Journal of Thermal Analysis, Vol. 36 (1990) 639-643

THE SYSTEM KPO_3 –$Y(PO_3)_3$

G. Czupińska and *T. Znamierowska*

DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF ENGINEERING AND ECONOMICS, ACADEMY OF ECONOMICS, 53345 WROCLAW, POLAND

(Received June 5, 1989)

The previously unknown binary system KPO_3-$Y(PO_3)_3$ has been examined by thermal, X-ray and microscopic analysis and its phase diagram provided. The existence of the compound $KY(PO_3)_4$ has been confirmed. Its melting point (700°, incongruent) and basic parameters of the unit cell (monoclinic system, space group $P2_1/n$, lattice parameters: a = 7.36, b = 8.36, c = 14.39 Å, $\beta = 96.1°$) have been determined. The new, so far unknown, compound has been discovered and assigned the formula $K_2Y(PO_3)_5$. It has been found that it forms peritectoidally (in the solid phase) at 642°.

The literature on rare-earth elements and their compounds with other chemical elements is abundant. Double condensed phosphates of rare-earths and alkali metals are of fundamental importance because of the wide range of their application (laser and luminescent materials) [1-6]. Most publications deal with methods of synthesis and X–ray structural investigations, but the number of papers describing basic research on phase equilibria, especially in systems M^IPO_3-$Ln(PO_3)_3$ (M^I-alkali metal, Ln-rare-earth element) is continuously increasing. As can be concluded from these publications, two types of mixed metaphosphates $M^ILn(PO_3)_4$ and $M^I_2Ln(PO_3)_5$ which form peritectically have been discovered [7-10]. The present work describes the results of our investigations on the system KPO_3-$Y(PO_3)_3$. This system has not been known until now, only the occurrence of the compound $KY(PO_3)_4$ has been mentioned in the literature [11].

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Experimental

The following starting materials were used: Y_2O_3, 99.99% (ZOCh), H_3PO_4 85% analytical grade (Xenon), KH_2PO_4 analytical grade (POCh) and K_2CO_3 analytical grade (POCh).

Poassium metaphosphate KPO_3 was obtained from KH_2PO_4 by sintering at 300° for 30 min.

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°. Yttrium ultraphosphate YP_5O_{14} was obtained from Y_2O_3 and H_3PO_4. The initial compounds mixed together in stoichiometric ratio were sintered for 3 days at 200, 300 and 700°.

The binary system KPO_3-$Y(PO_3)_3$ was examined by differential thermal (DTA), X-ray powder diffraction, microscopic in reflected light analysis and IR spectroscopy.

Samples for the study weighing from 0.5 to 3g were prepared from potassium and yttrium metaphosphates. The parent substances were mixed carefully and ground, then pressed into pellets and pre-synthesized by sintering at 600° for 24h. Thermal analysis during cooling was carried out at a speed of 5-10 deg min^{-1}. The temperature was measured with a Pt/PtRh 10 thermocouple which was calibrated against the melting points of NaCl and K_2SO_4 and the polymorphic transition temperature of K_2SO_4 (583°). Thermal analysis during heating was performed on 0.5 g samples using a derivatograph type 3427 (MOM, Hungary) within the temperature range 20 to 1000°, at a heating rate of 10 deg min^{-1}. High-purity alumina was used as the standard reference material.

The initial components and the new phases formed in the system KPO_3-$Y(PO_3)_3$ were identified by X-ray powder diffraction on a HZG-4 diffractometer with CuK_α-radiaton. The purity of reagents and phase structure of the substance was controlled microscopically in reflected light. Infrared spectra were recorded on an IR-75 Specord spectrophotometer using samples in the form of KBr pellets.

Results and discussion

The binary system KPO_3-$Y(PO_3)_3$ has not been previously known and has been studied in this laboratory over a full range of compositions and

