Phase Equilibria in the 14.4.43aO

EXPERIMENTAL

Samples of the YPO_4 — $Ba_3(PO_4)_2$ system were obtained from the starting orthophosphates. These reagents were synthesized from the following original compounds of analytical grade: $BaCO_3$, $BaHPO_4$, Y_2O_3 99.99%, H_3PO_4 85%. $Ba_3(PO_4)_2$ was synthesized by sintering a 1:1 stoichiometric ratio of $Ba_2P_2O_7$ and $BaCO_3$ at 1300°C for 6 h. $Ba_2P_2O_7$ was prepared from $BaHPO_4$ by a complete dehydration at 900°C for 1 h. 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, brought to boil in a reflux condenser and held there for 6 h. The precipitated YPO_4 was filtered, washed several times with hot distilled water, and dried at 200°C.

Samples for thermal analysis were synthesized by classical solid state reaction. The initial compounds were weighed in the appropriate amounts, strictly mixed, ground in an agate mortar (for homogenization) and then presynthesized by sintering in air. The conditions for the synthesis were determined experimentally. The attainment of an equlibrium state was monitored by X-ray phase analysis and differential thermal analysis (DTA).

The phase diagram of the binary system YPO_4 — $Ba_3(PO_4)_2$ has been determined by DTA, X-ray powder diffraction and microscopy in reflected light. The DTA of heating in air was carried out in a derivatograph of the type C (MOM, Hungary) between 20–1400°C (heating rate 5°/min; platinum cup; the masses of samples: 0.2 to 0.7 g). As standard substance high-purity Al_2O_3 was used. DTA of cooling in air was performed in a home-made furnace with a Pt30Rh winding (the mass of a sample: 3 g). Temperature was recorded by a Pt/Pt10Rh thermocouple, which was standardized against the melting points of $Ca_2P_2O_7$, K_2SO_4 and NaCl.

The high-temperature thermal investigation above 1400°C was carried out in argon in a horizontal, resistance furnace, with a molybdenum winding. The tested samples were pressed into pellets, sintered (for presynthesis), placed into small boats (made from Pt30Rh) and then fused. The temperature was measured by an optical pyrometer, calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$.

The quenching technique was also used for phase determination. Specimens equilibrated in a furnace (with a Pt30Rh winding) were quenched in ice. Freezing a specimen from the horizontal furnace was not possible (molybdenum easy oxidized at elevated temperature). The maximum cooling rate in this furnace, starting at 1800°C, was *ca*. 20°/min.

The X-ray powder analysis was performed by Siemens D5000 and HZG-4 diffractometers (Guinier camera, Cu-K_α radiation, Ni filter). The phase purity of the reagents and the phase composition of the alloys were controlled microscopically. Microsections were made from molten and crystallized samples and examined in reflected light.

RESULTS AND DISCUSSION

The phase diagram of the YPO_4 — $Ba_3(PO_4)_2$ system, shown in Fig. 1, is determined over the full composition range (in the subsolidus region) from room temperature to 1950°C. As it was found from initial thermal experiments, all the samples melted at temperatures above 1400°C. Therefore, in order to obtain the liquidus and solidus curves, heteromolar mixtures of the initial orthophosphates were presynthesized in the solid phase. The presynthesis consisted in heating the mixtures at 900°C for 2 h, which was followed by heating at 1450°C for 45 min. After each stage of the heating the samples were cooled to room temperature and thoroughly rubbed. Such obtained sinters were pressed into pellets and fused in a horizontal furnace. The melting (or the start melting) temperatures were read pyrometrically, therefore, the liquidus and solidus curves have a suggested position and are drawn by dashed lines.

Specimen of the composition 76.6 wt% $Ba_3(PO_4)_2$, 23.4 wt% YPO_4 melted at the highest temperature (1950°C). $Ba_3(PO_4)_2$ – poor specimens, in the composition range from *ca.* 45 to 76 wt% $Ba_3(PO_4)_2$, melted at the same temperature *ca.* 1800°C. It was recognized that elucidation of this striking behaviour of the above series of specimens could be found by investigation of phase dependences in the subsolidus region.

