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Investigation of the system ThO_2–NpO_2–P_2O_5. Solid solutions of thorium–neptunium (IV) phosphate–diphosphate

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Abstract

Considering that phosphate matrices could be potential candidates for the immobilization of actinides or for the final disposal of the excess plutonium from dismantled nuclear weapons, the chemistry of thorium phosphates has been re-examined. In the ThO_2–P_2O_5 system, the thorium phosphate–diphosphate $Th_4(PO_4)_4P_2O_7$ (TPD) can be synthesized by wet and dry chemical processes. The substitution of thorium by other tetravalent actinides like uranium or plutonium can be obtained for $0 < x < 3.0$ and $0 < x < 1.63$, respectively. In this work, we report the chemical conditions of synthesis of thorium–neptunium (IV) phosphate–diphosphate solid solutions $Th_{4-x}Np_x(PO_4)_4P_2O_7$ (TNPD) with $0 < x < 1.6$ from a mixture of thorium and neptunium (IV) nitrates and concentrated phosphoric acid. From the variation of the cell parameters and volume, the maximum substitution of Th^{4+} by Np^{4+} in the TPD structure is evaluated to 2.08 (which corresponds to about 52 mol% of thorium replaced by neptunium (IV)). The field of existence of solid solutions $Th_{4-x_U-x_{Np}-x_{Pu}}U_{x_U}Np_{x_{Np}}Pu_{x_{Pu}}(PO_4)4P_2O_7$ has been calculated. These solid solutions should be synthesized for $5x_U + 7x_{Np} + 9x_{Pu} \leqslant 15$. In the NpO_2–P_2O_5 system, the unit cell parameters of $Np_2O(PO_4)_2$ were refined by analogy with $U_2O(PO_4)_2$ which crystallographic data have been published recently. For $Np_2O(PO_4)_2$ the unit cell is orthorhombic with the following cell parameters: $a = 7.033(2)$ Å, $b = 9.024(3)$ Å, $c = 12.587(6)$ Å and $V = 799(1)$ Å^3. The unit cell parameter obtained for α-NpP_2O_7 ($a = 8.586(1)$ Å) is in good agreement with those already reported in literature. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In the framework of nuclear waste management we already reported the synthesis and characterization of the thorium phosphate–diphosphate $Th_4(PO_4)_4P_2O_7$ (TPD) which is a material very resistant to corrosion [1–3]. Aiming at the immobilization of ^{239}Pu (α, $T_{1/2} = 24\,500$ yr) and its daughter ^{235}U (α, $T_{1/2} = 7.04 \times 10^8$ yr) and the final disposal needed for the excess plutonium from dismantled nuclear weapons, we described the synthesis and the characterization of solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ (TUPD) and $Th_{4-x}Pu_x(PO_4)_4P_2O_7$ (TPPD) obtained by substitution of thorium by uranium (IV) or plutonium (IV) in the TPD lattice. The maximum x values were found to be equal to 3.00 and 1.63 for uranium (IV) and plutonium (IV), respectively [4].

Studies concerning leaching tests of such solid solutions are under progress and will be published soon. They confirm the good properties already obtained for the pure thorium phosphate–diphosphate during leaching tests in water or acidic media [2].

However, we never discussed about the substitution of thorium by neptunium (IV) which is produced by decay of ^{241}Pu (β^-, $T_{1/2} = 14.35$ yr) leading to ^{241}Am (α, $T_{1/2} = 432.2$ yr). This nuclide has also a short decay time and produces ^{237}Np (α, $T_{1/2} = 2.14 \times 10^6$ yr) by decay. Considering this long decay time, the contribution of the neptunium isotope ^{237}Np to the global radiotoxicity of actinides becomes very important after about 10^6 yr of storage. In these conditions it appeared also necessary to study the behavior of neptunium in the thorium phosphate–diphosphate structure.

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The ionic radius of neptunium (IV) for the eightfold coordination number ($^{[8]}r_{\mathrm{Np}} = 0.98$ Å) is close to that of the other tetravalent actinides like thorium ($^{[8]}r_{\mathrm{Th}} = 1.05$ Å), uranium ($^{[8]}r_{\mathrm{U}} = 1.00$ Å) and plutonium ($^{[8]}r_{\mathrm{Pu}} = 0.96$ Å) [5]. Considering the results obtained for TUPD and TPPD solid solutions, it should be possible to replace large amounts of thorium by neptunium (IV) in the TPD structure. Nevertheless, the chemistry of neptunium is very complicated due to the existence of several oxidation states. It is known that at least, three oxidation states (IV), (V) and (VI) are stable in solution for this element. Moreover, the pentavalent neptunium (NpO_2^+) tends to disproportionate in acidic medium into neptunium (IV): Np^{4+} and (VI): NpO_2^{2+}.

