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# Synthesis, characterization, and structure determination of the orthorhombic $U_2(PO_4)(P_3O_{10})$

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## Abstract

$\beta$ - $UP_2O_7$  has been synthesized under hydrothermal conditions ( $\theta = 500^\circ\text{C}$ ,  $P = 200$  MPa), using  $UO_2$  and  $H_3PO_4$ .  $\beta$ - $UP_2O_7$  crystallizes in the orthorhombic space group  $Pn2_1a$ , with  $a = 11.526$  (2) Å,  $b = 7.048$  (2) Å,  $c = 12.807$  (2) Å and  $Z = 4$ . Its structure has been determined through direct methods and difference Fourier synthesis and has been refined to  $R = 0.0396$ . The structure is built on  $UO_8$  polyhedral chains along the  $b$ -axis.  $PO_4^{3-}$  and  $P_3O_{10}^{5-}$  groups coexist in the structure and the latter groups form non-linear chains. Cohesion of the structure is made through the linkage of  $UO_8$  chains by  $PO_4$  and  $P_3O_{10}$  groups leading to the formula  $U_2(PO_4)(P_3O_{10})$  instead of  $\beta$ - $UP_2O_7$ . Vibrational and optical spectra confirm the results obtained by X-ray diffraction. DTA–TGA measurements show that the transformation of  $U_2(PO_4)(P_3O_{10})$  to the cubic  $\alpha$ - $UP_2O_7$  occurs at  $\theta = 870^\circ\text{C}$ .

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## 1. Introduction

The chemistry of tetravalent actinide phosphates has been extensively re-examined since 1994. This renewed interest was correlated with the evidence that  $U_3(PO_4)_4$ ,  $(U_2O_3)P_2O_7$ ,  $(UO)_2P_2O_7$  and  $Th_3(PO_4)_4$  compounds do not exist [1]. These formulae must be replaced by  $U(UO_2)(PO_4)_2$  for the first two compounds [2],  $U_2O(PO_4)_2$  [3] for the third and  $Th_4(PO_4)_4P_2O_7$  [4] for the last one.  $U(UO_2)(PO_4)_2$  can be synthesized in air at  $1170^\circ\text{C}$  through several routes involving wet and dry chemistry methods. The diuranium oxide phosphate,  $U_2O(PO_4)_2$  can only be prepared through heat treatments under inert conditions.  $Th_4(PO_4)_4P_2O_7$  and  $U(UO_2)(PO_4)_2$  form limited or complete solid solutions with actinides [5–7]. Several precursors of these solids have also been synthesized using wet chemistry methods ( $UCIPO_4 \cdot 2H_2O$  [8,9],  $UBrPO_4 \cdot 2H_2O$  [9] and  $UOHPO_4$  [10]) or hydrothermal reaction ( $Th_2(PO_4)_2HPO_4 \cdot H_2O$ ,  $Th(OH)PO_4$  and  $Th_2O(PO_4)_2$  [11]).

Tetravalent thorium and uranium diphosphates have been synthesized for a long time. Both are stable in the cubic and orthorhombic form [12–14]. These compounds are respectively noted  $\alpha$ - $ThP_2O_7$ ,  $\alpha$ - $UP_2O_7$  and  $\beta$ - $ThP_2O_7$ ,  $\beta$ - $UP_2O_7$ . These solids were synthesized only in powder form. The ab initio structure determination of  $\alpha$ - $UP_2O_7$  was recently reported by Cabeza et al. [15] from XRD powder measurements.

Up to now, no crystal data of  $\beta$ - $UP_2O_7$  and  $\beta$ - $ThP_2O_7$  have been reported in the literature, while these solids play an important role in the reactions involved in the formation of  $U(UO_2)(PO_4)_2$ ,  $U_2O(PO_4)_2$  and  $Th_4(PO_4)_4P_2O_7$  at high temperature. The determination of the structure of  $\beta$ - $UP_2O_7$  from single-crystal measurements is reported in this work. It is completed by spectrometric and thermogravimetric measurements.

## 2. Experimental

### 2.1. Hydrothermal synthesis conditions

The double capsule technique was used for the hydrothermal syntheses. A mixture of 300 mg of

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Ni+NiO and 100 mg of water was loaded into a platinum capsule (30 mm long, 3.6 mm diameter and 0.1 mm thick wall) sealed by welding. The platinum capsule containing the initial reactants including 200 mg of orthophosphoric acid (15 M) and 150 mg of  $\text{UO}_{2.12}$  was put into an outer gold capsule (60 mm long, 5 mm diameter and 0.1 mm thick wall). The gold capsule was then welded shut. A pre-experimental rupture test was made by heating the gold capsule in an oven at  $\theta = 120^\circ\text{C}$ , followed by weighing to check for leaks. The oxygen fugacity was fixed at  $10^{-22}$  atm by the Ni/NiO buffer [16].

Runs were conducted in the 300–780°C temperature range, at  $P = 200$  MPa.  $\beta$ - $\text{UP}_2\text{O}_7$  single-crystals were always obtained, indicating that the product is stable in these conditions. They crystallize in the orthorhombic system. The cubic variety was never observed in these synthesis conditions while it is always obtained upon using wet or dry chemistry methods [1,8]. The size of the dark green crystals is up to 1 mm in length.