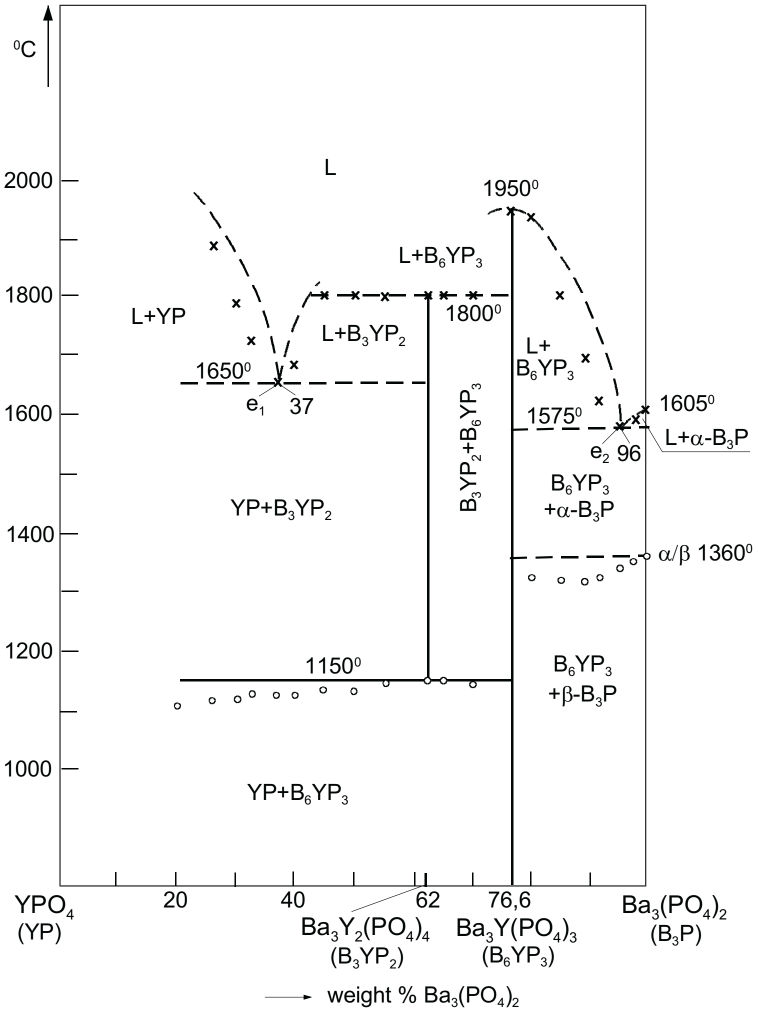

Figure 1. Phase diagram of the system YPO_4–$Ba_3(PO_4)_2$; ○ – DTA, x – optical.

The data for the subsolidus region were obtained from DTA during heating and cooling and by X-ray powder diffraction. For these reasons, the heteromolar mixtures of YPO_4 and $Ba_3(PO_4)_2$ orthophosphates underwent diversified thermal processes. The following heat treatments were used: (1) heating in the solid phase (for presynthesis, see conditions above), which was followed by cooling to room temperature, (2) heating to a temperature at which the samples became partly fused or completely melted, and then cooling to room temperature.

Phase composition of the products obtained was identified by X-ray powder diffraction. As a result, the occurrence of the intermediate compound $Ba_3Y(PO_4)_3$, known from [1,8], was noted in the system YPO_4—$Ba_3(PO_4)_2$. It formed at the molar ratio 1:1 of the initial orthophosphates (76.6 wt. % $Ba_3(PO_4)_2$, 23.4 wt. % YPO_4). X-ray phase analysis also showed at room temperature that, in the $Ba_3(PO_4)_2$-rich part, specimens consisted of a mixture of the orthophosphates $Ba_3Y(PO_4)_3$ and $Ba_3(PO_4)_2$. In the remaining composition range they were a mixture of YPO_4 and $Ba_3Y(PO_4)_3$. The $Ba_3Y(PO_4)_3$ melts congruently at 1950 ± 20° C, and it is stable down to room temperature. According to [8], the compound crystallizes in a regular structure of eulytite with the lattice parameter a = 10.4655 Å. $Ba_3Y(PO_4)_3$ and $Ba_3(PO_4)_2$ phosphates give a simple eutectic system with the composition 96 wt. % $Ba_3(PO_4)_2$ and 4 wt. % YPO_4 and it melts at 1575 ± 20°C. The congruent character of the melting of $Ba_3Y(PO_4)_3$ and the position of the eutectic in the phase diagram were confirmed by microscopy in reflected light.

The results described above suggested that only one intermediate compound, *i.e.* $Ba_3Y(PO_4)_3$, occurrs in the system YPO_4—$Ba_3(PO_4)_2$. It was striking, however, that in the DTA-cooling (1400 to 20°C) curves both for the specimens sintered and for the melted ones in the composition range YPO_4 — $Ba_3Y(PO_4)_3$, a strong thermal effect appeared at a 1150°C. In contrast, in the DTA curves for the specimen of the composition of $Ba_3Y(PO_4)_3$ no thermal effects were observed below 1400°C.

