JOURNAL OF SOLID STATE CHEMISTRY 92, 130–135 (1991)

The System YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$

WŁADYSŁAWA SZUSZKIEWICZ AND TERESA ZNAMIEROWSKA

Department of Inorganic Chemistry, Faculty of Engineering and Economics, Academy of Economics, 53345 Wroclaw, Poland

Received May 31, 1990; in revised form October 18, 1990

The ternary system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ has been investigated by differential thermal analysis, powder X-ray diffraction, and microscopy in reflected light. Its phase diagram and isothermal section at room temperature have been determined. The system contains only one double phosphate which is formed at the 1 : 1 molar ratio YPO_4 : $Ca_3(PO_4)_2$, i.e., $Ca_3Y(PO_4)_3$. © 1991 Academic Press, Inc.

Introduction

The present work is the second part of our investigation on the double calcium–yttrium orthophosphates. Previously the system YPO_4–$Ca_3(PO_4)_2$ was studied and its phase diagram determined (*1*). It was found that the system contains only one intermediate compound of the formula $Ca_3Y(PO_4)_3$. This orthophosphate melts congruently at 1790°C and it is stable down to 1215°C. At this temperature it decomposes into YPO_4 and β-$Ca_3(PO_4)_2$. Calcium–yttrium orthophosphate $Ca_3Y(PO_4)_3$ exhibits a polymorphic transition at 1255°C. The low-temperature β-modification crystallizes in the cubic system (a = 9.835 Å, V = 951.3 Å^3). Because of the interesting properties of $Ca_3Y(PO_4)_3$ further tests in the ternary system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ have been made. This system is not well known. It is limited by three side systems: YPO_4–$Ca_3(PO_4)_2$ (*1*), $Ca_3(PO_4)_2$–$Ca_2P_2O_7$, and YPO_4–$Ca_2P_2O_7$. The system $Ca_3(PO_4)_2$–$Ca_2P_2O_7$ was examined by several authors (*2–4*). It was examined in our laboratory as well. We have found (*5*) that calcium orthophosphate does not form solid solutions with calcium pyrophosphate but both these compounds form a simple eutectic system. The system YPO_4–$Ca_2P_2O_7$ has not been investigated previously.

Experimental

Samples for investigations of the YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ system were prepared from the following original compounds: Y_2O_3, 99.99%, H_3PO_4, 85% analytical grade, $CaCO_3$, analytical grade, $CaHPO_4$, analytical grade.

In our laboratory we have synthesized YPO_4, $Ca_3(PO_4)_2$, $Ca_2P_2O_7$, and $Ca_3Y(PO_4)_3$. Yttrium orthophosphate YPO_4 was obtained from the following solution: 0.4 wt% Y_2O_3, 15 wt% P_2O_5 (as H_3PO_4), 84.6 wt% distilled water. The mixture was placed in a round-bottomed flask and was brought to a boil in a reflux condenser and held there for 6 hr. The precipitated YPO_4 was filtered, washed several times with hot distilled water, and dried at 200°C. Calcium orthophosphate $Ca_3(PO_4)_2$ was synthesized by sintering a 1 : 1 stoichiometric ratio $Ca_2P_2O_7$

0022-4596/91 $3.00

Copyright © 1991 by Academic Press, Inc.
All rights of reproduction in any form reserved.

and $CaCO_3$ at 1350°C for 1 hr. Calcium pyrophosphate $Ca_2P_2O_7$ was obtained from $CaHPO_4$ by heating at 900°C for 1.5 hr. The double orthophosphate $Ca_3Y(PO_4)_3$ was prepared by one of the methods from our laboratory, described in Ref. (*6*). This orthophosphate was obtained by sintering a 1 : 3 stoichiometric ratio of Y_2O_3 and $Ca_2P_2O_7$ at 1400°C for 2 hr and then quenching in ice.

The ternary system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ was examined by differential thermal analysis (heating, cooling), powder X-ray diffraction, and microscopy in reflected light.

The differential thermal analysis of heating and cooling in air was performed in a furnace constructed in our laboratory (with Pt30Rh winding). Three-gram samples were used. In the thermal analysis a derivatograph type 3427 (MOM, Hungary) was used as well. Operating conditions were as follows: sensitivity TG, 500 mg; DTA, 1/10; DTG, 1/10; speed of heating, 10°/min; platinum cup, in an air atmosphere. The standard substance used was high-purity Al_2O_3. Temperatures were read by means of a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of $Ca_2P_2O_7$, K_2SO_4, and NaCl.

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 $Ca_3(PO_4)_2$ and Na_3PO_4.

Accuracy of temperature readings in the thermal analysis up to 800°C was ±1.5°C, above 800°C, ± 3°C, while in the visual methods it was ±10°C and for an optical pyrometer, ±20°C.

