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Phase equilibria in the system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$

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Abstract

The ternary system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$ has been investigated by differential thermal analysis, powder X-ray diffraction and microscopy in reflected light and its phase diagram has been determined. The system contains only one double phosphate which is formed at 1:1 molar ratio of $CePO_4$:Na_3PO_4, i.e. $Na_3Ce(PO_4)_2$.

INTRODUCTION

Investigations of sodium–cerium(III) phosphates have been carried out in our laboratory for several years [1–4].

The present work is the second part of our investigations on double cerium–sodium orthophosphates. Previously, the system $CePO_4$–Na_3PO_4 was studied and its phase diagram determined [4]. It was found that the system contains only one intermediate compound, $Na_3Ce(PO_4)_2$, which melts incongruently at 1550 °C. This orthophosphate is stable down to room temperature and exibits a polymorphic transition at 1060 °C. The low-temperature modification has an orthorhombic (lattice type P) unit cell with parameters: $a = 14.074(1)$, $b = 16.039(1)$, $c = 18.607(1)$ Å and $V = 4200.21$ Å^3. Continuing our previous work on double sodium–cerium phosphates, we present here the current results of our study on the ternary system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$. The phase diagram of this system has not been published before now. It is limited by three side systems: $CePO_4$–Na_3PO_4, Na_3PO_4–$Na_4P_2O_7$ and $CePO_4$–$Na_4P_2O_7$. The first and second systems are known. The last has not been investigated before.

EXPERIMENTAL

Samples for investigations of the $CePO_4$–Na_3PO_4–$Na_4P_2O_7$ system were prepared from the following original analytical-reagent-grade materials: $Ce(NO_3)_3 \cdot 6H_2O$, $NH_4H_2PO_4$, $Na_3PO_4 \cdot 12H_2O$ and Na_2HPO_4.

$CePO_4$, Na_3PO_4, $Na_4P_2O_7$ and $Na_3Ce(PO_4)_2$ were synthesized in our laboratory. Cerium(III) orthophosphate was prepared by the method given in ref. 3. Sodium orthophosphate Na_3PO_4 was obtained by slow dehydration of $Na_3PO_4 \cdot 12H_2O$ at 200 °C, 300 °C and further at 600 °C. Sodium pyrophosphate was synthesized from Na_2HPO_4 by heating at 200 °C and 500 °C over 5 h. The double orthophosphate was prepared by sintering at 1:1 stoichiometric ratio of $CePO_4$ and Na_3PO_4 at 1100 °C for 24 h.

The ternary system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$ was examined by differential thermal analysis (cooling and heating), powder X-ray diffraction, microscopy in reflected light and IR absorption. The differential thermal analysis of heating was performed by means of a derivatograph (type 3427, MOM, Hungary), heating rate 10 °C min^{-1}, platinum cup and air atmosphere. The standard substance used was high-purity Al_2O_3. The differential thermal analysis of cooling was performed in a furnace constructed in our laboratory (with Pt30Rh winding), under air. Temperatures were measured by means of a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of $Ca_2P_2O_7$, K_2SO_4, NaCl and the polymorphic transition point of K_2SO_4 (583 °C). High-temperature thermal studies above 1400 °C were carried out in a horizontal resistance furnace with molybdenum winding, under argon. The examined samples were pressed into pellets, placed in boats made from noble metal alloys, and fused. Temperatures were read by means of an optical pyrometer which was calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$.

A quenching technique was also used for phase determination.

The phases were identified by X-ray powder diffraction with an HZG-4 diffractometer and Cu Kα radiation.

The phase structure of the products was also monitored microscopically in reflected light.

A Specord IR-75 spectrophotometer was used for the IR absorption specroscopy, using pellets formed by mixing the specimens with KBr.

RESULTS AND DISCUSSION

Examinations of phase equilibria in the ternary system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$ began by determining the phase diagram of the system $CePO_4$–$Na_4P_2O_7$. It was discovered that samples from this binary system, which are rich in sodium pyrophosphate $Na_4P_2O_7$, readily form glasses. However, using slow cooling (approx. 2 °C min^{-1}) and frequent grafting, highly crystallized samples can be obtained. Because of its susceptibility to glass formation, there are usually no thermal effects connected with crystallization on the DTA curves. They are more distinct on the DTA curves of heating.

