

Phase Diagram for a Portion of the System $\text{Ce}_2\text{O}_3\text{-Na}_2\text{O-P}_2\text{O}_5$ Rich in P_2O_5

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The phase diagram for a portion of the ternary system $\text{Ce}_2\text{O}_3\text{-Na}_2\text{O-P}_2\text{O}_5$ rich in P_2O_5 has been worked out. The durability of two cerium phosphates, $\text{CeP}_3\text{O}_{14}$ and CeP_3O_9 , was investigated and the melting point of $\text{CeP}_3\text{O}_{14}$ determined (1064°C congruently). Phase diagrams of the two binary systems $\text{CeP}_3\text{O}_9\text{-CeP}_3\text{O}_{14}$ and $\text{NaCe}(\text{PO}_3)_4\text{-CeP}_3\text{O}_{14}$ are presented. © 1989 Academic Press, Inc.

Introduction

As can be concluded from the literature, during the last several years, vast possibilities of using rare-earth elements and their compounds in different fields, e.g., in ceramic industry, metallurgy, luminophore technology, etc., have been found. For instance, double-condensed lithium-lanthanum phosphates are valuable materials for quantum electronics, ultraphosphates $\text{NdP}_5\text{O}_{14}$ and $\text{LiNdP}_4\text{O}_{12}$ are used as laser materials, and the phosphates YPO_4 , YP_5O_{14} , and $\text{GdP}_5\text{O}_{14}$ show luminescence when they are activated with different rare-earth elements.

In this paper, results of an investigation of the phase diagram for a portion of the ternary system $\text{Ce}_2\text{O}_3\text{-Na}_2\text{O-P}_2\text{O}_5$ rich in P_2O_5 is reported. In this composition range only the phase diagram of the system $\text{CeP}_3\text{O}_9\text{-NaPO}_3$ is known (1). Binary compounds rich in P_2O_5 , i.e., NaPO_3 , $\text{CeP}_5\text{O}_{14}$, and CeP_3O_9 , are known and have been investigated. However, the published data concern mainly the methods of synthesis,

crystalline structure, polymorphism, and durability (2-8).

Experimental

Reagent-grade CeO_2 , 99.9%, H_3PO_4 85% analytical grade (Xenon), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ analytical grade, and $\text{NH}_4\text{H}_2\text{PO}_4$ analytical grade were used as starting materials. Cerium ultraphosphate $\text{CeP}_5\text{O}_{14}$ was obtained from CeO_2 and H_3PO_4 . A mixture of CeO_2 and H_3PO_4 of molar ratio $\text{P/Ce} = 10$ was placed in a porcelain crucible and then vaporized slowly until a thick, transparent mass was obtained. The mass was then sintered in a gold crucible at 700°C for 24 hr. The obtained hard product was ground in agate mortar and then washed several times with distilled water and dried at 200°C.

Cerium metaphosphate $\text{Ce}(\text{PO}_3)_3$ was obtained in two ways: (a) by sintering cerium ultraphosphate $\text{CeP}_5\text{O}_{14}$ at 960°C for 100 hr, which decomposes $\text{CeP}_5\text{O}_{14}$ to $\text{Ce}(\text{PO}_3)_3$, and (b) from cerium oxide CeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ by sintering the mixture of these compounds stoichiometrically at 250, 500,

and 900°C for 2, 5, and 15 hr, respectively. Sodium metaphosphate NaPO_3 was obtained by complete dehydration of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ at 300°C for 0.5 hr and then at 500°C for 2 hr. $\text{NaCe}(\text{PO}_3)_4$ was obtained by sintering the mixture composed of 1 mole of $\text{Ce}(\text{PO}_3)_3$ and 1 mole NaPO_3 at 750°C for 20 hr.

