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SYNTHESES OF MIXED METAPHOSPHATES $KY(PO_3)_4$ AND $K_2Y(PO_3)_5$

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In the ternary system Y_2O_3-K_2O-P_2O_5 the binary system KPO_3-$Y(PO_3)_3$ has been examined. There are two intermediate metaphosphates $KY(PO_3)_4$ and $K_2Y(PO_3)_5$ in it. On the basis of thermal analysis and powder X-ray diffraction, the methods of synthesizing these compounds were prepared.

From numerous publications on lanthanides and their compounds many deal with alkalimetal-lanthanide phosphates, and within this group several are concerned with mixed metaphosphates of these chemical elements [1-4]. Two types of mixed metaphosphates with formulas $M^{I}Ln(PO_3)_4$ and $M^{I}_2Ln(PO_3)_5$ (where: M = alkali metals, Ln = lanthanides) were found to exist [5-8]. Literature information on these compounds deals mainly with methods of synthesis and X-ray investigations. However, there are very few examinations of phase equilibria in the system $M^{I}PO_3$-$Ln(PO_3)_3$. Therefore, the phase diagram of the system KPO_3-$Y(PO_3)_3$ is not known. The occurrence of the compound $KY(PO_3)_4$ is only mentioned in reference [9].

Experimental

Samples for thermal investigations were prepared from ready reagents or from reagents synthesized in this laboratory. The following compounds were used: potassium dihydrophosphate KH_2PO_4 analytical grade, potassium carbonate K_2CO_3 analytical grade, yttrium oxide Y_2O_3, 99.99% and H_3PO_4 85% analytical grade.

Potassium metaphosphate KPO_3 was prepared from KH_2PO_4 by heating at 300° for 0.5 h and then at 500° for 2 h. Yttrium metaphosphate $Y(PO_3)_3$ was obtained from Y_2O_3 and H_3PO_4. The initial components were mixed

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carefully and sintered for 3 days at 200, 300 and 900°. Yttrium ultraphosphate YP_5O_{14} was synthesized from Y_2O_3 and H_3PO_4. The starting materials mixed together in stoichiometric ratio were sintered for 3 days at 200, 300 and 700°.

The investigations were carried out by differential thermal analysis, powder X-ray diffraction, microscopy in reflected light and IR spectroscopy. In the thermal analysis a derivatograph type 3427 (MOM, Hungary) was used within the temperature range 20-1450°, at a heating rate of 10 deg/min, platinum cup, air atmosphere. Typical samples varied from 250 mg to 500 mg. High-purity alumina was used as the standard material. Powder X-ray analysis was performed with an HZG-4 diffractometer with $CuK_{\bar{\alpha}}$ radiation.

Results

The phase diagram of the KPO_3-$Y(PO_3)_3$ system was examined and determined in this laboratory. The existence of the $KY(PO_3)_4$ compound was confirmed on the basis of thermal and X-ray analyses. It was also discovered that in this system one more, previously unknown mixed metaphosphate with the formula $K_2Y(PO_3)_5$ occurs. The conditions of obtaining them were examined as well. Both metaphosphates were found to form with difficulty, especially $K_2Y(PO_3)_5$ and complex conditions of synthesis were necessary. Despite numerous attempts, phase pure preparations were not obtained.

Figure 1 presents the thermal curves of the compound $KY(PO_3)_4$. The effect at 700° occurring on DTA curve was found to be connected with the decomposition of $KY(PO_3)_4$. $Y(PO_3)_3$ was identified (X-ray analysis) in products of decomposition. Therefore, the sintering of stoichiometric quantities of KPO_3 and $Y(PO_3)_3$ at 600° for 48 h is the best method to obtain the $KY(PO_3)_4$. X-ray analysis of the obtained product showed the presence of $KY(PO_3)_4$ and small quantities of $Y(PO_3)_3$. The fact is reflected in a minute effect on DTA curve at 648° (Fig. 1) which results from the eutectic.

Numerous attempts to obtain the $K_2Y(PO_3)_5$ phosphate using different initial materials showed that the mixture of both compounds: $K_2Y(PO_3)_5$ and $KY(PO_3)_4$ is obtained. It is reflected on DTA curve of a sample with the composition of the $K_2Y(PO_3)_5$ compound (Fig. 2). The effect at 642° is connected with the decomposition of the phosphate $K_2Y(PO_3)_5$ in solid phase. The other two effects at 650 and 715° were interpreted as follows. Because thermal analysis is performed at a rate of 10 deg/min, the decomposition of

$K_2Y(PO_3)_5$ begins with partial formation of the $KY(PO_3)_5$ phosphate at 642°. Thus, the effect at 650° may result from further decomposition and from the eutectic. The third effect at 715° is connected with a decomposition of $KY(PO_3)_4$.

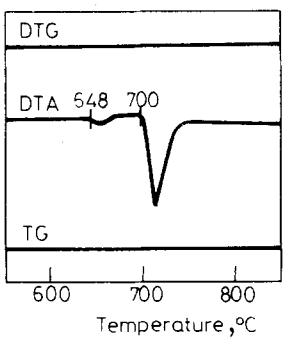

Fig. 1 DTA, TG and DTG curves of $KY(PO_3)_4$

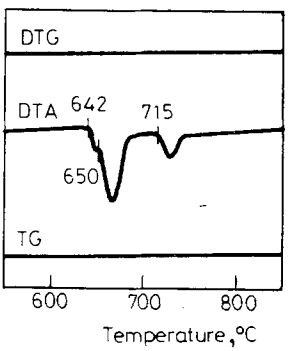

Fig. 2 DTA, TG and DTG curves of $K_2Y(PO_3)_5$

On the basis of thermal and powder X-ray diffraction two methods of synthesizing the mixed metaphosphate $K_2Y(PO_3)_5$ were prepared: 1) stoichiometric mixture of KPO_3 and $Y(PO_3)_3$ was sintered at 450, 500 and 550° for 3 days at each temperature, 2) the mixture of K_2CO_3 and YP_5O_{14} at the molar ratio 1:1 was sintered at 450 and 500° for 3 days at each temperature. More phase pure preparation is synthesized by the second method.

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Zusammenfassung — Im Dreikomponentensystem Y_2O_3-K_2O-P_2O_5 wurde das binäre System KPO_3-$Y(PO_3)_3$ untersucht. Darin existieren zwei intermediäre Metaphosphate $KY(PO_3)_4$ und $K_2Y(PO_3)_5$. Unter Anwendung thermoanalytischer und röntgenographischer Verfahren wurden die Methoden zur Herstellung dieser Verbindungen ausgearbeitet.