In this work, we applied the results obtained from the studies of TUPD and TPPD solid solutions to neptunium (IV). We confirmed these results by synthesizing the solid solutions $Th_{4-x}Np_x(PO_4)_4P_2O_7$ with $x = 0.4$, 0.8 and 1.6.

We also reported the results of our investigation on the system NpO_2–P_2O_5: the unit cell parameters of the neptunium (IV) diphosphate α-NpP_2O_7 and the dineptunium oxide phosphate $Np_2O(PO_4)_2$ were refined and are presented in this paper.

2. Experimental procedures

2.1. Syntheses

In our previous works concerning the thorium phosphate chemistry, we have shown that for a mole ratio $r = \mathrm{Th}/\mathrm{PO_4}$ in the range $0.5 < r < 1$, only the thorium phosphate–diphosphate ($r = \frac{2}{3}$) is well defined at high temperature. For all other ratios, the system obtained is polyphase [1,6]. For this reason, all syntheses were performed using the mole ratio

$$r = \frac{\mathrm{Th} + \mathrm{Np}}{\mathrm{PO_4}} = \frac{2}{3}.$$

Solid solutions of thorium–neptunium (IV) phosphate–diphosphate (TNPD) were prepared by wet methods of synthesis from a mixture of thorium nitrate, neptunium nitrate and phosphoric acid solutions. Thorium nitrate solution was prepared by dissolving 300 g of $Th(NO_3)_4 \cdot 5H_2O$ in 250 ml of 4 M nitric acid. The concentration of the thorium nitrate solution was determined by α liquid scintillation (using the PERALS spectrometer) as previously described [7]. It is equal to (2.13 ± 0.02) M which corresponds to (504.5 ± 3.9) g l^{-1} of thorium.

The initial solution of neptunium was prepared by dissolving neptunium dioxide NpO_2 in 4 M nitric acid (NpO_2 sample was first heated at 500°C for 4 h in order to get the complete dissolution of the powder in nitric acid). After evaporation, the final neptunium concentration in the dark yellow–green solution was equal to (0.209 ± 0.002) M which corresponds to (49.6 ± 0.5) g l^{-1} of neptunium while the free acidity was measured to 3.68 M. Several metal impurities were found in this solution by ICP/AES measurement: mainly iron (100 ppm), calcium (70 ppm), sodium and aluminum (40 ppm). Some radioactive impurities like uranium (40 ppm) and plutonium (25 ppm) isotopes were also present. The concentration of protactinium ^{233}Pa ($T_{1/2} = 27.0$ d) which is produced by α decay of ^{237}Np ($T_{1/2} = 2.14 \times 10^6$ yr) was also determined. From this measurement it appeared that this nuclide is in secular equilibrium with ^{237}Np.

The concentration of the phosphoric acid solution was determined by potentiometry using a 0.1 M sodium hydroxide solution in inert atmosphere to avoid any problem of carbonates. The measured concentration was equal to (4.97 ± 0.02) M.

Thorium and neptunium nitrate solutions were mixed with the phosphoric acid solution in the following mole ratio values Th/Np = 9, 4, 1.5 and 0 in order to synthesize thorium–neptunium (IV) solid solutions $Th_{4-x}Np_x(PO_4)_4P_2O_7$ with $x = 0.4$, 0.8, 1.6 and 4.0, respectively. For all the solids, the mole ratio $r = (\mathrm{Th} + \mathrm{Np})/\mathrm{PO_4}$ was fixed to 2/3 with a phosphoric acid excess of 1.5%. The conditions of synthesis of TNPD as well the yield of syntheses are reported in Table 1. Aiming at the synthesis of the neptunium phosphate–diphosphate '$Np_4(PO_4)_4P_2O_7$' (NPD), the mole ratio Np/PO$_4$ was fixed to 0.663. During the mixing we did not observe any modification of the color of the solution probably because of the darkness of the neptunium solution. At this stage neither gelation nor precipitation occurred. The mixtures were slowly evaporated between 100°C and 200°C in porcelain crucibles for at least 4 h until the residue is dried. The resulting residues were greyish green colored as mentioned in the literature for $Np(HPO_4)_2$ [8]. They were ground in water, evaporated and heated in alumina nacelles at 300°C for 2 h (to evaporate the volatiles like nitric acid or

Table 1
Conditions of synthesis of $Th_{4-x}Np_x(PO_4)_4P_2O_7$

Solid solution	$r = (\mathrm{Th+Np})/\mathrm{PO_4}$	Th/Np	Yield of synthesis (%)
$Th_{3.6}Np_{0.4}(PO_4)_4P_2O_7$	0.660	8.98	99.1
$Th_{3.2}Np_{0.8}(PO_4)_4P_2O_7$	0.657	4.08	99.2
$Th_{2.4}Np_{1.6}(PO_4)_4P_2O_7$	0.662	1.50	98.3

water) then, at 1000°C for 14 h with a rate of 3°C min^{-1}. The samples obtained after heating were homogeneous and turquoise-green colored which seems to be characteristic of tetravalent neptunium.

