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THE FORMATION AND STABILITY OF HYDRATED AND ANHYDROUS URANYL PHOSPHATES

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ABSTRACT

The stabilities of the hydrated uranyl phosphates $(UO_2)_3(PO_4)_2 \cdot 4\,H_2O$, $UO_2HPO_4 \cdot 4\,H_2O$, and $UO_2(H_2PO_4) \cdot 3\,H_2O$ have been reinvestigated. The compounds identified by thermal analysis have been prepared isothermally and characterised by their strongest X-ray reflections. During dehydration, oxygen was not evolved and the crystalline compounds $(UO_2)_3(PO_4)_2$, $(UO_2)_2P_2O_7$, $UO_2(PO_3)_2$, and probably $(UO_2)_3P_4O_{13}$ were found. At still higher temperatures, the uranyl phosphates are reduced. The decomposition products lose phosphorus oxide above 1300—1400°C. The present results are summarized in a tentative pseudo-binary phase diagram UO_x (x = 3 to 2)—$UO_2(PO_3)_2$.

INTRODUCTION

Extensive studies have been published on the conditions of formation [1—3] and the thermal stabilities [3—15] of the hydrated uranyl phosphates, but conflicting decomposition paths still remain. The anhydrous materials have been obtained, but their nature has not been investigated. Only the polymerisation of the phosphate groups in $UO_2(PO_3)_2$ has been studied [10], whereas interest was more concentrated on the reduction of uranium at higher temperatures [10—12, 16].

As part of a study on the uranyl phosphates and arsenates, the dehydration of the hydrates, as well as the formation and stability of the anhydrous compound in the system UO_3—$UO_2(PO_3)_2$ have been investigated. Compositions between $UO_2(PO_3)_2$ and P_2O_5 have not been studied because a low-temperature (~400°C) reduction in that region has been reported [17].

EXPERIMENTAL

Materials

The starting materials were the hydrated uranyl phosphates $(UO_2)_3(PO_4)_2 \cdot 4\,H_2O$ and $UO_2HPO_4 \cdot 4\,H_2O$, prepared as described by Schaekers

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[11] and Schreyer [18], and $UO_2(H_2PO_4)_2 \cdot 3\,H_2O$ prepared according to Kamo and Ohashi [10]. To evaporate all traces of acetone, which had been used to wash the precipitates, the compounds were left under continuous suction in a desiccator containing a saturated NaCl solution for 8 h. Thereafter, they were left in the desiccator for at least one week to reach equilibrium. In this way, well-crystallised samples were obtained.

In accordance with earlier observations [4], compound $H_{11}(UO_2)_2(PO_4)_5$ could not be prepared. It seems doubtful whether the compound exists, because its preparation conditions and crystallographic data are rather simular to those of $UO_2(H_2PO_4)_2 \cdot 3\,H_2O$ [2].

The anhydrous uranyl phosphates $(UO_2)_3(PO_4)_2$, $(UO_2)_2P_2O_7$, and $UO_2(PO_3)_2$ were prepared from their hydrates. It was assumed that the uranium—phosphorus ratio was not altered during the drying process.

Chemical analysis

The hydrates were characterised by chemical analysis. Uranium was determined by means of a computerised potentiometric titration [19,20] and phosphorus by means of an acid—base titration after separation of the uranium from the solution using a cation exchanger. The water content was determined thermogravimetrically. The results are given in Table 1.

Physical measurements

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out with a Netzsch, type STA-429, apparatus. The effluent gas was analysed (EGA) with a water- and an oxygen-sensitive probe using a Panametric hygrometer model 1000 and a Teledyne analyser model 311, respectively. About 150 mg samples in alundum cups were heated at a heating rate of 2.5°C min^{-1} in a stream of dry nitrogen, air, or oxygen, up to 1500°C. The uncertainty in the observed temperatures was within 20°C.

The high-temperature X-ray (HTX) exposures were taken with a Nonius—Guinier III camera (Cu K_α-radiation, $\lambda = 1.5418$ Å). The samples were heated at 1.5°C min^{-1} in air up to 1000°C.