The phase purity of reagents and phase structure of the products were studied microscopically. From molten and crystallized samples microsections which were polished and examined in reflected light were prepared.

The initial components and the phases formed in the ternary system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ were identified by powder X-ray diffraction with a HZG-4 diffractometer (Guinier camera) with Cu$K\alpha$ radiation.

Results and Discussion

The YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ system has been examined by differential thermal, X-ray, and microscopy with reflected light methods. The first step was to determine the phase diagram of the side binary system YPO_4–$Ca_2P_2O_7$, which is presented in Fig. 1.

It was discovered that during cooling molten samples form glasses easily. The phenomenon occurs mainly in the part of the system which is rich in $Ca_2P_2O_7$. Slow cooling (2°/min) and frequent seeding were used to obtain crystallized samples. The liquidus curve within the composition range 60–100 wt% of $Ca_2P_2O_7$ was determined by the differential thermal analysis of cooling. Samples richer in YPO_4 melt above 1400°C. To determine the liquidus curve within this composition range the samples were presynthesized by sintering at 1000°C, pelletized, and fused in a furnace with molybdenum winding. Melting points of these samples were determined by means of an optical pyrometer. Temperatures determined with an optical pyrometer are to larger or smaller degrees lowered (according to the composition of sample). Therefore, the suggested position of the liquidus curve is drawn with a dashed line (Fig. 1). Equilibria in the solid phase were investigated by differential thermal analysis on both heating and cooling. YPO_4 and $Ca_2P_2O_7$ were discovered to form a simple eutectic system. The eutectic temperture is 1310°C, composition: 73 wt% $Ca_2P_2O_7$, 27 wt% YPO_4. Calcium pyrophosphate $Ca_2P_2O_7$ occurs in three polymorphic

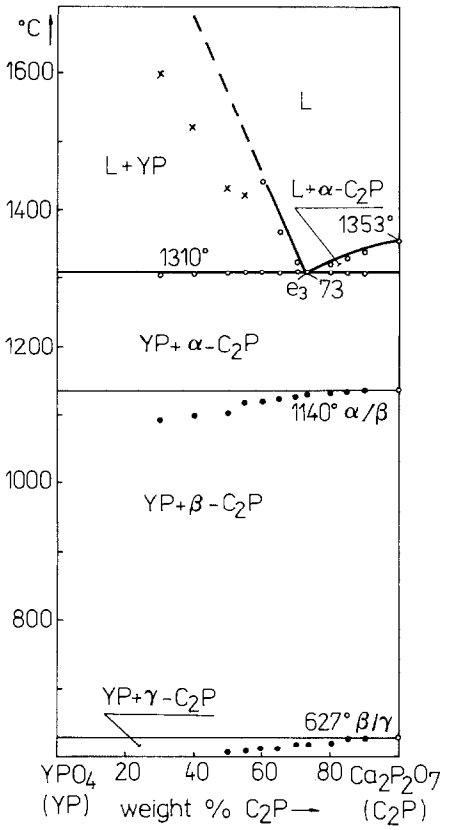

FIG. 1. Phase diagram of the system YPO_4–$Ca_2P_2O_7$. (○) Thermal analysis of cooling, (●) thermal analysis of heating.

modifications (*7*). The temperatures of transitions for pure compounds are: α/β, 1140°C and β/γ, 627°C. In the YPO_4–$Ca_2P_2O_7$ system, transition β/γ is characterized by a very weak and small lowered thermal effect during both heating and cooling, and the transition α/β by a strong thermal effect on the DTA heating curves and a very weak one on the DTA cooling curves. Using X-ray diffraction, it was discovered that within the composition range 0–50 wt% YPO_4, the high-temperature α-$Ca_2P_2O_7$ transition stabilizes during rapid cooling.

The examinations of the YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ system indicated that $Ca_3Y(PO_4)_3$ gives a section with $Ca_2P_2O_7$, which is not known so far. It was determined in this laboratory across the full composition and temperature range. Samples for investigations were prepared in two ways: (a) from Y_2O_3 and $Ca_2P_2O_7$ or (b) from $Ca_3Y(PO_4)_3$ and $Ca_2P_2O_7$. Because $Ca_3Y(PO_4)_3$ was found to decompose (*1*), samples rich in this compound were presynthesized at 1400°C and quenched. Therefore, it was assumed that more reliable results are obtained by means of thermal analysis of cooling. Thermal examinations of heating were performed as well, in order to check the behavior of samples under those conditions. It was discovered that, in the part of the system rich in $Ca_2P_2O_7$, analogous effects occurred on the DTA curves during both heating and cooling. However, in the part of the system rich in $Ca_3Y(PO_4)_3$, considerable differences occurred. Namely, during the

