JOURNAL OF SOLID STATE CHEMISTRY 88, 406–410 (1990)

The System YPO_4–$Ca_3(PO_4)_2$

WŁADYSŁAWA SZUSZKIEWICZ AND TERESA ZNAMIEROWSKA

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

Received November 1, 1989; in revised form March 19, 1990

The phase diagram of system YPO_4–$Ca_3(PO_4)_2$ has been determined by differential thermal, X-ray, and microscopic methods. The system contains one intermediate compound, which melts congruently at 1790°C. The compound is stable over the temperature range 1790–1215°C but decomposes into YPO_4 and $Ca_3(PO_4)_2$ at lower temperatures. It exhibits a polymorphic transition at 1255°C. The low-temperature modification has a body-centered cubic unit cell with parameters $a = 9.835$ Å and $V = 951.3$ Å^3.

Introduction

Recently, there has been great interest in double orthosphosphates of alkali and rare earth metals resulting from their uses in optics and electronics. Two types of these compounds, $M^I_3Ln^{III}(PO_4)_2$ (*1–3*) and $M^I_3Ln^{III}_2(PO_4)_3$ (*4*) (where M^I = alkali metals, Ln = rare earth and Y), are known. Previous reports have included the methods of synthesis and the results of X-ray examinations. According to Ref. (*2*), investigations of the thermal stability of compounds $M^I_3Ln(PO_4)_2$ (where M^I = K, Rb; Ln = rare earth, Sc, and Y) showed that they can be divided into two groups: (a) melting within the temperature range 1700–1850°C and (b) melting within the temperature range 1150–1280°C or below.

Double orthophosphates, according to their composition, occur in the system $Ln^{III}PO_4$–$M^I_3PO_4$. The present paper presents the results of a study of the previously unknown YPO_4–$Ca_3(PO_4)_2$ system. Double calcium–yttrium orthophosphates are also unknown. In 1981, Ref. (*5*) reported on the synthesis and structure of double calcium orthophosphates with rare earth elements. According to the authors, $Ca_3Ln(PO_4)_3$ compounds (where Ln = La–Gd, excluding Pm) have the $Bi_4(SiO_4)_3$ eulytite structure.

Experimental

The following reagents were used: Y_2O_3, 99.99%; H_3PO_4, 85% analytical grade; $CaHPO_4$, analytical grade; and $CaCO_3$, analytical grade.

Calcium pyrophosphate $Ca_2P_2O_7$ was obtained from $CaHPO_4$ by heating at 900°C for 1.5 hr. Calcium orthophosphate $Ca_3(PO_4)_2$ was prepared by sintering a 1 : 1 stoichiometric ratio of $Ca_2P_2O_7$ and $CaCO_3$ at 1350°C for 1 hr. After the first heating the samples were ground for better blending. Yttrium orthophosphate YPO_4 was obtained from the following solution: 0.4 wt% of Y_2O_3, 15 wt% of P_2O_5 (as H_3PO_4), 84.6 wt% of distilled water. The mixture was placed in a round-bottomed flask, brought

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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.

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

Samples for thermal analysis were prepared from YPO_4 and $Ca_3(PO_4)_2$ in the following way: weighed components were carefully mixed, ground, pressed into pellets, placed in boats, and fused in a vertical resistance furnace with molybdenum winding, under argon. Temperatures were read by means of an optical pyrometer which was calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$. The differential thermal analysis of heating and cooling was performed in a furnace constructed in this laboratory, under air. Boats and furnace winding from noble metal alloys were used. 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. Within the temperature range 20–1500°C a derivatograph type 3427 (MOM, Hungary) was used, as well as speed of heating at 10°C/min, a platinum cup, and air atmosphere. High-purity Al_2O_3 was used as the standard material.

A quenching technique was also used for phase determination. The phases were identified by the X-ray powder diffraction.

The phase purity and the phase structure of the products were studied microscopically. Microsections were prepared from molten and crystallized samples, which were polished and examined in reflected light.