## 2.2. Electron-probe microanalysis

The compositions of the synthesized phases were determined by electron-probe microanalyses using a CAMECA SX50 electron microprobe equipped with four wavelength-dispersive spectrometers. The instrument operating conditions were 15 kV accelerating voltage, 10 nA probe current and 1  $\mu\text{m}$  probe diameter. The standards used were sintered  $\text{UO}_{2.12}$  for uranium and  $\text{KTiPO}_4$  for phosphorus determinations. Counting times on standards and samples were 10 s on the peak maximum and 5 s on the background. The oxygen contents were calculated by stoichiometry. Oxidation states were fixed at +IV for uranium (as proved in the following sections) and at +V for phosphorus. The composition of the precipitated single crystals was determined by electron-probe micro-analysis and the U/P ratio was unambiguously equal to 1/2.

## 2.3. Thermal measurements

DTA-DTG measurements were performed using a Setaram TG92–16.5 mg of the ceramic were put in an alumina boat. The sample was heated to 1200°C with a heating rate of  $5^\circ\text{C min}^{-1}$  and cooled to room temperature with a cooling rate of  $5^\circ\text{C min}^{-1}$ .

## 2.4. Vibration spectroscopies

The Raman spectrum was recorded with a Dilor XY spectrophotometer. An objective with a  $80\times$  magnification was linked to the spectrophotometer allowing the analyses of single crystals. The incident radiation was produced by a Spectra-Physics argon(-ion) laser ( $\lambda_0 = 514.5$  nm). The spectral resolution was around

$2\text{ cm}^{-1}$  with a slit width of 150  $\mu\text{m}$ . The laser power was 1000 mW. The infrared spectrum of the solid was recorded on a 150 mg KBr–2 mg  $\text{UP}_2\text{O}_7$  mixture plate, with a Nicolet 210 FT-IR spectrophotometer.

## 2.5. X-Rays

A parallelepiped-like single crystal was mounted on a goniometric system for structural analysis. Data were collected on a “Nonius Kappa CCD area Detector.” In all 598 images were collected with a 100 s exposition time for each image. The data collection and the cell refinement were, respectively, performed by COLLECT [17] and SCALEPACK on the HKL program [18]. Data reduction was realized by SCALEPACK and DENZO in HKL. To solve the structure, SIR97 program was used [19]. Empirical absorption correction was made by using spherical harmonic functions using the SORTAV program [20].  $T_{\text{min}}$  and  $T_{\text{max}}$  transmission factor values are, respectively, equal to 0.21 and 0.45. The reliability factor of the mean equivalent reflections ( $R_{\text{int}}$ ) calculated before and after the correction is 0.12 and 0.09, respectively.

The diffraction conditions yielded two possible space groups,  $Pnma$  and  $Pn2_1a$ . The model was first refined in the centrosymmetric space group  $Pnma$ , but features such as partially occupied sites and improbable polyhedral geometries indicated that this was not the correct space group. In fact, the orthorhombic form of uranium diphosphate  $\beta$ - $\text{UP}_2\text{O}_7$  crystallizes in the space group  $Pn2_1a$ . The experimental data and data collection parameters are reported in Table 1. The unit-cell parameters are  $a = 11.526$  (2),  $b = 7.048$  (2) and  $c = 12.807$  (2) Å. This result is in good agreement with that reported by Douglass and Staritsky [13]:  $a = 11.526$ ,  $b = 12.810$  and  $c = 7.045$  Å and by Burdese and Borlera [14]:  $a = 11.521$ ,  $b = 12.767$  and  $c = 7.044$  Å.

## 3. Results and discussion

The atomic positions are reported in Table 2. The anisotropic displacement factor<sup>1</sup> was refined only for the uranium and phosphorus atoms. Only the  $B_{\text{iso}}$  temperature factors were refined for the oxygen atoms. Selected interatomic distances and angles calculated from Table 1 are reported in Table 3.

### 3.1. Description of the structure

#### 3.1.1. Uranium coordination polyhedron

In the structure, uranium atoms are eight-fold coordinated and form  $\text{UO}_8$  dodecahedra (Fig. 1a). Six U–O bond lengths are within the 2.216–2.39 Å range,

<sup>1</sup> Deposited as supplementary information in a .CIF file.