The experiments were performed with differential thermal analysis (DTA), X-ray powder diffraction techniques, and microscopic analysis in reflected light. Thermal analysis was performed with samples of 0.5 and 3 g prepared in the following way: weighed components were mixed in a weighting bottle, ground in agate mortar, pressed into disks, placed in a gold crucible, and precalcined at 500°C for several days. The thermal analysis (DTA) was performed using a derivatograph Type 3427 (Hungarian, MOM) with photographic recording over the temperature range 20 to 1200°C. Operating conditions were as follows: sensitivity TG, 500 mg; DTA, 1/10; DTG, 1/10; speed of heating 10°/min, platinum crucible. The standard substance used was Al_2O_3 . Temperature was measured with a thermocouple which was standardized using the melting points of the following substances: NaCl , K_2SO_4 , and the polymorphic transition temperature of K_2SO_4 (583°C). Differential thermal analysis (DTA) was used to investigate the liquidus and solidus relations, because above 900°C there is a composition change caused by the evaporation of P_2O_5 . In addition, the samples crystallize with difficulty and readily form glasses. The purity of reagents and phase structure of the substances were controlled microscopically. Microsections were prepared from melted and crystallized samples, which were polished and microscopically examined in reflected light.

A quenching technique was also used for phase determination. Specimens equilibrated in an electric furnace were quenched in water. Phase identification was made

with $\text{CuK}\alpha$ radiation from an HZG-4 diffractometer.

Results and Discussion

Before investigating phase dependencies for a portion of the ternary Ce_2O_3 - Na_2O - P_2O_5 system rich in P_2O_5 , thermal experiments were carried out to determine the melting point of the ultraphosphate, $\text{CeP}_5\text{O}_{14}$. Experiments have shown that it is labile at higher temperatures. There is a strong endothermic effect which starts at about 900°C on the differential curve (DTA) of heating $\text{CeP}_5\text{O}_{14}$. This effect is accompanied by a two-stage decrease in mass of about 4% in the first stage. The isothermal measurement of mass decrement at 900°C was carried out in order to examine the course of $\text{CeP}_5\text{O}_{14}$ decomposition. It was noted that, after about 150 hr, $\text{CeP}_5\text{O}_{14}$ decomposes completely to form $\text{Ce}(\text{PO}_3)_3$. This phenomenon was found while studying the final product by powder X-ray diffraction techniques. For this reason immersed platinum ampoules have been used to determine fusion temperature of $\text{CeP}_5\text{O}_{14}$. The decomposition of $\text{CeP}_5\text{O}_{14}$ is minimized under such conditions. It has been discovered that cerium ultraphosphate fuses congruently at 1064°C. Congruent formation of $\text{CeP}_5\text{O}_{14}$ is confirmed by microscopic observations in reflected light. Molten and quickly cooled $\text{CeP}_5\text{O}_{14}$ forms glass very easily. Figure 1 illustrates cerium ultraphosphate microphotography: white, primarily separated crystals of $\text{CeP}_5\text{O}_{14}$ are surrounded by glass.

The stability of cerium polyphosphate $\text{Ce}(\text{PO}_3)_3$ was also tested in this way. Durif (3) reported that $R(\text{PO}_3)_3$ ($R = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Tb}$) decomposes into $R\text{PO}_4$ and liquid. This decomposition was also observed in this laboratory. DTA measurements gave a decomposition temperature of ~1200°C.

In the present work, which concerns a

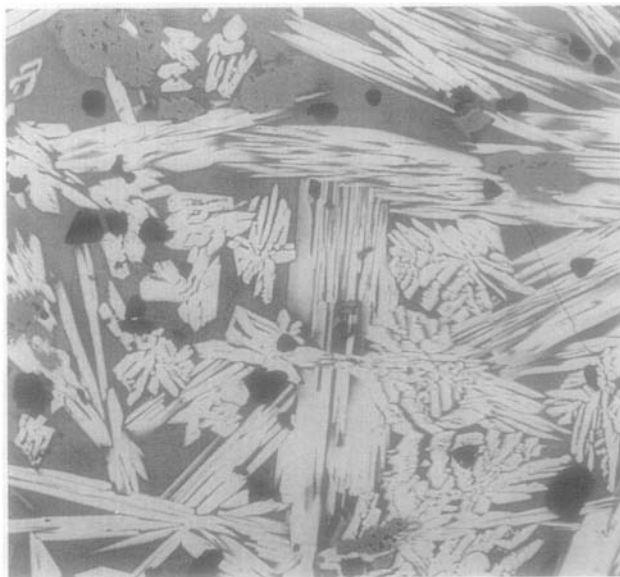


FIG. 1. Composition: CeP₅O₁₄ (white crystals).