Results and Discussion

The previously unknown phase diagram of system YPO_4–$Ca_3(PO_4)_2$ has been examined in this laboratory across the full composition range (Fig. 1). The liquidus and solidus curves were determined by observing the behavior of pellets in the furnace with the temperatures read by means of an optical pyrometer. Subsolidus phase equilibria were determined by the differential thermal analysis on cooling. Molten samples were sintered at 1500°C and cooled quickly. Then they were ground, placed in platinum crucibles, and put into a furnace heated to 1500°C, and thermal analysis of cooling was performed.

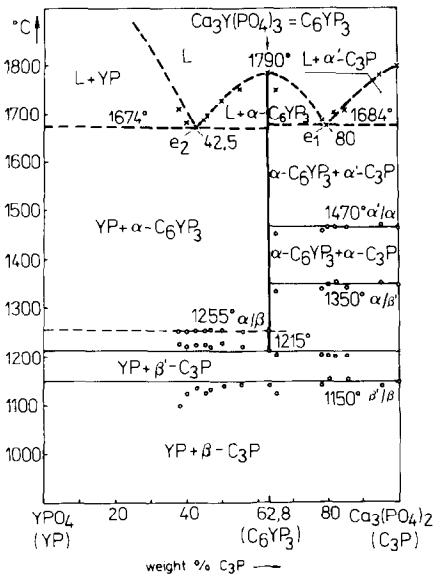

FIG. 1. Phase diagram of the system YPO_4–$Ca_3(PO_4)_2$. *o*, thermal analysis; x, optical.

It was discovered that the system contains one intermediate compound which is formed at the 1:1 molar ratio YPO_4:$Ca_3(PO_4)_2$ (62.8 wt% of $Ca_3(PO_4)_2$, 37.2 wt% YPO_4), i.e., $Ca_3Y(PO_4)_3$. This double orthophosphate melts at 1790°C. The conditions of synthesis and the thermal stability of $Ca_3Y(PO_4)_3$ were examined. This compound was formed when stoichiometric quantities of the initial orthophosphates are fused, cooled slowly down to approx 1500–1600°C, sintered at this temperature for 2 hr, and then cooled

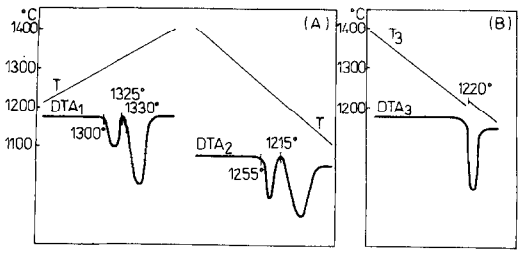

FIG. 2. T and DTA curves recorded during heating and cooling of $Ca_3Y(PO_4)_3$.

quickly. If a sample of stoichiometric composition of this compound is (a) sintered within the range 1500–1600°C or (b) fused, and then cooled slowly (10°C/min) down to room temperature, a mixture of YPO_4 and β-$Ca_3(PO_4)_2$ is obtained. Efforts to synthesize $Ca_3Y(PO_4)_3$ from different chemical reagents (e.g., $Ca_2P_2O_7$ and Y_2O_3, $CaCO_3$ and $Y(PO_3)_3$) were made and the results are presented in Ref. (*6*).

The behavior of $Ca_3Y(PO_4)_3$ during heating, cooling, and in the presence of excess YPO_4 and $Ca_3(PO_4)_2$ was examined with differential thermal analysis. Figure 2 shows T and DTA behavior of $Ca_3Y(PO_4)_3$ for two procedures: (A) during heating and cooling and (B) when the sample is put into a furnace heated up to 1400°C and cooled down.

There are three thermal effects at 1300, 1325, and 1330°C on the DTA_1 (heating) curve, while there are only two effects at 1255 and 1215°C on the DTA_2 (cooling) curve. Overcooling amounting to approx 10°C occurs on the T_3 curve in Fig. 2B, and it is accompanied by one strong thermal effect on the DTA_3 curve. These thermal analyses of heating and cooling were also performed for other samples from the YPO_4–$Ca_3(PO_4)_2$ system. For procedure A, the DTA curves were similar to those shown in Fig. 2A. But when the thermal analysis of cooling was performed according to procedure B, the results were different. Two effects occurred on the DTA curves within the composition range YPO_4–$Ca_3Y(PO_4)_3$. Within the composition range $Ca_3Y(PO_4)_3$–$Ca_3(PO_4)_2$, one effect occurred on the DTA curves (similarly to the ones shown in Fig. 2B). There was always smaller or larger overcooling on curve T.