Table 1  
Crystal data and structure refinement for  $U_2(PO_4)(P_3O_{10})$

|   |  |
|---|--|
| Empirical formula                           | $U_2(PO_4)(P_3O_{10})$   |
| Formula weight                              | 3295.76 g mol <sup>-1</sup>  |
| Temperature                                 | 293(2) K   |
| Wavelength                                  | 0.71070 Å  |
| Crystal system, space group                 | $Pn2_1a$   |
| Unit-cell dimensions                        | $a = 11.526(2)$ Å<br>$b = 7.048(2)$ Å<br>$c = 12.807(2)$ Å           |
| Volume                                      | 1040.4(4) Å <sup>3</sup>   |
| Z, Calculated density (g.cm <sup>-3</sup> ) | 4, 5.260   |
| Absorption coefficient                      | 31.79 mm <sup>-1</sup>   |
| $F(000)$                                    | 1424   |
| Crystal size                                | 0.040 × 0.025 × 0.05 mm  |
| Theta range for data collection             | 2.38–30.56°  |
| Index ranges                                | $-16 \leq h \leq 16$ , $-8 \leq k \leq 10$ ,<br>$-16 \leq l \leq 18$ |
| Reflections collected/unique                | 16949/1711 [ $R(int) = 0.09$ ]                                       |
| Completeness to $\theta = 30.56$            | 99.9%  |
| Refinement method                           | Full-matrix least-squares on $F^2$                                   |
| Data/restraints/parameters                  | 1711/1/113   |
| Final R indices [ $I > 2\sigma(I)$ ]        | $R_1 = 0.0396$ , $R_{w2} = 0.0794$                                   |
| R indices (all data)                        | $R_1 = 0.0549$ , $R_{w2} = 0.0882$                                   |
| Largest diff. peak and hole                 | 3.63 and $-2.40$ e Å <sup>-3</sup>                                   |

Table 2  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for  $U_2(PO_4)(P_3O_{10})^a$

| Atom  | x        | y        | z        | $U_{eq}^a$ |
|-------|----------|----------|----------|------------|
| U(1)  | 5294(1)  | 2151(2)  | 6727(1)  | 8(1)       |
| U(2)  | 1389(1)  | 7174(1)  | 6897(1)  | 9(1)       |
| P(1)  | -470(3)  | 7123(17) | 8827(3)  | 10(1)      |
| P(2)  | 7091(3)  | 2190(15) | 8706(3)  | 10(1)      |
| P(3)  | 1635(4)  | 7440(8)  | 4076(3)  | 11(2)      |
| P(4)  | 3382(4)  | 6684(8)  | 9039(3)  | 18(1)      |
| O(14) | 90(2)    | 8820(3)  | 8269(17) | 19(5)      |
| O(13) | 176(16)  | 5370(2)  | 8332(14) | 8(4)       |
| O(11) | -285(8)  | 6970(4)  | 9993(8)  | 19(3)      |
| O(12) | -1763(8) | 6980(3)  | 8569(7)  | 16(2)      |
| O(22) | 6500(13) | 410(2)   | 8275(12) | 14(4)      |
| O(21) | 8367(9)  | 1990(4)  | 8762(8)  | 21(2)      |
| O(23) | 6610(13) | 3800(2)  | 8069(12) | 10(4)      |
| O(33) | 730(9)   | 7270(3)  | 3268(7)  | 15(3)      |
| O(31) | 2785(11) | 6610(2)  | 3748(11) | 32(4)      |
| O(32) | 1302(9)  | 6677(18) | 5133(9)  | 20(3)      |
| O(41) | 2361(10) | 7542(16) | 8470(9)  | 13(3)      |
| O(42) | 4499(9)  | 6677(17) | 8565(9)  | 16(3)      |
| O(44) | 3425(10) | 7552(15) | 10172(9) | 13(3)      |
| O(43) | 3300(2)  | 4510(5)  | 9320(2)  | 109(9)     |

<sup>a</sup>  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

the other one are higher than 2.57 Å. The O(22)–O(14) and O(23)–O(13) edges are common to the U(1)O<sub>8</sub> and U(2)O<sub>8</sub> groups; leading to UO<sub>8</sub> infinite zigzag chains along the *b*-axis (Fig. 1b). Both U(1)O<sub>8</sub> and U(2)O<sub>8</sub> dodecahedra are similar and each can be described as an orthogonal interpenetration of two types of irregular

Table 3  
Selected bond lengths (Å) and angles (deg) for  $U_2(PO_4)(P_3O_{10})$ , and symmetry transformations used to generate equivalent atoms

| Atom | Atom    | $d$ (Å)   | Atom | Atom    | $d$ (Å)    |
|------|---------|-----------|------|---------|------------|
| U(1) | O(11)#1 | 2.225(10) | U(2) | O(12)#2 | 2.216(10)  |
|      | O(13)#2 | 2.276(18) |      | O(42)#4 | 2.285(11)  |
|      | O(33)#3 | 2.301(10) |      | O(32)   | 2.288(12)  |
|      | O(21)#4 | 2.310(10) |      | O(22)#7 | 2.297(16)  |
|      | O(31)#5 | 2.328(13) |      | O(41)   | 2.320(11)  |
|      | O(14)#6 | 2.36(2)   |      | O(23)#4 | 2.389(15)  |
|      | O(23)   | 2.571(16) |      | O(14)   | 2.58(2)    |
|      | O(22)   | 2.713(16) |      | O(13)   | 2.635(19)  |
| P(1) | O(11)   | 1.513(11) | P(2) | O(21)   | 1.479(11)  |
|      | O(12)   | 1.530(10) |      | O(23)   | 1.505(17)  |
|      | O(14)   | 1.54(2)   |      | O(22)   | 1.528 (19) |
|      | O(13)   | 1.57(2)   |      | O(44)#8 | 1.577(12)  |
|      |         |           | P(3) | O(33)   | 1.475(11)  |
|      |         |           |      | O(43)#9 | 1.51(3)    |
|      |         |           |      | O(32)   | 1.506(12)  |
|      |         |           |      | O(31)   | 1.508(14)  |
|      |         |           | P(4) | O(42)   | 1.424(12)  |
|      |         |           |      | O(41)   | 1.510(12)  |
|      |         |           |      | O(43)   | 1.56(3)    |
|      |         |           |      | O(44)   | 1.575(12)  |

