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Phase equilibria in the system YPO_4–$Mg(PO_3)_2$

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Abstract

The previously unknown binary system YPO_4–$Mg(PO_3)_2$ has been examined by thermal, X-ray and microscopic analysis and its phase diagram is provided. A new compound has been discovered and assigned the formula $MgYP_3O_{10}$. This phosphate melts incongruently at 1080°C.

INTRODUCTION

There are no literature reports on the existence of mixed magnesium–lanthanide phosphates. There have been no systematic phase examinations of the system Y_2O_3–MgO–P_2O_5.

Phase equilibria in the YPO_4–$Mg(PO_3)_2$ system have been investigated in our studies on the ternary system Y_2O_3–MgO–P_2O_5.

EXPERIMENTAL

The following starting materials were used: Y_2O_3 99.99%, analytical grade; MgO, analytical grade, $MgHPO_4 \cdot 3H_2O$, analytical grade, and $NH_4H_2PO_4$, analytical grade.

Yttrium orthophosphate YPO_4 was obtained from the solution containing 0.4wt.% Y_2O_3, 15 wt.% P_2O_5 (as H_3PO_4), 84.6 wt.% distilled water by the method given in ref. 1. Yttrium metaphosphate $Y(PO_3)_3$ was obtained from Y_2O_3 and H_3PO_4. The initial components were mixed carefully and sintered for 3 days at 200, 300 and 900°C. Yttrium phosphate $Y_2P_4O_{13}$ was prepared from Y_2O_3 and $NH_4H_2PO_4$ by the method given in ref. 2.

Magnesium pyrophosphate $Mg_2P_2O_7$ was prepared from $MgHPO_4 \cdot 3H_2O$ by heating at 900°C for 1 h. Magnesium metaphosphate $Mg(PO_3)_2$ was prepared from $Mg_2P_2O_7$ and H_3PO_4 by heating at 900°C for 1 h.

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The binary system YPO_4–$Mg(PO_3)_2$ was examined by differential thermal analysis (heating), powder X-ray diffraction, and microscopy in reflected light.

The high temperature thermal studies were performed in a vertical resistance furnace with molybdenum winding, under argon. The samples examined 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 type 3427 derivatograph (MOM, Hungary) within the temperature range 20-1400°C at a heating rate of 10°C min^{-1}. High purity alumina was used as the standard substance. The temperature was measured with a Pt/Pt–10%Rh 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 Cu Kα radiation with an HZG-4 diffractometer.

RESULTS AND DISCUSSION

The system YPO_4–$Mg(PO_3)_2$ was examined in this laboratory by differential thermal analysis of heating and by X-ray methods. Figure 1 shows the phase diagram.

It was discovered that in the system there is an intermediate compound at the molar ratio YPO_4 to $Mg(PO_3)_2$ of 1:1. This compound was assigned the formula $MgYP_3O_{10}$. The tripolyphosphate $MgYP_3O_{10}$ is formed peritectically. The peritectic reaction is irreversible. For that reason, and because there is a susceptibility to form glasses in the system, thermal analysis of cooling could not be used. The phosphate $MgYP_3O_{10}$ does not show any polymorphic transitions. This phosphate is formed with difficulty, and several attempts were made to obtain it in pure form. On the basis of the examinations carried out, four methods of obtaining $MgYP_3O_{10}$ were established: (1) from the stoichiometric mixture of magnesium oxide MgO and yttrium metaphosphate $Y(PO_3)_3$ by sintering at 1000°C for 3 h; (2) from the stoichiometric mixture of phosphates YPO_4 and $Mg(PO_3)_2$ by partial melting at 1050°C, then slow cooling to 950°C and sintering at this temperature for 24 h; (3) from the stoichiometric mixture of phosphates $Y_2P_4O_{13}$ and $Mg_2P_2O_7$ by sintering at 900 and 1000°C for 24h at each temperature; (4) from the mixture composed of 1 mol of Y_2O_3, 2 mol of

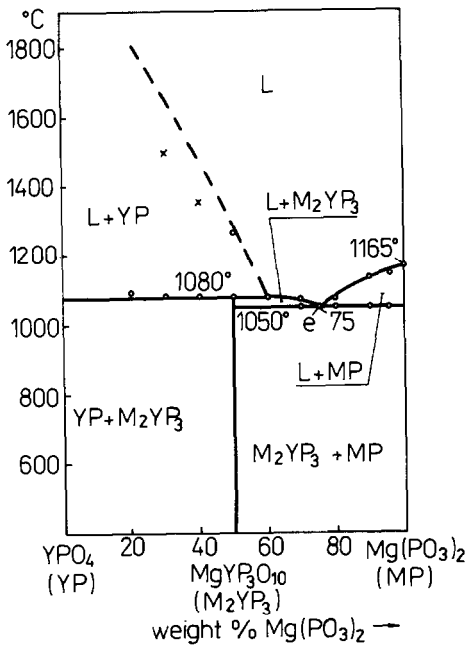

Fig. 1. Phase diagram of the system YPO_4–$Mg(PO_3)_2$. ○, thermal analysis; ×, optical analysis.

MgO and 6 mol of $NH_4H_2PO_4$ by sintering at 200, 300, 650 and 950°C for 24 h at each temperature. A pure $MgYP_3O_{10}$ phase could not be obtained by any of these methods. A preparation with the smallest amount of impurities in the form of foreign phases (YPO_4 and $Mg(PO_3)_2$) was obtained by the first method. $MgYP_3O_{10}$ is synthesized with most difficulty from the phosphates YPO_4 and $Mg(PO_3)_2$, and this product contains the most impurities, which are initial phosphates. Because of these difficulties, the phase diagram shown in Fig. 1 was established by the synthesis of samples from (1) YPO_4 and $MgYP_3O_{10}$ (over the composition range up to approximately 50 wt.% $Mg(PO_3)_2$), and (2) $MgYP_3O_{10}$ and $Mg(PO_3)_2$ (over the composition range from approximately 50–100 wt.% $Mg(PO_3)_2$). Samples for investigation were presynthesized by sintering the mixture of initial phosphates within the temperature range 1000–1050°C. The liquidus curve, over the composition range 60–100 wt.% $Mg(PO_3)_2$, was drawn on the basis of differential thermal analysis of heating. In the other part of the system, the melting points were measured with the use of an optical pyrometer, because there were no effects resulting from melting on the DTA curves. The tripolyphosphate $MgYP_3O_{10}$ melts incongruently, forming YPO_4 and a liquid rich in $Mg(PO_3)_2$ at 1080°C. The peritectic reaction finishes at approximately 60 wt.% $Mg(PO_3)_2$. In the YPO_4–$Mg(PO_3)_2$ system, a eutectic (Fig. 1) occurs at 1050°C, at a content of 75 wt.% $Mg(PO_3)_2$.

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