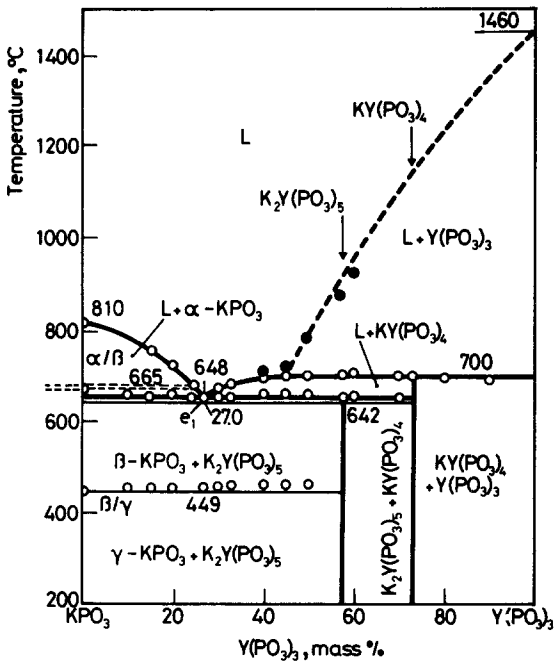

Fig. 1 Phase diagram of the system KPO_3 – $Y(PO_3)_3$ o – thermal analysis; • – visual

temperatures. Figure 1 presents its phase diagram. Studies have shown that the system KPO_3-$Y(PO_3)_3$ contains two intermediate compounds of 1:1 and 2:1 ratios, having the general formulas: $KY(PO_3)_4$ and $K_2Y(PO_3)_5$. The phosphate $KY(PO_3)_4$ melts incongruently to $Y(PO_3)_3$ and liquid at 700°. The compound $K_2Y(PO_3)_5$ forms peritectoidally (in the solid phase) at 642°. The peritectic point is at about 45 wt% of $Y(PO_3)_3$ and the eutectic temperature is 648°, the eutectic point corresponds to a concentration of 27 wt% of $Y(PO_3)_3$. The liquidus curve in the part of the system rich in $Y(PO_3)_3$ (over the composition range from approx 46 to 100 wt% of $Y(PO_3)_3$) was determined by visual observation as the thermal effects connected with melting were not observed on the DTA heating curves. Thermal analysis with cooling is not possible because of the irreversible decomposition of yttrium metaphosphate which can be noticed above 1000°. The visual observation consisted in taking notes of the temperature when the first traces of liquid

were seen, and of the temperature at which the sample liquefied completely and became transparent.

The investigations proved that double potassium-yttrium metaphosphates are difficult to obtain in a pure form, expecially $K_2Y(PO_3)_5$. As a result of many attempts, it was discovered that the most phase-pure compound $KY(PO_3)_4$ can be obtained by sintering a stoichiometric mixture of KPO_3 and $Y(PO_3)_3$ at 600° for 48h. But the X–ray analysis has always shown the presence of minute quantities of $Y(PO_3)_3$. Powder X-ray examinations were performed to determine the structure of $KY(PO_3)_4$. A series of reflections deriving from $KY(PO_3)_4$ was obtained after eliminating diffraction lines of $Y(PO_3)_3$ from the produced X–ray photographs. On the basis of X–ray powder analysis it was found that $KY(PO_3)_4$ crystallizes in the monoclinic system of the following unit cell parameters: a = 7.36, b = 8.36, c = 14.39 Å, β = 96.1°. These results suggested that $KY(PO_3)_4$ is isomorphic with $KYbP_4O_{12}$ [12].

The compound $K_2Y(PO_3)_5$ is even more difficult to obtain in a pure form than $KY(PO_3)_4$. Many attempts at obtaining $K_2Y(PO_3)_5$ from different initial materials showed that the final product is always a mixture of $K_2Y(PO_3)_5$ and $KY(PO_3)_4$. It was discovered that the sintering of equimolar mixture of K_2CO_3 and YP_5O_{14} at 450 and 500° for 3 days at each of these temperature is the most favourable method of synthesis.

Samples from the system KPO_3-$Y(PO_3)_3$ are hygroscopic and very liable to form glasses.

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This paper was included in the CPBP-01.18 problem and was financially supported by the Ministry of National Education.

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Zusammenfassung – Das zuvor unbekannte binäre System KPO_3-$Y(PO_3)_3$ wurde mittels Thermo-, Röntgendiffraktions- und mikroskopischer Analyse untersucht und das Phasendiagramm aufgestellt. Die Existenz der Verbindung $KY(PO_3)_4$ wurde dabei bekräftigt. Ihr Schmelzpunkt (700°, inkongruent) und die grundlegenden Parameter der Elementarzellen (monoklines System, Raumgruppe $P2_1/n$, Gitterkonstanten: $a = 7.36$, $b = 8.36$, $c = 14.39$ Å, $\beta = 96.1°$) wurden ermittelt. Weiterhin wurde eine neue, bislang unbekannte Verbindung mit der Formel $K_2Y(PO_3)_5$ entdeckt. Sie verfügt (in fester Phase) über ein Peritektikum bei 642°.