| Atom    | Atom | Atom    | Angle (deg) |
|---------|------|---------|-------------|
| O(11)   | P(1) | O(12)   | 110.3(6)    |
| O(11)   | P(1) | O(14)   | 117.1(13)   |
| O(12)   | P(1) | O(14)   | 111.2(13)   |
| O(11)   | P(1) | O(13)   | 105.9(12)   |
| O(12)   | P(1) | O(13)   | 108.7(11)   |
| O(14)   | P(1) | O(13)   | 102.9(5)    |
| O(21)   | P(2) | O(23)   | 117.6(11)   |
| O(21)   | P(2) | O(22)   | 112.6(12)   |
| O(23)   | P(2) | O(22)   | 105.5(6)    |
| O(21)   | P(2) | O(44)#8 | 110.2(6)    |
| O(23)   | P(2) | O(44)#8 | 103.5(8)    |
| O(22)   | P(2) | O(44)#8 | 107.1(8)    |
| O(33)   | P(3) | O(43)#9 | 105.1(13)   |
| O(33)   | P(3) | O(32)   | 114.9(7)    |
| O(43)#9 | P(3) | O(32)   | 100.3(13)   |
| O(33)   | P(3) | O(31)   | 113.2(8)    |
| O(43)   | P(3) | O(31)   | 112.9(11)   |
| O(32)   | P(3) | O(31)   | 109.7(7)    |
| O(42)   | P(4) | O(41)   | 120.0(7)    |
| O(42)   | P(4) | O(43)   | 98.6(11)    |
| O(41)   | P(4) | O(43)   | 116.8(11)   |
| O(42)   | P(4) | O(44)   | 111.4(7)    |
| O(41)   | P(4) | O(44)   | 108.3(15)   |
| O(44)   | P(4) | O(43)   | 99.7(12)    |

Symmetry transformations used to generate equivalent atoms: #1:  $-x+1/2, y-1/2, z-1/2$ ; #2:  $x+1/2, y, -z+3/2$ ; #3:  $-x+1/2, y-1/2, z+1/2$ ; #4:  $x-1/2, y, -z+3/2$ ; #5:  $-x+1, y-1/2, -z+1$ ; #6:  $x+1/2, y-1, -z+3/2$ ; #7:  $x-1/2, y+1, -z+3/2$ ; #8:  $-x+1, y-1/2, -z+2$ ; #9:  $-x+1/2, y+1/2, z-1/2$ .

tetrahedra: (O23, O22, O33, O31) and (O13, O21, O11, O14) for U(1)O<sub>8</sub>; (O13, O14, O42, O41) and (O12, O32, O23, O22) for U(2)O<sub>8</sub>.

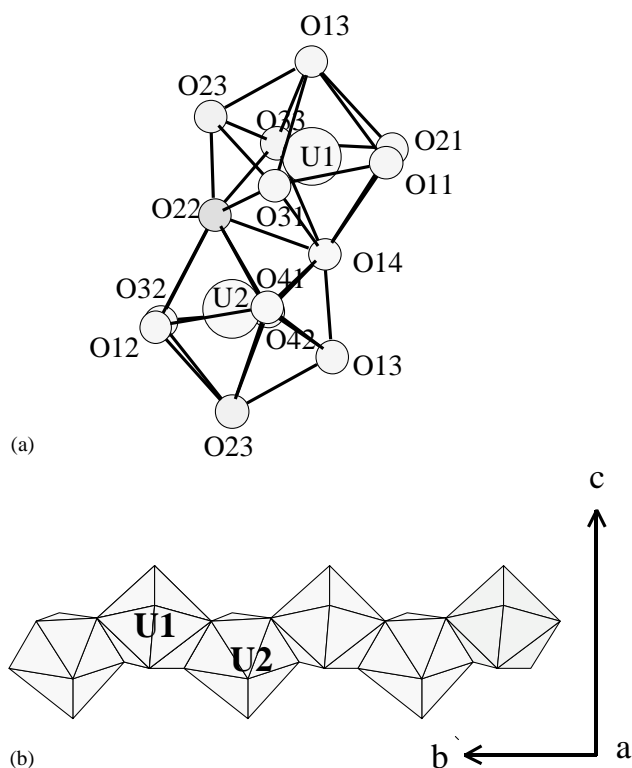


Fig. 1. (a) Perspective view of the eight-fold coordination polyhedron of uranium (IV) atom in  $U_2(PO_4)(P_3O_{10})$ . Both U(1) and U(2) positions are shown. (b) View of the  $UO_8$  chains formed along the  $b$ -axis.