Static experiments

For further characterisation, the hydrates found by TGA, were prepared by means of isothermal heating. The temperatures were taken from the TGA. After the sample had stabilised to the expected weight, its X-ray pattern was recorded with a Guinier—de Wolff camera.

Anhydrous samples of various compositions were brought into a dry box after isothermal heating (each 100°C from 300 to 1000°C) in air during about 15 h. Thereafter, X-ray diagrams of the samples were taken while they were protected from moisture with polythene foil (0.05 mm).

TABLE 1

Chemical analysis of the uranyl phosphate hydrates

Sample	Uranium (wt. %)		Phosphorus (wt. %)		Water (wt. %)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$(UO_2)_3(PO_4)_2 \cdot 4\,H_2O$	66.14 ± 0.05	66.61	5.78 ± 0.01	5.78	6.71 ± 0.03	6.72
$UO_2HPO_4 \cdot 4\,H_2O$	54.30 ± 0.01	54.34	7.08 ± 0.01	7.07	18.50 ± 0.09	18.51
$UO_2(H_2PO_4)_2 \cdot 3\,H_2O$	45.85 ± 0.09	45.95	12.00 ± 0.02	11.96	17.18 ± 0.06	17.38

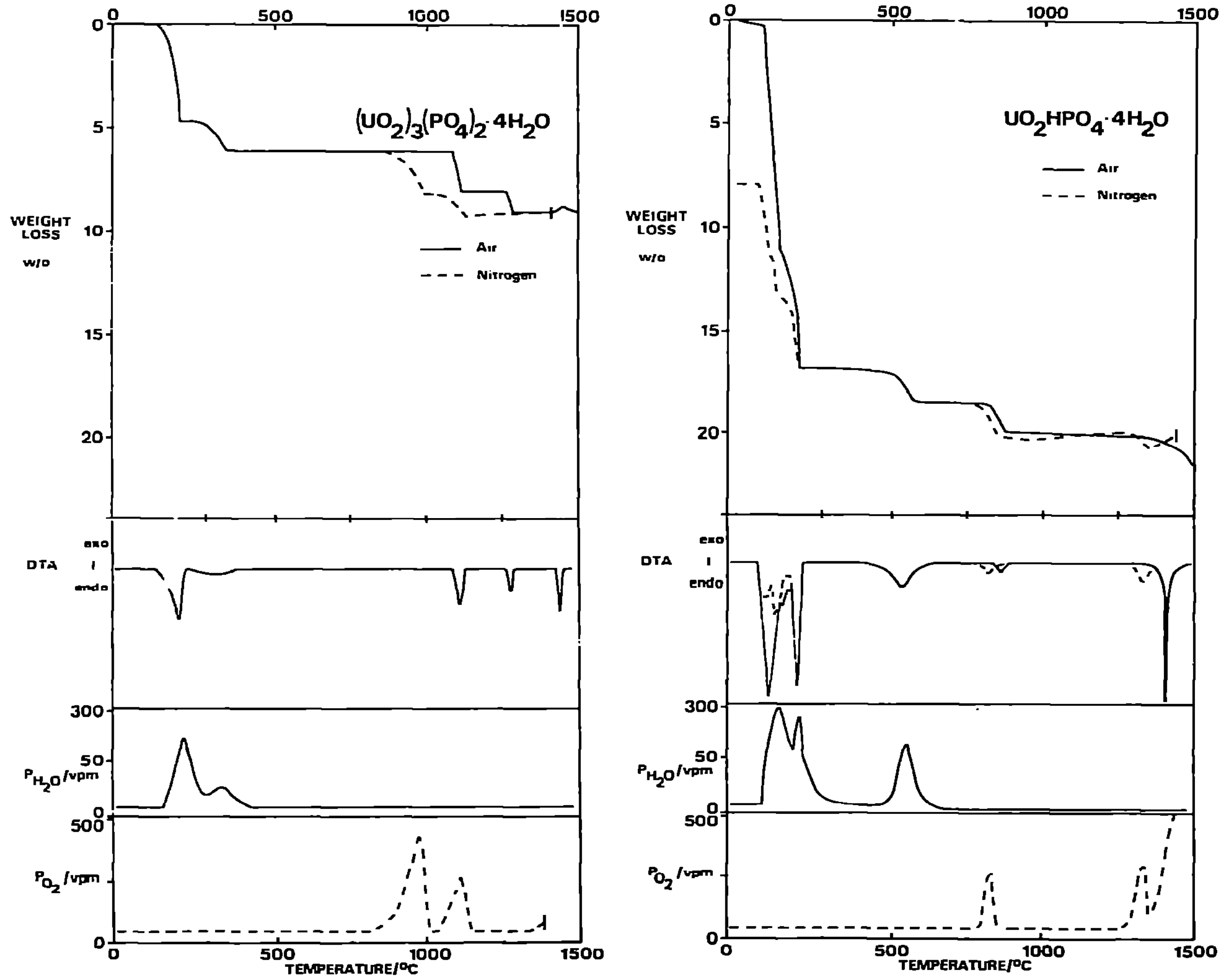
RESULTS AND DISCUSSION

Hydrates

Thermal analysis