2.2. Methods of characterization

The high temperature treatment was performed in an Adamel furnace in a glove box. X-ray powder diffraction diagrams of thorium-neptunium (IV) solid solutions were collected with a Jobin–Yvon CGR apparatus in glove box using Cu $K_{\alpha 1}$ ray. For all diagrams, silicon (JCPDS file number 27-1402) was added as internal reference in order to calibrate the angular positions of the diffraction lines. Both powders were mixed, ground in an agate mortar then put on an adhesive tape. Patterns were collected from 10° to 50° (2θ) each 0.01° with an acquisition time equal to 1.2 s step^{-1}. The peak positions were determined using the DIFFRACTINEL (INEL) program while the phases identification was performed using the DIFFRACTINEL PLUS program. The JCPDS – International Centre for Diffraction Database was also interrogated to study the existence of neptunium (IV) phosphate chemistry at the solid state.

In our previous work, we have already reported the synthesis and the characterization of the thorium phosphate–diphosphate [1]. Its crystal structure was solved ab initio from X-ray and neutron powder diffraction. The unit cell is orthorhombic with the following cell parameters: $a = 12.8646(9)$ Å, $b = 10.4374(8)$ Å, $c = 7.0676(5)$ Å and $V = 949.00(9)$ Å^3. It is then possible to study the deformation of the lattice for solid solutions $Th_{4-x}Np_x(PO_4)_4P_2O_7$ when thorium is partly replaced by the smaller neptunium (IV) cation. For all the solids, the unit cell parameters were refined using the U-fit program [9].

3. Results and discussion

3.1. The ThO_2–UO_2–P_2O_5 and ThO_2–PuO_2–P_2O_5 systems

In our previous study concerning the thorium-uranium (IV) phosphate-diphosphate solid solutions (TUPD) we used an electron probe microanalysis to verify whether the solids are single or polyphase [4]. This study showed that after heating at 1000°C, the powdered samples synthesized by wet methods of syntheses were homogeneous and single phase. We did not observe neither thorium (or uranium) diphosphates nor oxides.

The variations of the unit cell parameters of TUPD and TPPD solid solutions were studied in order to verify if uranium (IV) or plutonium (IV) takes the place of thorium in the thorium phosphate–diphosphate structure. From the deformation of the unit cell obtained, it is possible to give the formulation of the cell parameters and the cell volume of the solid solutions as a function of the average cation radius $^{[8]}r_{\text{cat}}$, i.e.:

$$^{[8]}r_{\text{cat}} = \frac{(4-x)\ ^{[8]}r_{\text{Th}} + x\ ^{[8]}r_{\text{M}}}{4}, \quad \text{where M} = \text{U, Pu}, \quad (1)$$

when, as example, x atoms of thorium are replaced by uranium (IV) or plutonium (IV) in the general formula $Th_{4-x}M_x(PO_4)_4P_2O_7$.

The relations obtained are

$$a = 4.400\ ^{[8]}r_{\text{cat}} + 8.2500, \quad (2)$$

$$b = 2.448\ ^{[8]}r_{\text{cat}} + 7.9597, \quad (3)$$

$$c = 2.112\ ^{[8]}r_{\text{cat}} + 4.8506, \quad (4)$$

$$V = 820.72\ ^{[8]}r_{\text{cat}} + 87.04, \quad (5)$$

from the study of $Th_{4-x}U_x(PO_4)_4P_2O_7$ and

$$a = 3.813\ ^{[8]}r_{\text{cat}} + 8.8609, \quad (6)$$

$$b = 3.164\ ^{[8]}r_{\text{cat}} + 7.1156, \quad (7)$$

$$c = 1.877\ ^{[8]}r_{\text{cat}} + 5.0962, \quad (8)$$

$$V = 842.11\ ^{[8]}r_{\text{cat}} + 64.63, \quad (9)$$

from the study of $Th_{4-x}Pu_x(PO_4)_4P_2O_7$.