### 3.1.2. Phosphorus coordination polyhedron

Four distinct positions of phosphorus atoms were observed in the structure. Each phosphorus atom is surrounded by four oxygen atoms and forms  $PO_4$  groups. The P(1) $O_4$  group forms a tetrahedral phosphate group with classical P(1)–O distances and O–P(1)–O angles (Table 3). The three other phosphorus groups P(2) $O_4$ , P(4) $O_4$  and P(3) $O_4$  are linked together by one vertex (O(44) and O(43) oxygen atoms) which leads to the existence of triphosphate groups. These groups are not linear and the P(2)–P(4)–P(3) angle (formed between the phosphorus atoms centered in the phosphate groups constituting the  $P_3O_{10}$  unit) is approximately  $96^\circ$  (Fig. 2). The two P–O–P angles of the  $P_3O_{10}$  group are equal to  $148$  and  $140^\circ$ . Furthermore, the P–P distances in this group are equal to  $3.00$  and  $2.96 \text{ \AA}$ . The P(4)–O distances and O–P(4)–O angles are not equal to the values generally determined for a phosphate group. This may be due to the central position of the P(4) atom in the  $P_3O_{10}$  group which leads to the distortion of this tetrahedron.

### 3.1.3. Cohesion of the structure

The U(1) $O_8$  polyhedron is linked to three  $PO_4$  groups and three  $P_3O_{10}$  groups by six vertices and to another  $P_3O_{10}$  group by one edge. The U(2) $O_8$  polyhedron is

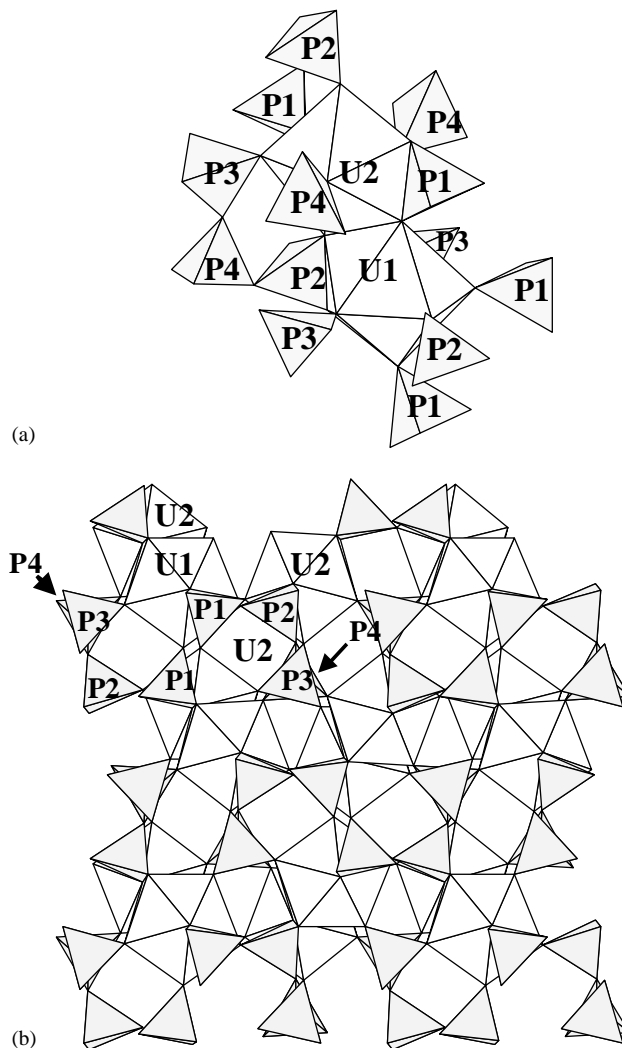


Fig. 2. (a) Representation of the arrangement between uranium (IV) coordination polyhedra, isolated phosphate groups (P(1)) and  $P_3O_{10}$  (P(3)–P(4)–P(2)) non-linear chains. (b) Projection of the structure of  $U_2(PO_4)(P_3O_{10})$  along the  $b$ -axis.

linked to two  $PO_4$  groups and four  $P_3O_{10}$  groups by six vertices and to another  $PO_4$  group by one edge. The  $P_3O_{10}$  group which share one edge with the U(1) $O_8$  polyhedron by one edge is attached to the U(2) $O_8$  polyhedron of the same chain by one vertex (Fig. 2). The cohesion of the structure is ensured by the linkage of  $UO_8$  chains by  $PO_4$  and  $P_3O_{10}$  groups. Each  $PO_4$  group maintains three different U-chains together. Each  $P_3O_{10}$  group binds together four different U-chains (Fig. 2b).

A similar type of phosphate-triphosphate arrangement has been reported for a monoclinic  $CsTa_2(PO_4)_2(P_3O_{10})$  compound [21]. In this product, the three  $PO_4^{3-}$  groups forming the  $P_3O_{10}^{5-}$  chain are arranged as a non-linear chain, as observed for the so-called  $\beta$ - $UP_2O_7$ . The P–P–P angle (formed between the phosphorus atoms centered in the phosphate groups constituting the  $P_3O_{10}$  unit) is also approximately  $90^\circ$ .