The results of the thermal analyses are shown in Fig. 1. The evolution of water, but not of oxygen, was detected during the dehydrations. This proves that no reduction of the compounds occurs during these heatings. Thus, the anhydrous compounds formed are phosphates in which uranium is hexavalent. The DTA only indicates the thermal effects due to the dehydrations involved. Disagreement with the literature over the decomposition temperatures are possibly caused by differences in the experimental conditions, such as equipment, heating rate, and sample size. It seems more interesting to compare the presently observed decomposition steps with previous publications.

The observed decomposition of $(UO_2)_3(PO_4)_2 \cdot 4\,H_2O$ via its monohydrate



(c)

(b)

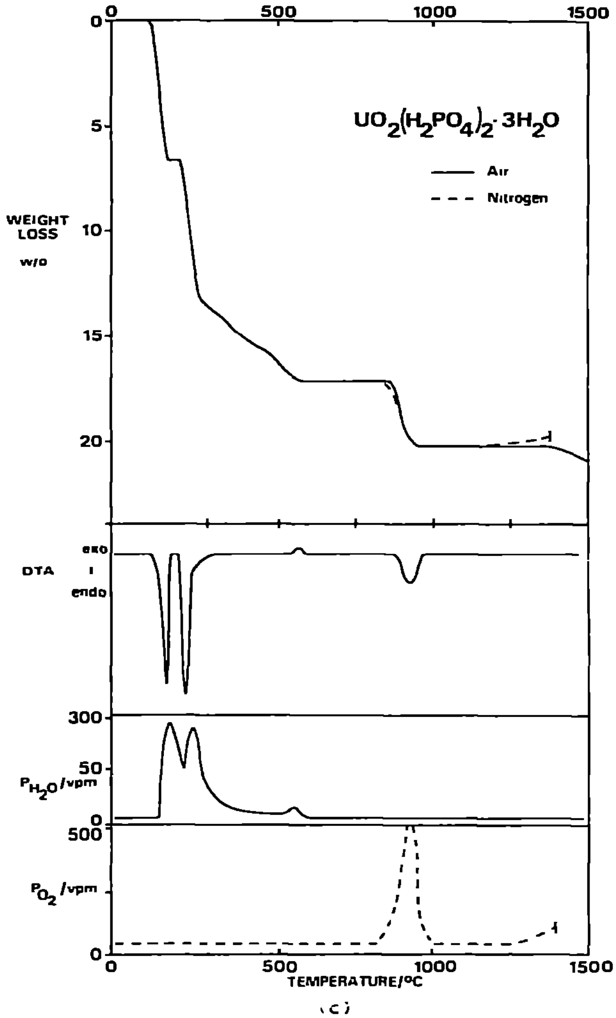


Fig. 1. Thermograms of uranyl phosphate hydrates in air and nitrogen. (a) $(UO_2)_3(PO_4)_2 \cdot 4\ H_2O$; (b) $UO_2HPO_4 \cdot 4\ H_2O$; (c) $UO_2(H_2PO_4)_2 \cdot 3\ H_2O$.

is in agreement with the findings of Schaekers [11], and Weigel and Hoffman [14]; the tetrahemi- or di-hydrates, which have been reported previously by Karpov and Ambartsumyan [5], and Domine-Berges [3], respectively, have not been found.