To interpret the above results, samples from the binary system under investigation were quenched from different temperatures. The resulting phases were identified by X-ray powder diffraction. These investigations showed that $Ca_3Y(PO_4)_3$ is stable within the temperature range 1790–1215°C. It decomposes into YPO_4 and β-$Ca_3(PO_4)_2$ at 1215°C.

Figure 3 shows the microphotography of a sample of the composition 64 wt% of $Ca_3(PO_4)_2$, 36 wt% of YPO_4; (a) fused, then sintered at 1600°C for 2 hr and cooled quickly down to room temperature, (b) fused, then sintered at 1600°C for 2 hr and at 1150°C for 2 days, and then cooled slowly (10°C/min) down to room temperature. Figure 3a shows primarily separated gray crystals of $Ca_3Y(PO_4)_3$ and the eutectic. Figure 3b shows the crystals of $Ca_3Y(PO_4)_3$ which have been decomposed to YPO_4 (white crystals) and $Ca_3(PO_4)_2$ (gray fields). This decomposition is also observed in the eutectic.

The phosphate $Ca_3Y(PO_4)_3$ has a polymorphic transition at 1255°C (Fig. 2A—DTA_2 curve). The low-temperature β-$Ca_3Y(PO_4)_3$ is stable and transforms into the high-temperature modification (α) with difficulty. β-$Ca_3Y(PO_4)_3$ can be synthesized by the method described in this paper. The carried out investigations showed that an addition of $Ca_3(PO_4)_2$ stabilizes the β-$Ca_3Y(PO_4)_3$ form and the presence of YPO_4 accelerates the $\alpha \rightleftharpoons \beta$ transition.

The structure of low-temperature β-$Ca_3Y(PO_4)_3$ was determined by the powder X-ray analysis. Table I presents the X-ray powder diffraction data for this modification. It was found that β-$Ca_3Y(PO_4)_3$ has a body-centered cubic unit cell with the fol-