portion of the system Ce₂O₃-Na₂O-P₂O₅ rich in P₂O₅, there are two binary systems: Ce(PO₃)₃-CeP₅O₁₄ and Ce(PO₃)₃-NaPO₃. The first of them, i.e., Ce(PO₃)₃-CeP₅O₁₄, has not been known before. Figure 2 shows the phase diagram of this system examined in this laboratory on the basis of DTA heat-

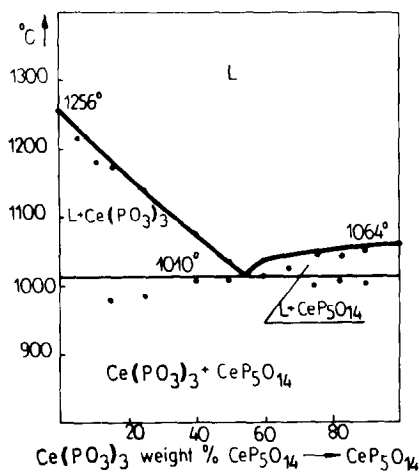


FIG. 2. Phase diagram of the system Ce(PO₃)₃-CeP₅O₁₄.

ing. The initial phosphates give a eutectic at 1010°C at composition 55 wt% of CeP₅O₁₄.

The second system, Ce(PO₃)₃-NaPO₃, is already known (1) and agrees with the results of the present authors. The NaCe(PO₃)₄ compound occurs in this system and it decomposes on heating in a peritectic reaction at 865°C. NaCe(PO₃)₄ gives a binary section with CeP₅O₁₄, which is not known so far.

Figure 3 shows the phase diagram of the system NaCe(PO₃)₄-CeP₅O₁₄ examined in our laboratory on the base of DTA heating. This system, in the top part of the phase diagram, shows a ternary nature resulting from the peritectic reaction taking place. In the high-temperature part, up to 760°C, four phases occur, viz.: liquid L, phosphates Ce(PO₃)₃, CeP₅O₁₄, and NaCe(PO₃)₄. As a result of the peritectic reaction liquid L and Ce(PO₃)₃ become used up to yield NaCe(PO₃)₄ crystals. Below 760°C the system has a binary nature and only CeP₅O₁₄ and NaCe(PO₃)₄ exist.

Figure 4 shows the DTA data on the composition containing 5-90 wt% of NaPO₃,

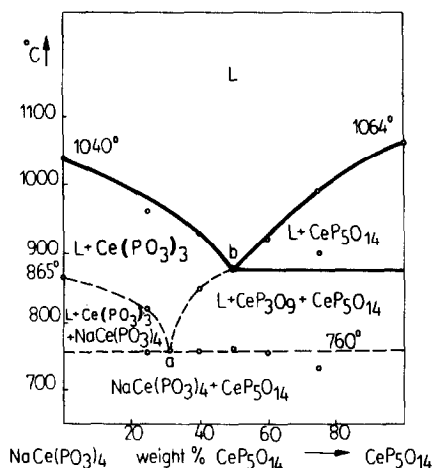


FIG. 3. Phase diagram of the system $\text{NaCe}(\text{PO}_3)_4$ - $\text{CeP}_5\text{O}_{14}$.

95–10 wt% of $\text{CeP}_5\text{O}_{14}$. The precalcined mixtures of $\text{CeP}_5\text{O}_{14}$ and NaPO_3 , weighed at specific weight ratios, were investigated by thermal analysis of heating.

Phase composition of the mixtures after thermal analysis was examined by X-ray

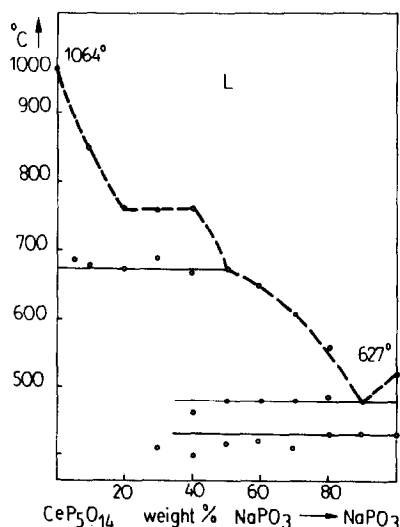


FIG. 4. DTA heating data for precalcined compositions containing 5–90 wt% of NaPO_3 , 95–10 wt% of $\text{CeP}_5\text{O}_{14}$.