The decomposition path of $UO_2HPO_4 \cdot 4\ H_2O$ leads via its monohydrate and UO_2HPO_4 to $(UO_2)_2P_2O_7$, and will be discussed in combination with the results of the static experiments.

$UO_2(H_2PO_4)_2 \cdot 3\ H_2O$ decomposes via its monohydrate and $UO_2H_2P_2O_7$ to $UO_2(PO_3)_2$. This is in agreement with the observations by Kamo and Ohashi [10].

Static experiments

Most intermediate and final compounds described above have been prepared and crystallized at temperatures obtained from the thermal analyses. Their formation is in agreement with the changes of mass involved during

TABLE 2

Interplanar spacings of the strongest intensities of uranyl phosphates

The *d* values are uncorrected and the intensities are visually estimated.

Compound	*d* (Å)					100 I/I_0				
$(UO_2)_3(PO_4)_2 \cdot 1\ H_2O$	4.80	3.49	2.82	1.915	2.19	100	95	70	70	70
$(UO_2)_3(PO_4)_2 \cdot {\sim}0.5\ H_2O$	4.20	5.22	3.26	3.02	3.53	100	80	80	80	60
γ-$(UO_2)_3(PO_4)_2$	4.80	2.75	6.40	3.55	1.770	100	100	80	80	70
β-$(UO_2)_3(PO_4)_2$	3.50	3.25	2.75	4.78	1.775	100	100	90	60	60
α-$(UO_2)_3(PO_4)_2$ (750°C)	4.80	2.75	7.05	3.50	3.57	100	70	60	40	40
$UO_2HPO_4 \cdot 2\ H_2O$ *	2.99	3.55	5.75	4.90	4.57	100	70	60	60	50
$UO_2HPO_4 \cdot 1\ H_2O$	5.22	4.20	3.54	4.25	2.98	100	100	80	70	60
$(UO_2)_2P_2O_7$	3.55	4.27	5.20	11.9	5.40	100	95	80	70	70
$(UO_2)_3P_4O_{13}$ *	4.80	3.50	7.15	2.75	4.02	100	80	60	60	50
$UO_2(H_2PO_4)_2 \cdot 1\ H_2O$	6.22	4.42	3.32	4.32	2.82	100	90	70	70	70
$UO_2H_2P_2O_7$	5.70	6.75	3.00	3.48	4.72	100	50	50	40	30
γ-$UO_2(PO_3)_2$	4.42	7.90	5.90	3.69	3.43	100	80	80	80	80
β-$UO_2(PO_3)_2$ (650°C)	4.05	3.47	4.25	5.45	6.05	100	90	70	40	40
α-$UO_2(PO_3)_2$ (780°C)	4.10	3.50	4.30	5.58	6.10	100	95	95	50	50

* Poorly crystalline samples.

these isothermal experiments. Only UO_2HPO_4 does not become crystalline. The five strongest reflections of the new compounds are given in Table 2.

In contradiction to the observations during the thermal analysis of $UO_2HPO_4 \cdot 4\ H_2O$, a dihydrate of this compound is formed. It can be prepared either by passing dry nitrogen at ambient temperature over the tetrahydrate or by rehydration of the monohydrate.

Several authors have published observations on the thermal decomposition of the tetrahydrate. Some of them reported the formation of a dihydrate [14,15] and some did not [9,12,13]. From the present observations, it becomes clear that the dihydrate does exist, but that the experimental conditions determine if it can be observed.

The very hygroscopic $(UO_2)_3(PO_4)_2$ probably forms a hemihydrate after a short exposure to humid air. This compound also has not been observed by thermal analysis.