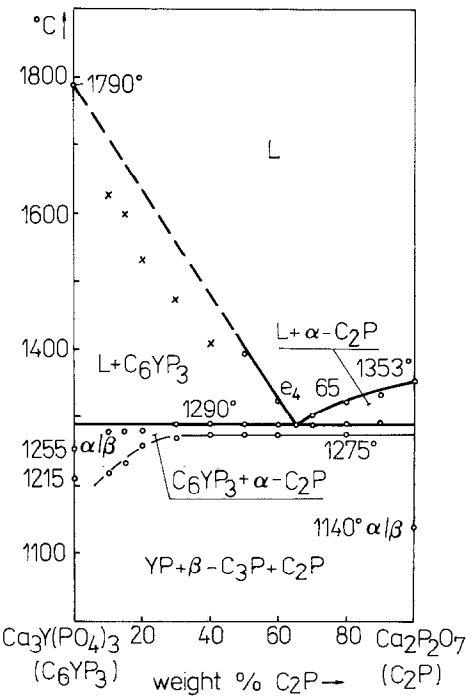

FIG. 2. Phase diagram of the system $Ca_3Y(PO_4)_3$–$Ca_2P_2O_7$. (○) Thermal analysis; (×) optical.

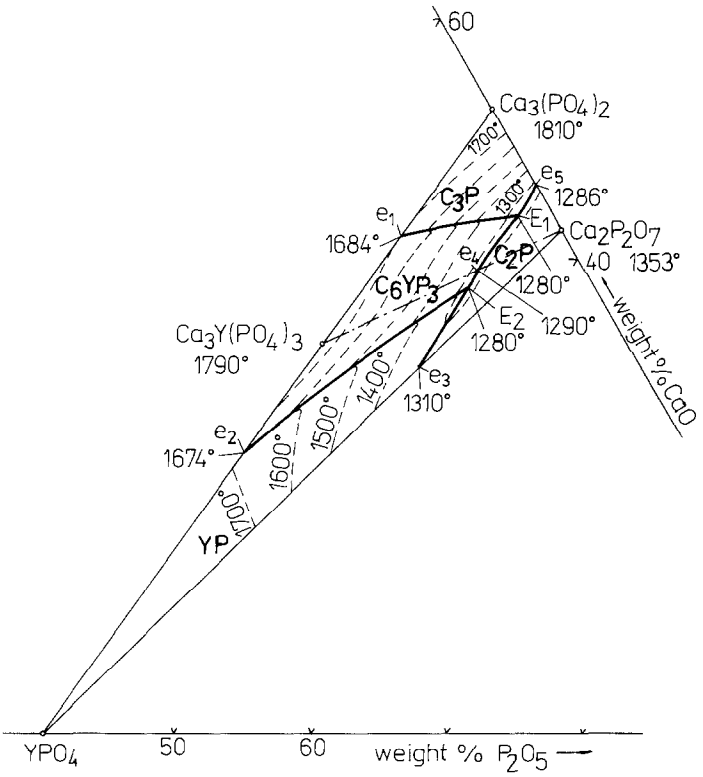

FIG. 3. Phase diagram of the system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$. YP -YPO_4; C_6YP_3 -$Ca_3Y(PO_4)_3$; C_3P- $Ca_3(PO_4)_2$; C_2P -$Ca_2P_2O_7$.

thermal analysis of heating, within the temperature range 1200–1350°C, three effects appeared on the DTA curves. During the thermal analysis of cooling, within the same temperature range, only one or two effects appeared on the DTA curves. If only one effect occurred on the DTA curve, it was always accompanied by overcooling within 20–40°C. Such phenomena were observed during the investigations of the YPO_4–$Ca_3(PO_4)_2$ binary system. They were described and interpreted in Ref. (*1*). The phase composition of samples from the system $Ca_3Y(PO_4)_3$–$Ca_2P_2O_7$, melted and cooled slowly down to the room temperature, was identified by X-ray powder analysis. The obtained results confirmed that the phosphate $Ca_3Y(PO_4)_3$ decomposes into YPO_4 and $Ca_3(PO_4)_2$.

On the basis of the performed examinations, the phase diagram of the system $Ca_3Y(PO_4)_3$–$Ca_2P_2O_7$ was determined. It is presented in Fig. 2.

