation were started by determining the phase diagram of the side-system $CePO_4$–$Ce(PO_3)_3$. Samples for investigations were prepared from the initial phosphates and were synthesized by sintering at 900°C for 20 h. The results proved that $CePO_4$ and $Ce(PO_3)_3$ form a eutectic at 1180°C. Its composition is 85 wt% of $Ce(PO_3)_3$, 15 wt% of $CePO_4$. Figure 1 presents the phase diagram of the system $CePO_4$–$Ce(PO_3)_3$ within the composition range 60–100 wt% of $Ce(PO_3)_3$ and within the temperature interval up to 1400°C. $CePO_4$ occurs in two polymorphic modifications. The temperature of the transition $\alpha \to \beta$ is 620°C [11]. This transition can be observed in the form of not very strong thermal effects in the DTA heating curves over the whole binary system under investigation.

Two double phosphates, $NaCeP_2O_7$ and $NaCe(PO_3)_4$, occur in the partial ternary system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$. According to their composition, these phosphates occur in the side-system $CePO_4$–$NaPO_3$ and $NaPO_3$–$Ce(PO_3)_3$ respectively. Our studies proved that $NaCe(PO_3)_4$ forms two previously unknown sections: $NaCeP_2O_7$–$NaCe(PO_3)_4$ and $CePO_4$–$NaCe(PO_3)_4$.

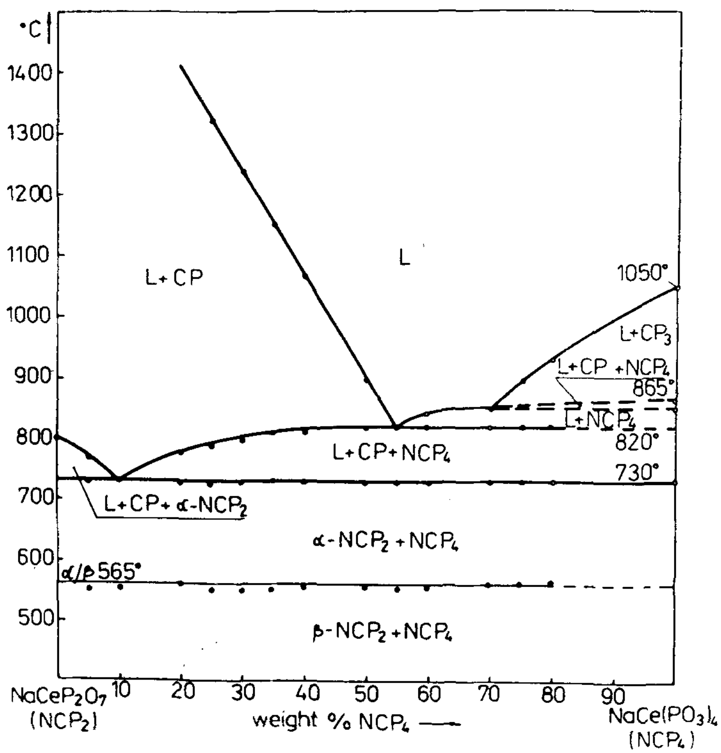

Fig. 2 Phase diagram of the system $NaCeP_2O_7$–$NaCe(PO_3)_4$

Figure 2 shows the phase diagram of the section $NaCeP_2O_7$–$NaCe(PO_3)_4$ which was determined in our laboratory. Samples were prepared from the initial phosphates and presynthesized by sintering within the temperature interval 650–700°C for 24 h. This section is a polyphase which results from the peritectic reaction occurring here. Above 730°C, five phases occur: liquid *L* and $NaCeP_2O_7$, $NaCe(PO_3)_4$, $CePO_4$ and $Ce(PO_3)_3$. As a result of the peritectic reaction, liquid *L* and $CaPO_4$ and $Ce(PO_3)_3$ are used up to form $NaCeP_2O_7$ and $NaCe(PO_3)_4$ crystals. The system is binary below 730°C. The liquidus curve was drawn within the composition range 20–100 wt% of $NaCe(PO_3)_4$.

Figure 3 shows the phase diagram of the system $CePO_4$–$NaCe(PO_3)_4$. Samples were prepared from the initial phosphates and presynthesized by sintering at 700–750°C for 48 h. This section is a polyphase at higher temperatures. Above 830°C, there are four phases: liquid *L* and $NaCe(PO_3)_4$, $CePO_4$ and $Ce(PO_3)_3$. It results from the peritectic reaction occurring here. As a result of this reaction, liquid *L* and $Ce(PO_3)_3$ are used up to form $NaCe(PO_3)_4$ crystals. According to the Gibbs phase equation, this reaction proceeds at the constant temperature of 830°C. Below 830°C, there are only two phases, $CePO_4$ and $NaCe(PO_3)_4$, and the system is binary. The transition α/β-$CePO_4$ can be observed at 620°C over the whole system $CePO_4$ – $NaCe(PO_3)_4$, in the form of not very strong thermal effects in the DTA heating curves.