According to literature reports, sodium pyrophosphate $Na_4P_2O_7$ occurs in several polymorphic modifications. Our examinations show that during

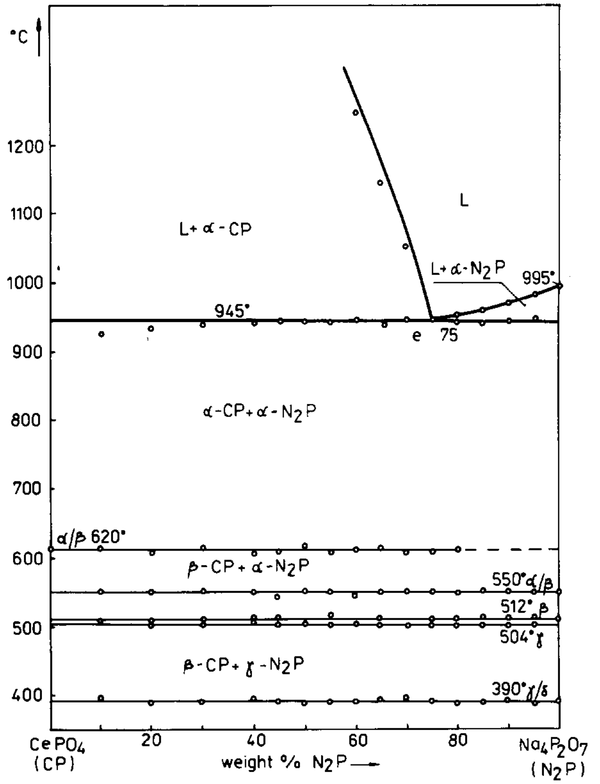

Fig. 1. Phase diagram of the system $CePO_4$–$Na_4P_2O_7$.

thermal analysis of an $Na_4P_2O_7$ sample (heating and cooling) quite large thermal effects appear on the DTA curves at 550 and 390 °C, with two more overlapping effects at 512 and 504 °C. These effects result from the following polymorphic transitions of sodium pyrophosphate: $\alpha \rightarrow \beta$, 550 °C, $\beta \rightarrow \gamma$, 512–504 °C (the $\beta \rightarrow \gamma$ transition occurs over a small temperature range) and $\gamma \rightarrow \delta$, 390 °C. These transitions occur over the whole $CePO_4$–$Na_4P_2O_7$ system and are accompanied by strong thermal effects on the DTA curves.

Cerium orthophosphate $CePO_4$ occurs in two polymorphic modifications and the temperature of the $\alpha \rightarrow \beta$ transition is 620 °C [3]. The thermal effect resulting from this transition is shown by samples with compositions within the range 20–100 wt.% $CePO_4$ (80–0 wt.% $Na_4P_2O_7$).

Figure 1 presents the phase diagram of the system $CePO_4$–$Na_4P_2O_7$ determined by thermal analysis of heating, X-ray diffractometry and microscopy. The liquidus curve was estimated only within the composition range 60–100 wt.% $Na_4P_2O_7$. Samples richer in $CePO_4$ melt at very high temperatures, much above 1400 °C. As can be seen from Fig. 1, $CePO_4$ and $Na_4P_2O_7$ form a simple eutectic system. The temperature of the

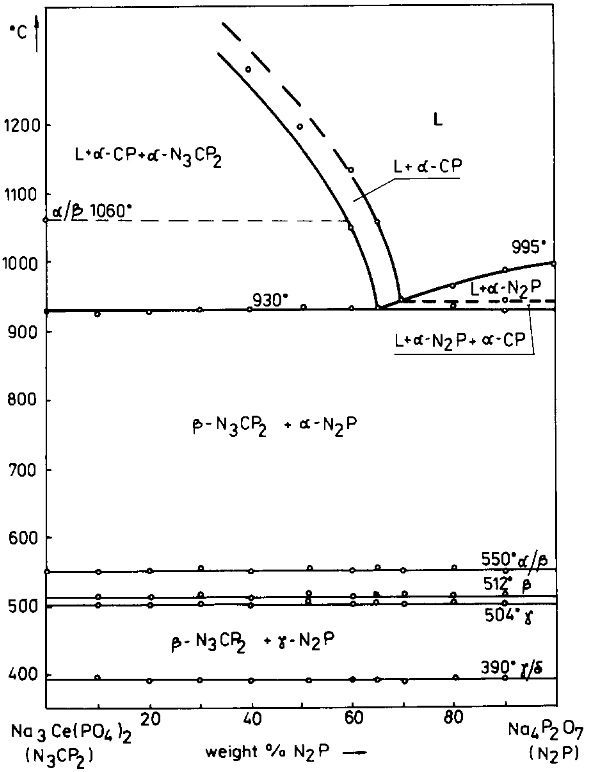

Fig. 2. Phase diagram of the system $Na_3Ce(PO_4)_2$–$Na_4P_2O_7$.

eutectic is 945 ° C, and the composition is 75 wt.% $Na_4P_2O_7$ and 25 wt.% $CePO_4$.