TABLE 3

Comparison of the decomposition temperatures of uranium phosphates in air

Reaction	Temperature range (°C)	
	This work	Other workers [ref.]
$3\,(UO_2)_3(PO_4)_2 \rightleftharpoons U_3O_8 + 3\,U_2O_3P_2O_7 + 2\,O_2\uparrow$	1090—1120	1060—1090 [12]
$U_3O_8 + 3\,U_2O_3P_2O_7 \rightleftharpoons 3\,U_3O_5P_2O_7 + O_2\uparrow$	1260—1300	1200—1282 [12]
$(UO_2)_2P_2O_7 \rightleftharpoons U_2O_3P_2O_7 + \frac{1}{2}\,O_2\uparrow$	790—885	800—880 [16]
$U_2O_3P_2O_7 \rightleftharpoons (UO)_2P_2O_7 + \frac{1}{2}\,O_2\uparrow$ *	>1280?	1200—1340 [16]
$UO_2(PO_3)_2 \rightleftharpoons UP_2O_7 + O_2\uparrow$	845—965	900—1000 [10]

* Not observed in air; the figures given are in nitrogen.

Anhydrous compounds

Thermal analysis

Our results obtained by the thermal analyses (Fig. 1) are quite similar to the results published by Schaekers [11,12,16] and Kamo and Ohashi [10]. The observed mass losses and the oxygen evolution are in agreement with the decomposition reactions previously found; only minor differences in the temperatures have been observed. The decomposition reactions and the presently found temperatures are given in Table 3. At lower oxygen pressures, all decompositions occur at lower temperatures. This has previously been reported by Schaekers [11,12] for $(UO_2)_3(PO_4)_2$ and $(UO_2)_2P_2O_7$. We have obtained similar results for $UO_2(PO_3)_2$ and agree with his conclusion that, although the reaction products do not reoxidise noticeably, the reactions are nevertheless reversible. The X-ray diagrams obtained from the residues after thermal analysis (1500°C) indicate a shift to compounds with less phosphorus. This indicates the evolution of phosphorus oxide, with which Schaekers [12,16] explained the weight loss at 1300—1400°C. In contradiction to his findings, we do not unequivocally observe the decomposition in nitrogen of $U_2O_3P_2O_7$ into $(UO)_2P_2O_7$ which has been reported to take place at about 1200—1340°C. This reaction might occur simultaneously with the evolution of phosphorus oxide, which starts at 1280°C, but no final conclusions can be drawn presently.

In addition, the mixtures of the uranyl phosphates and amorphous UO_3 in the compositions 87.7, 70.5, 53.9, 45.5 and 40.0 at.% U * have been thermally analysed. They appear to decompose like the constituent compounds.

Static experiments

All samples on isothermal heating (the same compositions as mentioned previously) appear to decompose prior to melting. This is in contradiction to

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* Throughout this paper, at.% U = 100 U/(U + P).

the findings of Kamo and Ohashi [10], who have reported that $UO_2(PO_3)_2$ melts at about 650°C during the thermal analysis. Because we found that precrystallised samples (at 650°C) do not melt, we suggest that the high heating rate they used (12°C min^{-1}) does not permit a full dehydration, and that the samples have dissolved in their water of hydration.

Primarily, three crystalline anhydrous uranyl phosphates, ortho-, pyro-, and meta-phosphates, have been observed. The glassy mass obtained in the composition range between $(UO_2)_2P_2O_7$ and $UO_2(PO_3)_2$ crystallizes after prolonged heating (1 week between 600 and 700°C). The still poorly crystalline sample shows a distinct X-ray pattern. From experiments with additional mixtures at 37.0, 39.2, 41.2, 43.6, 44.6 and 47.8 at.% U, it has been concluded that the composition of the compound is close to $(UO_2)_3P_4O_{13}$. This new compound has not been investigated. Its strongest X-ray reflections are given in Table 2.