powder diffraction and the following phases were discovered: NaPO_3 , $\text{NaCe}(\text{PO}_3)_4$, $\text{CeP}_5\text{O}_{14}$, and $\text{Ce}(\text{PO}_3)_3$. For this reason, the described mixtures underwent a diversified heat treatment and each phase obtained was identified by X-ray diffraction techniques. The following various heat treatments were used:

(i) the samples were melted, crystallized with grafting, and cooled slowly to room temperature (Fig. 5A);

(ii) the samples were melted, crystallized with grafting, sintered over the temperature range 450 to 700°C (according to the composition), and then quenched from these temperatures (Fig. 5B);

(iii) the samples were sintered over the temperature range 450 to 700°C (according to the composition) for a few hours and then cooled slowly to room temperature (Fig. 5C);

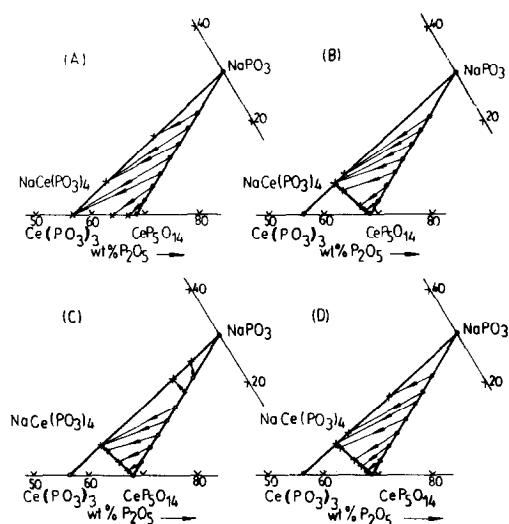


FIG. 5. Position of samples: (O) initial composition; (x) composition after heat treatment. Data are shown for (A) samples melted and cooled to room temperature (i); (B) samples melted, sintered (450–700°C), and quenched (ii); (C) samples sintered (450–700°C) and cooled to room temperature (iii); (D) samples sintered (450–700°C) and quenched (iv).

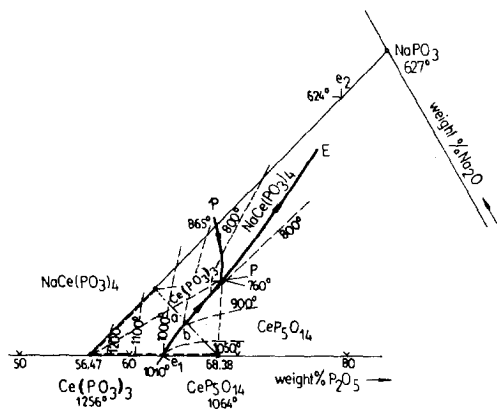


FIG. 6. Phase diagram of the system Na₂O-Ce₂O₃-P₂O₅.

(iv) the samples were sintered over the temperature range 450 to 700°C (according to the composition) for a few hours and then quenched from these temperatures (Fig. 5D).

Figures 5A, 5B, 5C, and 5D illustrate the phase composition of the samples, before and after using the heat treatment described above, which was identified on the grounds of the X-ray investigation. It was noted that, according to the thermal treatment and compositions used, reactions that lead to considerable change in the phase constitutions take place in the initial mixtures (CeP₅O₁₄ + NaPO₃).

On the basis of the results presented

here, a phase diagram for the system Ce₂O₃-Na₂O-P₂O₅ in a P₂O₅-rich portion was suggested and shown in Fig. 6. There is a triple peritectic point *P* in the field shown. The *p^p* curve corresponds to a solidification of the double peritectic point according to the reaction: $L_{p^p} + Ce(PO_3)_3 \rightarrow NaCe(PO_3)_4$. Other curves correspond to a solidification of the double eutectic point. During solidification of the melts, corresponding to the points of Ce(PO₃)₃-NaCe(PO₃)₄-P-CeP₅O₁₄ field triple peritectic quadrangle, a triple peritectic reaction takes place:



at 760°C (*L_P* denotes the liquid whose composition corresponds to point *P*).

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