Two extensive reviews of polyphosphate chemistry [22,23] indicate that many monovalent cation triphosphates ( $\text{Na}_5\text{P}_3\text{O}_{10}$ ,  $\text{Ag}_5\text{P}_3\text{O}_{10}$ ,  $\text{K}_3\text{H}_2\text{P}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ , etc.), divalent and monovalent–divalent cation triphosphates ( $\text{Be}_2\text{NH}_4\text{P}_3\text{O}_{10}$ ,  $\text{Zn}_2\text{NH}_4\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$ , etc.) and trivalent and monovalent–trivalent cation triphosphates ( $\text{ScNaHP}_3\text{O}_{10}$ ,  $\text{MnM}^{\text{I}}\text{HP}_3\text{O}_{10}$ , etc.) are stable under various conditions. Triphosphates of higher valency cations have been prepared but the atomic arrangements proposed by the authors need to be revised [22]. The compounds which were prepared are  $\text{Th}_5(\text{P}_3\text{O}_{10})_4 \cdot 14.5\text{H}_2\text{O}$ ,  $\text{ThKP}_3\text{O}_{10}$ ,  $(\text{UO}_2)_5\text{Na}_5(\text{P}_3\text{O}_{10})_3 \cdot 19\text{H}_2\text{O}$ , and  $(\text{UO}_2)\text{Na}_3\text{P}_3\text{O}_{10} \cdot 8\text{H}_2\text{O}$ . These products were not obtained in our work even though we used sodium for some experiments.

Averbuch-Pouchot and Durif indicate that the triphosphate anion structure can be determined with reasonable accuracy from no more than 20 atomic arrangements [23]. The parameters that these authors considered as essential to describe the  $\text{P}_3\text{O}_{10}$  group are the P–P distances and the P–P–P and P–O–P angles. These groups are non-linear and the P–P–P angle can vary from  $84.5^\circ$  to  $151.3^\circ$ . In the  $\beta\text{-UP}_2\text{O}_7$  compound, the P–P–P angle determined ( $96^\circ$ ) is included in this range. Furthermore, the P–P distance and P–O–P angles determined for the  $\beta\text{-UP}_2\text{O}_7$  structure are in the range generally observed. It can also be noted that the central phosphorus atom of the triphosphate group is not located on a binary axis, as observed for half of the structural studies of compounds containing a triphosphate group [23].

The new data set concerning  $\beta\text{-UP}_2\text{O}_7$  leads to reconsider the formula of this compound which was already the case for  $\text{U}_3(\text{PO}_4)_4$ ,  $(\text{U}_2\text{O}_3)\text{P}_2\text{O}_7$  and  $\text{Th}_3(\text{PO}_4)_4$ . Consequently, its formula should be written  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$  instead of  $\beta\text{-UP}_2\text{O}_7$  and it should be called uranium phosphate triphosphate.

### 3.2. Optical spectroscopy

The UV-visible absorption spectrum was recorded on  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ . The main bands corresponding to the tetravalent uranium ( $5f^2$ ) are reported in Table 4. They are observed at 440, 450–500, 500–550, 550–690 and 800 nm, respectively, for the  $^3\text{P}_2$ ,  $^3\text{I}_6$ ,  $^3\text{P}_1$ ,  $^1\text{G}_4$ – $^1\text{D}_2$ – $^3\text{P}_0$  and  $^3\text{H}_6$  uranium (IV) levels as already described for the

Table 4  
Wavelength and assignment of uranium (IV) levels in  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$

| Wavelength (nm) | Assignment                                       |
|-----------------|--|
| 800             | $^3\text{H}_6$                                   |
| 550–690         | $^1\text{G}_4$ – $^1\text{D}_2$ – $^3\text{P}_0$ |
| 500–550         | $^3\text{P}_1$                                   |
| 450–500         | $^3\text{I}_6$                                   |
| 440             | $^3\text{P}_2$                                   |

spectra of  $\text{U}(\text{UO}_2)(\text{PO}_4)_2$ ,  $\text{U}_2\text{O}(\text{PO}_4)_2$ ,  $\text{UCiPO}_4 \cdot 2\text{H}_2\text{O}$  and  $(\text{Th}_{1-x}\text{U}_x)_4(\text{PO}_4)_4\text{P}_2\text{O}_7$  solid solutions [3]. Moreover, the four typical bands of the uranyl group, usually observed between 350 and 450 nm [2] are not present in the spectrum of  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ , which is consistent with the structural and chemical results.

### 3.3. Infrared and Raman spectroscopy

Raman and infrared spectra of  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$  were recorded at room temperature (Fig. 3). The spectrum is much more complicated than that of the cubic form which only exhibits six distinct peaks [24–26]. On this spectrum, the peak located at  $737\text{ cm}^{-1}$  (infrared spectrum) was assigned to the symmetric stretching of the P–O–P bond. Hubin [24] noted that the infrared spectra of isotype orthorhombic thorium diarsenate or diphosphate are much more complicated than those obtained for cubic compounds. This author explained the differences observed by the distortion of the P–O–P (As–O–As) angle in the  $\text{P}_2\text{O}_7$  ( $\text{As}_2\text{O}_7$ ) group.