As a result of the examinations performed and the results obtained, the previously unknown diagram of the ternary system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$ with solidification isotherms has been suggested (Fig. 4).

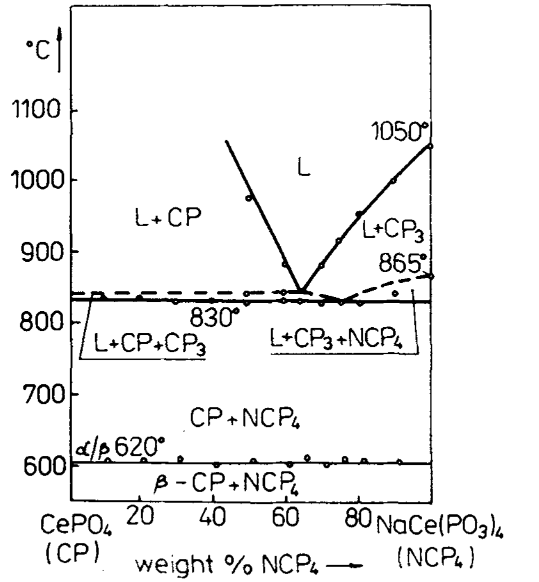

Fig. 3 Phase diagram of the system $CePO_4$–$NaCe(PO_3)_4$

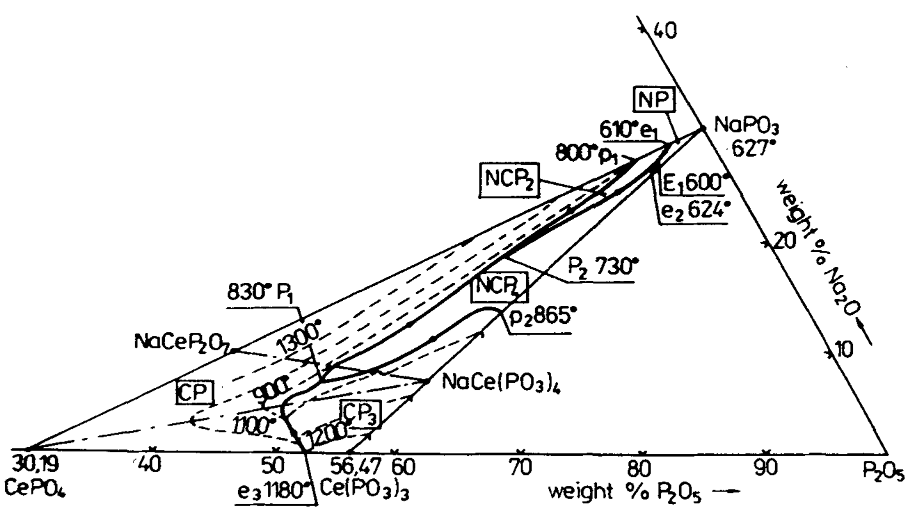

Fig. 4 Phase diagram of the system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$, CP=$CePO_4$, CP_3=$Ce(PO_3)_3$, NCP_2=$NaCeP_2O_7$, NCP_4=$NaCe(PO_3)_4$, NP=$NaPO_3$

In the side-system $CePO_4$–$NaPO_3$, a binary peritectic reaction occurs at 800°C. As a result of this reaction, the compound $NaCeP_2O_7$ is formed. In the side-system $NaPO_3$–$Ce(PO_3)_3$, binary peritectic reaction occurs at 865°C and the compound $NaCe(PO_3)_4$ is formed. This is reflected in the partial ternary system under investigation in the form of two ternary peritectics. Ternary peritectic reactions proceed according to the following scheme:

$$1)\ L_{P_1} + Ce(PO_3)_3 \rightarrow CePO_4 + NaCe(PO_3)_4 \quad \text{at } 830°C$$

$$2)\ L_{P_2} + CePO_4 \rightarrow NaCeP_2O_7 + NaCe(PO_3)_4 \quad \text{at } 730°C$$

(L_{P_1} = liquid with composition corresponding to point P_1,
L_{P_2} = liquid with composition corresponding to point P_2.)

In the system $CePO_4$–$NaPO_3$–$Ce(PO_3)_3$, ternary eutectic E_1 occurs at the constant temperature of approx. 600°C. In the composition range under consideration, there are five primary crystallization fields of binary and ternary compounds. These fields are separated by peritectic and eutectic curves.

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Zusammenfassung — Mittels DTA, Pulverröntgendiffraktion und Auflichtmikroskopie wurde das ternäre System $CePO_4$-$NaPO_3$-$Ce(PO_3)_3$ untersucht. In diesem System existieren zwei Doppelphosphate: $NaCeP_2O_7$ und $NaCe(PO_3)_4$. Sowohl $NaCeP_2O_7$ als auch $NaCe(PO_3)_4$ schmelzen inkongruent bei 800 beziehungsweise 865C. In dieser Region fand man die Existenz der zwei Systeme $NaCeP_2O_7$–$NaCe(PO_3)_4$ und $CePO_4$–$NaCe(PO_3)_4$. Die diesbezüglichen Phasendiagramme werden angegeben.