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THE SYSTEM YPO_4– $Mg_3(PO_4)_2$– $Mg_2P_2O_7$

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Phase equilibria in the systems YPO_4–$Mg_3(PO_4)_2$, YPO_4–$Mg_2P_2O_7$ and YPO_4– $Mg_3(PO_4)_2$ –$Mg_2P_2O_7$ have been examined by thermal, X-ray and microscopic methods. Their phase diagrams have been provided.

Keywords: phase diagrams, phase equilibria microscopic – thermal, X-ray methods

Introduction

During examinations of the ternary system Y_2O_3– MgO– P_2O_5, the partial system YPO_4– $Mg_3(PO_4)_2$– $Mg_2P_2O_7$ was investigated.

The system YPO_4– $Mg_3(PO_4)_2$– $Mg_2P_2O_7$ is surrounded by three side binary systems. Two of them: YPO_4– $Mg_3(PO_4)_2$ and YPO_4– $Mg_2P_2O_7$ have not been examined before and the third one $Mg_3(PO_4)_2$– $Mg_2P_2O_7$ has been investigated by Berak [1].

As results from literature reports systematic phase examinations in the partial system YPO_4– $Mg_3(PO_4)_2$– $Mg_2P_2O_7$ have not been carried out, either. No mixed magnesium– yttrium phosphates have been obtained. There are only few literature data on mixed alkaline earth metals– lanthanide phosphates. Reference [2] describing barium and strontium– lanthanide orthophosphates was published in 1970. In 1980 McCarthy *et al.* [3] reported on calcium– lanthanide orthophosphates. As results from references [2, 3] there exist binary orthophosphates with the formula $M_3Ln(PO_4)_3$ (where M = Sr, Ba, Ca, Ln = La-Gd). These compounds have the $Bi_4(SiO_4)_3$ eulytite structure.

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Experimental

The following starting materials were used: Y_2O_3, 99.99% (ZOCh), H_3PO_4, 85% analytical grade (Xenon), MgO, analytical grade (POCh) and $MgHPO_4 \cdot 3H_2O$, analytical grade (BDH– England).

Yttrium orthophosphate YPO_4 was obtained from a solution containing 0.4 wt% of Y_2O_3, 15 wt% of P_2O_5 (as H_3PO_4), 84.6 wt% of distilled water by the method given in reference [4].

Magnesium pyrophosphate $Mg_2P_2O_7$ was prepared from $MgHPO_4 \cdot 3H_2O$ by heating at 900°C for one hour.

Magnesium orthophosphate $Mg_3(PO_4)_2$ was prepared from $Mg_2P_2O_7$ and MgO by heating at 1200°C for 20 minutes.

The systems YPO_4– $Mg_3(PO_4)_2$, YPO_4– $Mg_2P_2O_7$ and YPO_4– $Mg_3(PO_4)_2$– $Mg_2P_2O_7$ were examined by differential thermal analysis (DTA), X-ray powder diffraction, and microscopic analysis in reflected light. Molten and sintered samples were used for thermal analysis. High temperature thermal studies above 1400°C were performed in a vertical resistance furnace with molybdenum winding, under argon. The examined samples were prepared as follows: the weighed components were mixed, ground, pressed into pellets, placed in platinum boats, precalcined at 1000°C and then fused. Temperatures were read by means of an optical pyrometer which was calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$. Thermal analysis during heating was performed on 0.5 g samples using a derivatograph type 3427 (MOM, Hungary) within the temperature range 20° to 1400°C at a heating rate of 10 $deg \cdot min^{-1}$. High purity alumina was used as the standard reference material. The temperature was measured with a Pt/Pt10Rh thermocouple which was calibrated against the melting points of $Ca_2P_2O_7$, K_2SO_4 and NaCl and the polymorphic transition temperature of K_2SO_4 (583°C).

The phase purity of the reagents 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.

Phase identification was made with CuK_α-radiation with an HZG-4 diffractometer.

Results and discussion

The system YPO_4–$Mg_3(PO_4)_2$ was examined for the first time in this laboratory. Samples for the investigations were synthesized from the starting phosphates and then underwent complex thermal treatment. Sintering temperatures: 800°–1300°C, time of sintering 30 min – 7 days. The sintered samples were either cooled slowly down to room temperature or frozen in ice. The samples were also heated without preliminary synthesis up to 1200°, 1250° and 1300°C and then frozen in ice. Molten samples were cooled with grafting. X-ray photographs of the samples prepared in this way always showed the mixture of YPO_4 and $Mg_3(PO_4)_2$, which means that the starting orthophosphates did not form new compounds. Figure 1 presents the phase diagram of the system YPO_4–$Mg_3(PO_4)_2$.