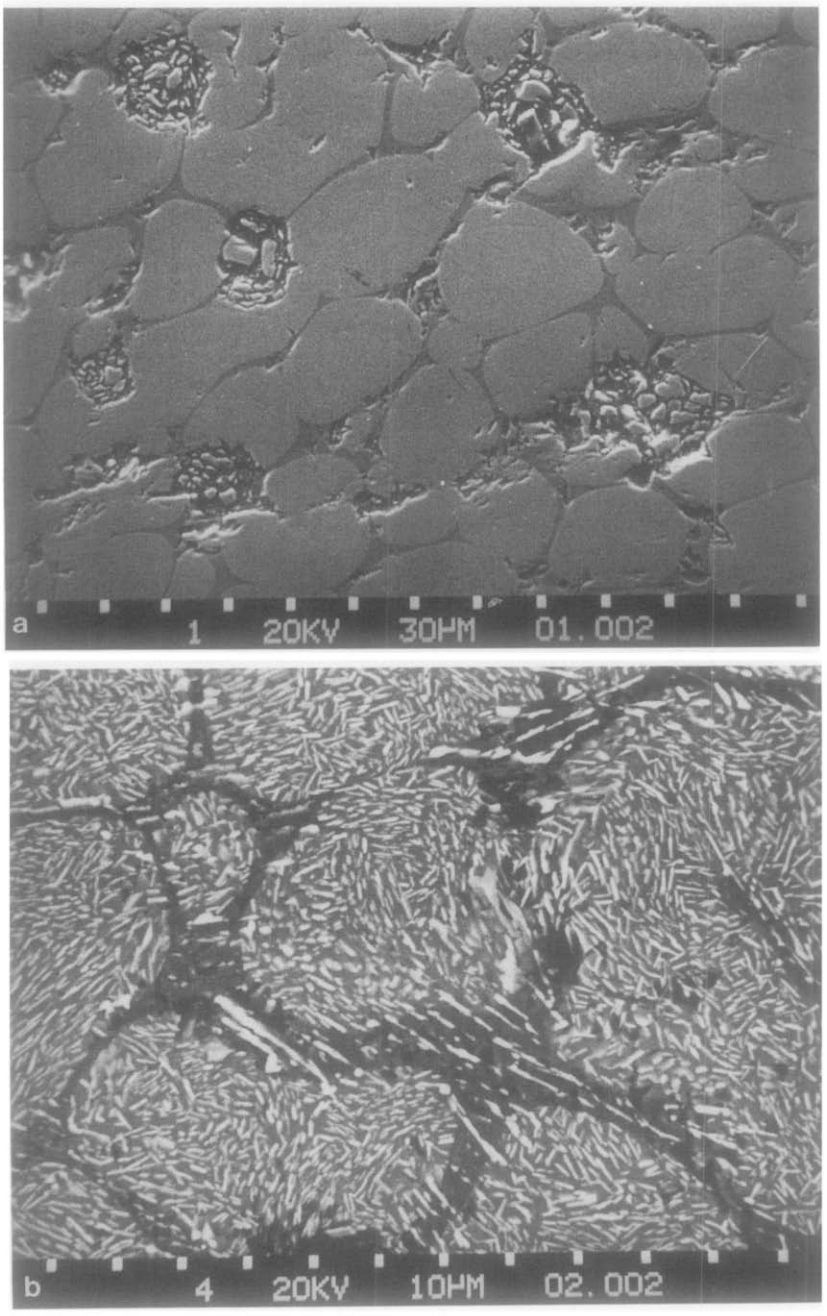

FIG. 3. Composition: 64 wt% of $Ca_3(PO_4)_2$, 36 wt% of YPO_4. (a) Fused, sintered at 1600°C, cooled quickly. Gray crystals, $Ca_3Y(PO_4)_3$. (b) Fused, sintered at 1600 and 1150°C, cooled slowly. White crystals, YPO_4; gray fields, $Ca_3(PO_4)_2$.

TABLE I

X-RAY ANALYSIS DATA FOR β-$Ca_3Y(PO_4)_3$ MODIFICATION

hkl	d_{obsd} (Å)	d_{calcd} (Å)	I/I_o
211	4.016	4.015	8
310	3.111	3.110	100
321	2.628	2.628	41
332	2.096	2.097	14
422	2.007	2.007	24
431	1.928	1.929	32
521	1.794	1.795	3
532	1.595	1.595	12
620	1.554	1.555	8
541	1.517	1.517	7
631	1.450	1.450	2
444	1.420	1.419	3
633	1.338	1.338	8

Note. Cubic system: a = 9.835 Å, V = 951.3 Å^3.

lowing parameters: a = 9.835 Å, V = 951.3 Å^3.

The data in Table I show that β-$Ca_3Y(PO_4)_3$ is isomorphous with $Ca_3Gd(PO_4)_3$ and $Ca_3Eu(PO_4)_3$, which have the eulytite structure. X-ray data of the two latter compounds are available in the Powder Diffraction File (*7*) as 29-325 and 29-321.

In accordance with Fig. 1, two eutectics occur in the YPO_4–$Ca_3(PO_4)_2$ system: e_1 at 1684°C, of the composition 80 wt% of $Ca_3(PO_4)_2$; and e_2 at 1674°C, of the composition 42.5 wt% of $Ca_3(PO_4)_2$. According to literature reports, calcium orthophosphate $Ca_3(PO_4)_2$ occurs in four polymorphic modifications with the following temperatures of transitions: α'/α—1470°C, α/β'—1350°C, and β'/β—1150°C. Only the α'/α transition gives a clear thermal effect in a phase pure compound. It is difficult to obtain the modification β. It was discovered in the present study that the presence of YPO_4 makes all transitions of $Ca_3(PO_4)_2$ proceed one after another, and β-$Ca_3(PO_4)_2$ is always obtained at room temperature.

Acknowledgments

The authors thank Dr. J. Matuszewski for performing the X-ray analyses. This paper was included in the CPBP-01.18 problem and was financially supported by the Ministry of National Education.

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