The discussed facts suggest supposition that: (1) phase dependences for the YPO_4-rich part of the system in question have a complicated character; (2) in this region, or at the molar ratio $YPO_4 : Ba_3(PO_4)_2 > 1$, another barium and yttrium orthophosphate can be formed. In fact, it results from literature that double orthophosphates of alkaline-earths and lanthanides, with the stoichiometry $M^{II}_3Ln(PO_4)_3$, are stable only at high temperature and at about 1200°C they decompose to $LnPO_4$ and $M^{II}_3(PO_4)_2$. However, the phosphate $Ba_3Y(PO_4)_3$ is stable down to room temperature. On the other hand, the about 1150°C effect appears in the DTA curves for the YPO_4-rich part of the system. Therefore, the following varied thermal investigations were undertaken.

The initial orthophosphates were mixed in the assumed molar ratios (in the range 45–76 wt. % $Ba_3(PO_4)_2$) and were: (1) sintered at 1200, 1350 or 1450°C, then frozen (in ice) from these temperatures, (2) presynthesized, pressed into pellets which were melted in the horizontal furnace and coolled (cooling rate 20°/min.). It was found by X-ray powder diffraction that the samples of these series were a mixture of the phosphates YPO_4 and $Ba_3Y(PO_4)_3$. In the X-ray patterns only for the melted specimens, in the composition range 62–76 wt% $Ba_3(PO_4)_2$, some additional diffuse spots of low intensity used to appear. This phase composition suggested that only one intermediate compound, *i.e.* $Ba_3Y(PO_4)_3$, occurs in the system. Thus, it was necessary to carry out additional investigations. The orthophosphates YPO_4 and $Ba_3Y(PO_4)_3$ in turn were used as the initial substance to produce specimens of the composition range in question.

An equimolar mixture of these compounds was thermally treated (in an atmosphere of argon in the horizontal furnace) by: (1) sintering at 1550°C for 30 min and cooling to room temperature, (2) sintering at 1650°C for 30 min and cooling to room temperature, (3) heating to 1810°C (the sample became partly melted) and cooling to room temperature. In each variant the cooling rate was 20°/min. The above thermal processing was repeated for the respective specimens encapsulated in (sealed) tubes made from a Pt30Rh alloy. This processing series was carried out to check whether the samples under argon would or would not decompose at high temperatures. The phase composition of the obtained products was X-ray inspected. X-ray patterns of the specimens thermally treated, as described in point 1), revealed spots originated from YPO_4 and the eulytite-structure phase. However, the phase composition of specimens treated, as in the next two points, was slightly different. In the composition range 45–60 wt% $Ba_3(PO_4)_2$ specimens were a mixture of YPO_4 and the eulytite-structure phase. Anyway, X-ray patterns of specimens from the composition range 62–76 wt% $Ba_3(PO_4)_2$ showed spots from the eulytite-structure phase and a few additional diffuse, low-intensity spots. The result of these experiments indicates that a second intermediate compound occurs in the system YPO_4 — $Ba_3(PO_4)_2$. It was assumed to be formed at the 2:1 molar ratio of the parent orthophosphates (*i.e.* YPO_4 and $Ba_3(PO_4)_2$) and has the formula $Ba_3Y_2(PO_4)_4$, melting incongruently at 1800 ± 20°C according to the reaction: $Ba_3Y_2(PO_4)_4 \rightarrow Ba_3Y(PO_4)_3$ + liquid. $Ba_3Y_2(PO_4)_4$ is stable only at high temperatures. At 1150°C it decomposes to YPO_4 and $Ba_3Y(PO_4)_3$. This decomposition is fast and the freezing from high temperature (*i.e.* 1650–1810°C), at the rate 20°/min, does not result in yielding the $Ba_3Y_2(PO_4)_4$ in the phase-purity form. Observations by microscopy in reflected light confirmed the peritectic character of the compound as well as its decomposition. For the above aspects, establishing the existence of the orthophosphate $Ba_3Y_2(PO_4)_4$ was essentially made difficult and its structure could not be determined. The phosphates YPO_4 and $Ba_3Y_2(PO_4)_4$ give an eutectic which melts at 1650 ± 20°C and has the composition 37 wt. % $Ba_3(PO_4)_2$, 63 wt. % YPO_4.

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