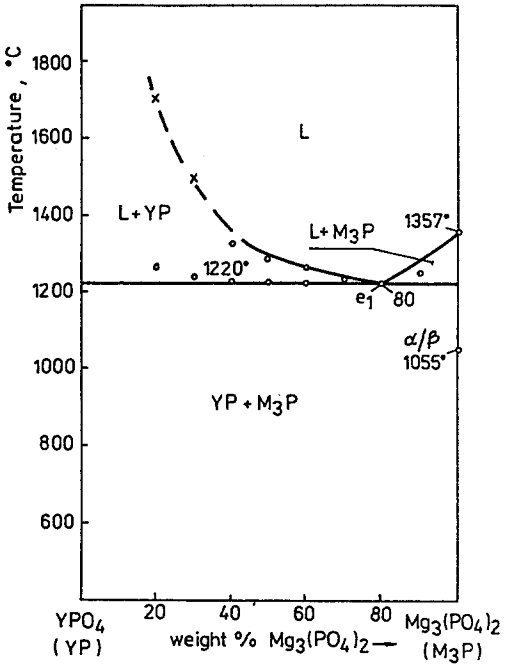

Fig. 1 Phase diagram of the system YPO_4 – $Mg_3(PO_4)_2$; o – thermal analysis, x – optical

$Mg_3(PO_4)_2$ melts congruently at 1357°C. YPO_4 forms with $Mg_3(PO_4)_2$ an eutectic e_1 at 80 wt% of $Mg_3(PO_4)_2$ at 1220°C. The liquidus curve over the composition range 40–100 wt% of $Mg_3(PO_4)_2$ was estimated on the basis of differential thermal analysis. In the other part of the system, the melting points were read by means of an optical pyrometer. In the YPO_4– $Mg_3(PO_4)_2$ system, the thermal effect resulting from the polymorphic transition α/β– $Mg_3(PO_4)_2$ occurring at 1055°C was not observed.

The system YPO_4– $Mg_2P_2O_7$ was investigated over the entire composition range up to approx. 1650°C. Figure 2 presents its phase diagram. Samples for examinations were prepared from the starting phosphates and treated preliminarily by sintering in the temperature interval 800°–1300°C. Refrigeration from different temperatures was used as well. The phase composition of the products obtained was identified with X-ray. It was discovered that the initial phosphates form a simple eutectic system. The temperature of the eutectic e_2 is 1300°C and the composition: 55 wt% of $Mg_2P_2O_7$ and 45 wt% of YPO_4. The liquidus curve over the composition range 55–100 wt% of $Mg_2P_2O_7$ was estimated on the basis of differential thermal analysis. In the other part of the system, the melting points were read by means of an optical pyrometer. The polymorphic transition β/γ – $Mg_2P_2O_7$ at 68°C produces strong thermal effects on the DTA curves over the whole system, while the effect of the α/β transition can be noticed only within the composition range 40–100 wt% of $Mg_2P_2O_7$.

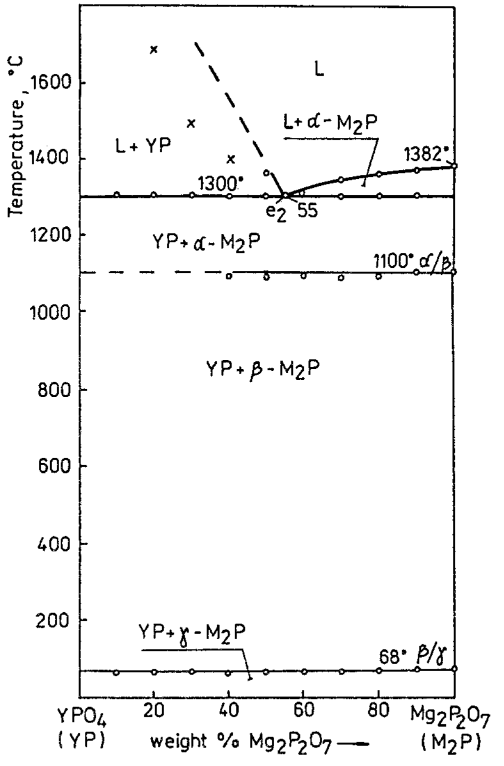

Fig. 2 Phase diagram of the system YPO_4 – $Mg_2P_2O_7$; o – thermal analysis, x – optical