According to Corbridge [27], the  $\text{P}_3\text{O}_{10}$  group (which can be written  $\text{O}_3\text{P}-\text{O}-\text{PO}_2-\text{O}-\text{PO}_3$ ) can be described for the vibrational spectra interpretation as an assembly of the vibrations of the  $\text{PO}_3$ ,  $\text{PO}_2$  and the P–O–P groups. In these conditions, for  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ , all the vibrations of the  $\text{PO}_2$ ,  $\text{PO}_3$ ,  $\text{PO}_4$  and P–O–P groups could be observed. Since these absorption bands generally overlap, it is not possible to give a more precise assignment than that proposed in Table 5. Moreover, the absence of the peak corresponding to the  $\text{UO}_2^{2+}$  group (observed at about  $892\text{ cm}^{-1}$  for  $\text{U}(\text{UO}_2)(\text{PO}_4)_2$ ) reveals that uranium is only present in the tetravalent oxidation state in this solid which is consistent with the dark-green color of the crystals obtained and the results suggested by study of optical spectroscopy.

As noted by Hubin and Tarte [26], the peak centered at  $737\text{ cm}^{-1}$  observed for the cubic  $\alpha\text{-UP}_2\text{O}_7$  is not observed on the Raman spectra of  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ . The P–O–P bond is not as marked in  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$  (that is

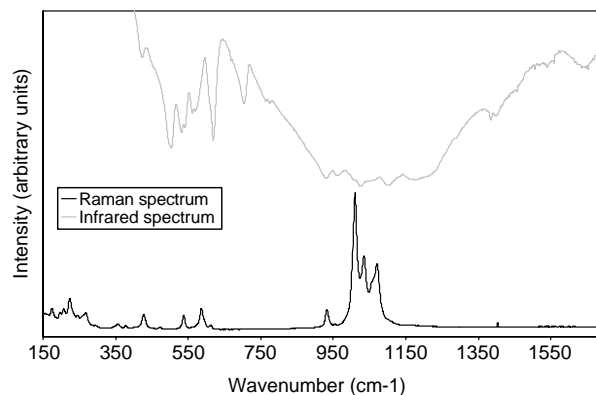


Fig. 3. Infrared and Raman spectra of  $\text{U}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ .

Table 5  
Assignment of the absorption bands observed in the infrared and Raman spectra for  $U_2(PO_4)(P_3O_{10})$

| Infrared spectra                 | Raman spectra         | Assignment  |
|----------------------------------|-----------------------|---|
| 1230 (w)                         |                       |   |
| 1094 (vs)                        | 1070 (s)<br>1057 (sh) | $\nu_{as}(P-O)$ in $PO_2$ , $PO_3$ and $PO_4$                                 |
|                                  | 1034 (s)              |   |
| 1020 (vs)                        | 1010 (vs)             |   |
| 946 (vs)                         | 932 (w)               | $\nu_s(P-O)$ in $PO_2$ , $PO_3$ and $PO_4$ , $\nu_{as}(P-O-P)$ in $P_3O_{10}$ |
| 704 (s)                          | Not observed          | $\nu_s(P-O-P)$ in $P_3O_{10}$   |
| 619 (w)564 (w)544–531 (s)503 (s) | 612 (vw)              |   |
|                                  | 586 (w)               | $\delta_{as}(O-P-O)$ in $PO_2$ , $PO_3$ and $PO_4$                            |
|                                  | 560 (vw)              |   |
|                                  | 538 (w)               |   |
| 425 (vw)                         | 471 (vw)              | $\delta_s(O-P-O)$ in $PO_2$ , $PO_3$ and $PO_4$                               |
|                                  | 427 (w)               |   |
|                                  | 377(vw)               |   |
|                                  | 356 (vw)              |   |
| /                                | 267 (w)               | Lattice vibrations  |
|                                  | 244 (vw)              |   |
|                                  | 224 (w)               |   |
|                                  | 208 (vw)              |   |
|                                  | 197 (vw)              |   |
|                                  | 175 (w)               |   |

vs = very strong, s = strong, w = weak, vw = very weak, sh = shoulder.

to say in the  $P_3O_{10}^{5-}$  group) as in  $\alpha-UP_2O_7$  where the  $P_2O_7^{4-}$  group exists as a proper unit. This may be due to the distortion of the central  $PO_4$  group of the non-linear “ $P_3O_{10}$ ” group noted from the structure determination of the compound. The peak observed at  $704\text{ cm}^{-1}$  in the infrared spectrum could be assigned to the symmetric stretching of the  $P-O-P$  bonds joining the central  $PO_4$  group (noted  $P(4)O_4$ ) to external  $PO_4$  groups (noted  $P(2)O_4$  and  $P(3)O_4$ ) in the  $P_3O_{10}$  group. The corresponding symmetric stretching may be at the same position of the symmetric stretching of the  $P-O$  bonds in the isolated phosphate groups.

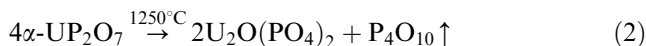
### 3.4. DTA–TGA measurements

DTA–TGA measurements were performed on  $U_2(PO_4)(P_3O_{10})$  in air up to  $1200^\circ\text{C}$ . No oxidation of tetravalent uranium into uranyl groups was observed. A weak DTA signal is observed at  $870^\circ\text{C}$ , indicating the presence of a reaction at this temperature. X-ray powder diffraction characterization of the compound after cooling to room temperature indicates that the initial uranium (IV) phosphate triphosphate  $U_2(PO_4)(P_3O_{10})$  was transformed into cubic uranium (IV) diphosphate  $\alpha-UP_2O_7$ . This reaction corresponds to an irreversible phase transition from the orthorhombic to the