Examinations of the system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$ showed that the mixed orthophosphate $Na_3Ce(PO_4)_2$ forms a previously unknown section with sodium pyrophosphate. Figure 2 presents the phase diagram of the system $Na_3Ce(PO_4)_2$–$Na_4P_2O_7$ which was determined by differential thermal analysis of heating, X-ray diffractometry and microscopy. This system is complex and is ternary is nature in the upper part. Above 930 ° C there are four phases: liquid L, $Na_3Ce(PO_4)_2$, $CePO_4$ and $Na_4P_2O_7$. As a result of a peritectic reaction, liquid L and orthophosphate $CePO_4$ are used up to form crystals of $Na_3Ce(PO_4)_2$. Below 930 ° C there are only two phases, $Na_3Ce(PO_4)_2$ and $Na_4P_2O_7$, and the system is binary in nature. The liquidus curve was estimated only within the composition range 40–100 wt.% $Na_4P_2O_7$. Samples richer in $Na_3Ce(PO_4)_2$ melt at very high temperatures, much above 1400 ° C. The polymorphic transitions of $Na_4P_2O_7$ occur over the whole $Na_3Ce(PO_4)_2$–$Na_4P_2O_7$ system and are accompanied by strong thermal effects on the DTA curves.

On the basis of these investigations and the results obtained, the phase diagram of the ternary system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$ with solidifica-

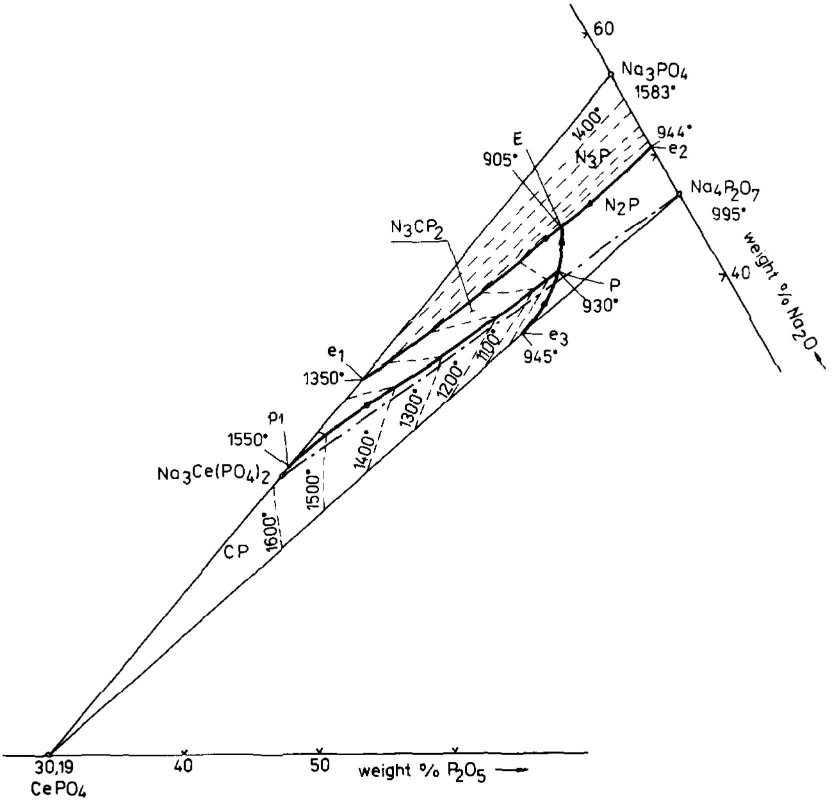

Fig. 3. Phase diagram of the system $CePO_4$–Na_3PO_4–$Na_4P_2O_7$. CP = $CePO_4$; N_3CP_2 = $Na_3Ce(PO_4)_2$; N_3P = Na_3PO_4, N_2P = $Na_4P_2O_7$.

tion isotherms can be suggested; it is presented in Fig. 3. In the side system $CePO_4$–Na_3PO_4, a binary peritectic reaction occurs at 1550 °C and, as a result of this reaction, $Na_3Ce(PO_4)_2$ forms; this is reflected in the ternary system under investigation in the form of the ternary peritectic P. As a result of the reaction of cerium orthophosphate $CePO_4$ and the liquid with the composition corresponding to point P, $Na_3Ce(PO_4)_2$ and $Na_4P_2O_7$ are formed according to the ternary peritectic reaction

$$L_p + CePO_4 \rightarrow Na_3Ce(PO_4)_2 + Na_4P_2O_7$$

This reaction, according to the Gibbs phase equation, takes place at the constant peritectic temperature, 930 °C. The ternary eutectic E of composition 9.9 wt.% Ce_2O_3, 44.1 wt.% Na_2O and 46 wt.% P_2O_5 occurs at 905 °C in the ternary system.

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