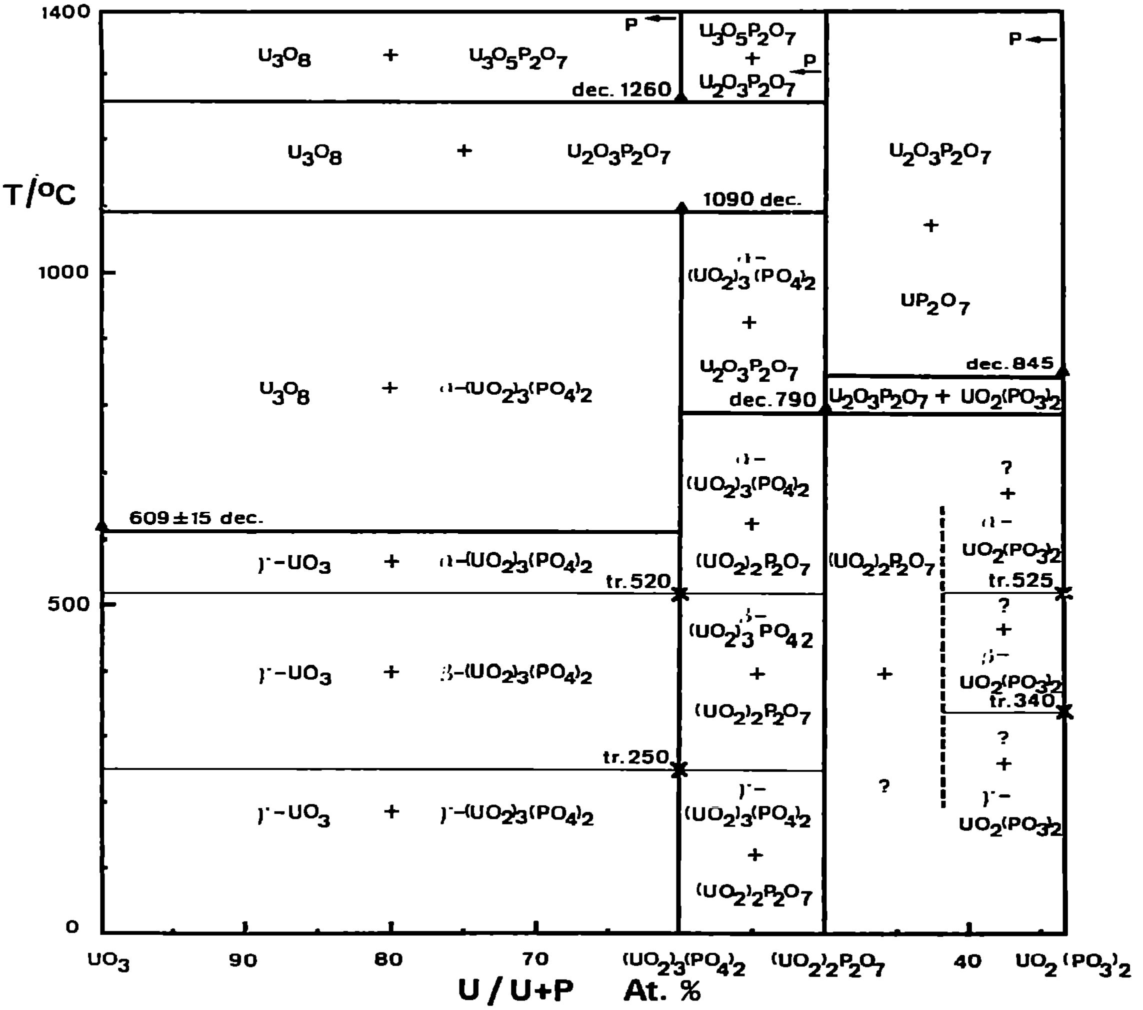

Fig. 2. Tentative pseudo-binary phase diagram UO_x ($x = 3$ to 2)—$UO_2(PO_3)_2$ at 21.7 kPa (0.214 atm) oxygen pressure. * = Phase transitions; P↑ = evolution of phosphorus oxide; ? = probably $(UO_2)_3P_4O_{13}$.

The compounds γ-$(UO_2)_3(PO_4)_2$, $(UO_2)_2P_2O_7$ and γ-$UO_2(PO_3)_2$ have been prepared from their hydrates after heating at, respectively, 500, 820 and 650°C in 1 atm oxygen for 15 h. As indicated by the prefix γ, two more high-temperature phases (β and α) have been observed on the HTX exposures. The transition temperatures can be read from the phase diagram given in Fig. 2, in which the present conclusions are summarised. In this figure, the decomposition temperature of γ-UO_3 has been calculated from the oxygen pressure measurements by Cordfunke and Aling [21], whereas the decomposition of U_3O_8 has been neglected. The accuracy of the temperatures given is about 20°C.

For characterisation purposes, the strongest reflections of the anhydrous uranyl phosphates have also been given in Table 2.

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