The liquidus and solidus curves within the composition range 50–100 wt% $Ca_2P_2O_7$ were drawn on the basis of the thermal analysis of cooling. The melting points of samples rich in $Ca_3Y(PO_4)_3$ were determined by means of an optical pyrometer (similarly with the system YPO_4–$Ca_2P_2O_7$, Fig. 1). It was discovered that an addition of calcium pyrophosphate, $Ca_2P_2O_7$ accelerates decomposition of $Ca_3Y(PO_4)_3$ (this compound decomposes at 1215°C). In the system $Ca_3Y(PO_4)_3$–$Ca_2P_2O_7$ the temperature of this decomposition changes with the composition of samples and occurs over the temperature range 1215 to 1275°C. Therefore, this sys-

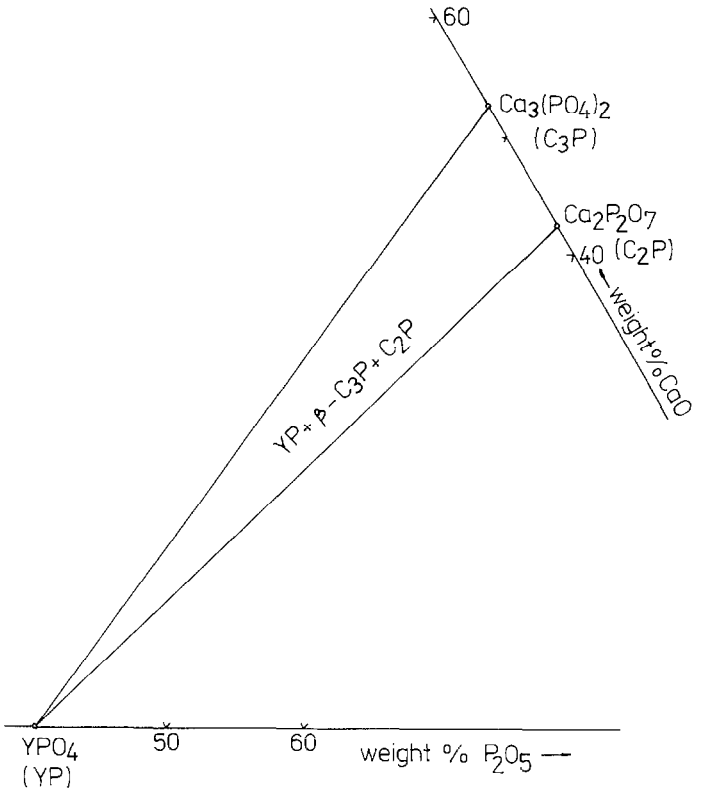

FIG. 4. Isothermal section at room temperature. Designations as in Fig. 3.

tem, only in the higher temperature range (above 1215–1275°C), has a binary nature, and initial phosphates form an eutectic at 65 wt% $Ca_2P_2O_7$, at 1290°C. In the low-temperature part (below 1215–1275°C) this system has a ternary nature and three phases appear: calcium pyrophosphate $Ca_2P_2O_7$, yttrium orthophosphate YPO_4, and calcium orthophosphate $Ca_3(PO_4)_2$. The second and third compounds are the products of $Ca_3Y(PO_4)_3$ decomposition. Thermal effects connected with the polymorphic transitions of $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$ were not found to occur in the system.

Fig. 3 presents the phase diagram of the system YPO_4–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ with its solidification isotherms. Phase equilibria shown in the figure occur only above 1215–1275°C. Above these temperatures, the composition range under investigation is divided into two partial ternary systems: (1) $Ca_3Y(PO_4)_3$–$Ca_3(PO_4)_2$–$Ca_2P_2O_7$ and (2) YPO_4–$Ca_3Y(PO_4)_3$–$Ca_2P_2O_7$. The first partial ternary system is a simple eutectic system containing a ternary E_1 eutectic: 2.50 wt% Y_2O_3, 43.75 wt% CaO, 53.75 wt% P_2O_5, and temperature 1280°C. The second partial system is also a simple eutectic system containing a ternary E_2 eutectic: 9.0 wt% Y_2O_3, 38.0 wt% CaO, 53.0 wt% P_2O_5, and temperature 1280°C.

Figure 4 shows an isothermal section at room temperature. No phosphate $Ca_3Y(PO_4)_3$ is visible since this compound is unstable and does not occur in the equilibrium state at room temperature.

References

1. W. SZUSZKIEWICZ AND T. ZNAMIEROWSKA, *J. Solid State Chem.*, submitted for publication.
2. G. TRÖMEL AND W. FIX, *Arch. Eisenhüttenw.* **4,** 209 (1961).
3. J. H. WELCH AND W. GUTT, *J. Chem. Soc.* **1961,** 4442.
4. E. R. KREIDLER AND F. A. HUMMEL, *Inorg. Chem.* **6,** 884 (1967).
5. J. BERAK AND T. ZNAMIEROWSKA, *Polish J. Chem.* (formely Roczniki Chemii) **47,** 1137 (1973).
6. W. SZUSZKIEWICZ AND T. ZNAMIEROWSKA, *J. Thermal Anal.*, submitted for publication.
7. J. BERAK AND T. ZNAMIEROWSKA, *Polish J. Chem.* (formely Roczniki Chemii) **46,** 1921 (1972).