The system YPO_4–$Mg_3(PO_4)_2$– $Mg_2P_2O_7$ was examined by preparing samples from the starting phosphates. Figure 3 presents its phase diagram. Solidification isotherms are marked on the diagram. It is a simple eutectic system. The ternary eutectic E_1 occurs at 1200°C. In the composition range under investigation, there are three primary crystallization fields of binary compounds which contact along lines: e_1E_1 – of binary eutectic (YPO_4 + $Mg_3(PO_4)_2$), e_2E_1 – of binary eutectic (YPO_4 + $Mg_2P_2O_7$) and e_3E_1 – of binary eutectic ($Mg_2P_2O_7$ + $Mg_3(PO_4)_2$). The primary crystallization field of YPO_4 occurs over the composition range $YPe_1E_1e_2$, of $Mg_3(PO_4)_2$ over $e_1M_3Pe_3E_1$, and of $Mg_2P_2O_7$ over $e_3M_2Pe_2E_1$.

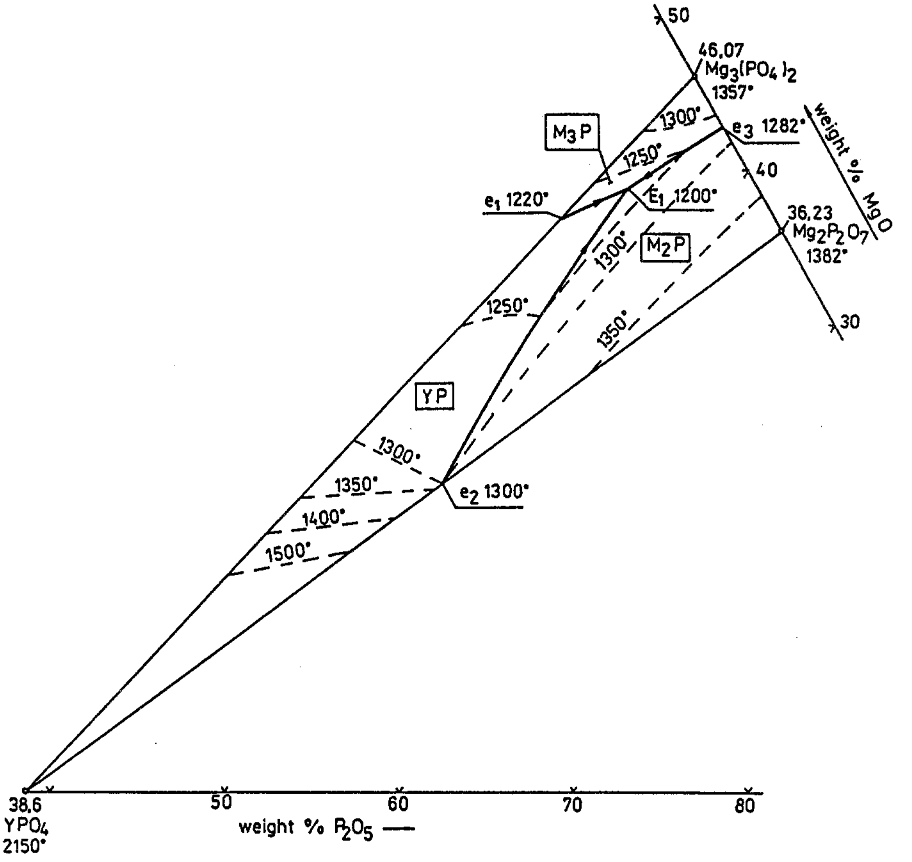

Fig. 3 Phase diagram of the system $YPO_4 - Mg_3(PO_4)_2 - Mg_2P_2O_7$, $YPO_4 = YP$, $Mg_3(PO_4)_2 = M_3P$, $Mg_2P_2O_7 = M_2P$

References

1 J. Berak, Rocz. Chem., 32 (1958) 17.
2 G. Blasse, J. Solid State Chem., 2 (1970) 27.
3 G. J. McCarthy and D. E. Phoertsch, J. Solid State Chem., 38 (1980) 128.
4 G. Czupinska and T. Znamierowska, Mater. Chem. Phys., 27 (1991) 217.

Zusammenfassung — Mittels thermischen, röntgenografischen und mikroskopischen Methoden wurden die Phasengleichgewichte in den Systemen $YPO_4 - Mg_3(PO_4)_2$, $YPO_4 - Mg_2P_2O_7$ und $YPO_4 - Mg_3(PO_4)_2 - Mg_2P_2O_7$ untersucht und deren Phasendiagramme ermittelt.