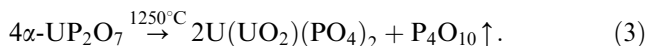
cubic structure:



Moreover, the behavior of  $\alpha-UP_2O_7$  at temperature higher than  $1200^\circ\text{C}$  has already been reported in the literature [2,3]. It decomposes into the diuranium oxide phosphate  $U_2O(PO_4)_2$  under inert conditions according to reaction [3]:



while it leads to uranium (IV) uranyl phosphate  $U(UO_2)(PO_4)_2$  in air as follows [2]:



Comparison between the cubic and orthorhombic forms of “ $UP_2O_7$ ” does not give evidence of a simple structural relationship between these arrangements. The uranium (IV) atom coordination polyhedron is lowered from the eight-fold coordination (orthorhombic structure) to the six-fold coordination in the cubic structure. Comparison between the unit-cell volumes of orthorhombic  $U_2(PO_4)(P_3O_{10})$  (which is synthesized under high-pressure conditions) and  $\alpha-UP_2O_7$  indicates that the former is much more compact than in the cubic  $\alpha-UP_2O_7$  (which is obtained by high-temperature reactions, under standard conditions). The volume expansion from orthorhombic  $U_2(PO_4)(P_3O_{10})$  to the cubic  $\alpha-UP_2O_7$  which can be calculated for one formula unit corresponds to 23.65%.

### References

- [1] V. Brandel, N. Dacheux, M. Genet, J. Solid State Chem. 121 (2) (1996) 467–472.
- [2] P. Bénard, D. Louer, N. Dacheux, V. Brandel, M. Genet, Chem. Mater. 6 (7) (1994) 1049–1058.
- [3] P. Bénard, D. Louer, N. Dacheux, V. Brandel, M. Genet, An. Quim. Int. Ed. 92 (1996) 79–87.
- [4] P. Bénard, V. Brandel, N. Dacheux, S. Jaulmes, S. Launay, C. Lindecker, M. Genet, D. Louer, M. Quarton, Chem. Mater. 8 (1) (1996) 181–188.
- [5] N. Dacheux, V. Brandel, M. Genet, K. Bak, C. Berthier, New J. Chem. 20 (3) (1996) 301–310.
- [6] N. Dacheux, R. Podor, V. Brandel, M. Genet, J. Nucl. Mater. 252 (3) (1998) 179–186.
- [7] N. Dacheux, A.C. Thomas, V. Brandel, M. Genet, J. Nucl. Mater. 257 (2) (1998) 108–117.
- [8] N. Dacheux, V. Brandel, M. Genet, New J. Chem. 19 (10) (1995) 1029–1036.
- [9] P. Bénard-Rocherulle, D. Louer, N. Dacheux, V. Brandel, M. Genet, J. Solid State Chem. 132 (2) (1997) 315–322.
- [10] V. Brandel, J.F. Le Du, N. Dacheux, R. Podor, M. Genet, C. R. Acad. Sci. Ser. IIC: Chim. 1 (9) (1998) 561–566.
- [11] V. Brandel, N. Dacheux, M. Genet, R. Podor, J. Solid State Chem. 159 (2001) 139–148.
- [12] P. Giorgio, Z. Kristallogr. 94 (1936) 311–312.
- [13] R.M. Douglass, E. Staritzky, Anal. Chem. 28 (1956) 1211–1212.
- [14] A. Burdese, M.L. Borlera, Ann. Chim. 53 (1963) 333–343.

- [15] A. Cabeza, M.A.G. Aranda, F.M. Cantero, D. Lozano, M. Martinez-Lara, S. Bruque, *J. Solid State Chem.* 121 (1996) 181–189.
- [16] R. Podor, M. Cuney, C. Nguyen Trung, *Am. Mineral.* 80 (1995) 1261–1268.
- [17] Nonius, (1998): COLLECT, Nonius BV, Delft, The Netherlands, 1998.
- [18] Z. Otwinowski, W. Minor, *Methods Enzymol.* 276 (1997) 307–326.
- [19] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 32 (1998) 115–119.
- [20] R.H. Blessing, *Acta Crystallogr. A* 51 (1995) 33–38.
- [21] G.G. Sadikov, V.P. Nikolaev, A.V. Lavrov, M.A. Porai-Koshits, *Dokl. Akad. Nauk SSSR* 264 (4) (1982) 862–867.
- [22] A. Durif, *Crystal Chemistry of Condensed Polyphosphates*, Plenum Press, New York, 1995.
- [23] M.T. Averbuch-Pouchot, A. Durif, *Topics in Phosphate Chemistry*, World Scientific Publishing, Singapore, 1996.
- [24] R. Hubin, *Spectrochim. Acta Part A* 27 (2) (1971) 311–319.
- [25] N. Dacheux, Ph.D. Thesis, Université de Paris-Sud, France, IPNO-T-95.04, 1995.
- [26] R. Hubin, P. Tarte, *Spectrochim. Acta Part A* 23 (6) (1967) 1815–1829.
- [27] D.E. Corbridge, in: M. Grayson, G. Wiley (Eds.), *Topics in Phosphorus Chemistry*, Griffith Ed., New York, 1966, p. 275.