The corresponding variations of the cell parameters and cell volume in terms of x for TUPD and TPPD solid solutions are gathered in Fig. 1. Thus, it is possible to apply these equations to the substitution of the thorium by the neptunium (IV) taking into account the ionic radius of the tetravalent neptunium for the eightfold coordination number ($^{[8]}r_{\text{Np}} = 0.98$ Å). The variations of the cell parameters and cell volume for $Th_{4-x}Np_x(PO_4)_4P_2O_7$ expected from Eqs. (2)–(5) on the one hand and from Eqs. (6)–(9) on the other hand, are presented in Table 2. Both are consistent. We will see in the following section that they are in very good agreement with those obtained from experiments.

In our previous published work [4] we reported that the maximum x value for the substitution of thorium by uranium (IV) is obtained for $x_{\text{U}} \approx 3.0$. The corresponding unit cell parameters are $\{a = 12.705(3)$ Å, $b = 10.334(5)$ Å, $c = 6.996(3)$ Å$\}$ while the cell volume is equal to $V = 918$ Å^3. It is then possible to determine the maximum x value ($x_{\max}$) for neptunium (IV) considering that these parameters correspond to the maximum deformation of the thorium phosphate–diphosphate unit cell.

As instance from Eq. (2), the resulting equation is

$$12.705 = \frac{4.4[(4-x_{\max})\ ^{[8]}r_{\text{Th}} + x_{\max}\ ^{[8]}r_{\text{M}}]}{4} + 8.250. \quad (10)$$

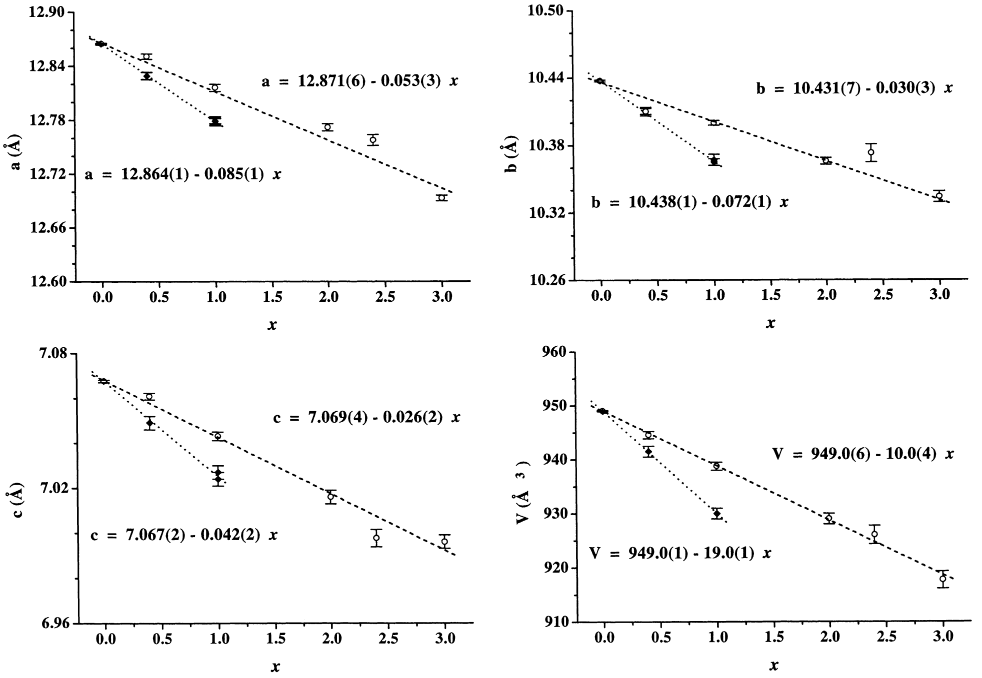

Fig. 1. Variation of the unit cell parameters and cell volume of $Th_{4-x}U_x(PO_4)_4P_2O_7$ (○) and $Th_{4-x}Pu_x(PO_4)_4P_2O_7$ (♦) as a function of x [4].

Table 2
Variations of the cell parameters expected for $Th_{4-x}Np_x(PO_4)_4P_2O_7$ in terms of x

Unit cell parameter	Expected variations (I) [a]	Expected variations (II) [a]
a (Å)	$12.870 - 0.077\,x$	$12.864 - 0.067\,x$
b (Å)	$10.430 - 0.043\,x$	$10.438 - 0.055\,x$
c (Å)	$7.068 - 0.037\,x$	$7.067 - 0.033\,x$
V (Å^3)	$948.8 - 14.4\,x$	$948.8 - 14.8\,x$

[a] Calculated from the studies of TUPD (I) and TPPD (II) solid solutions.

The resulting x_{max} values obtained from Eqs. (2)–(9) are gathered in Table 3. Considering the variation of the volume cell V which corresponds to the average variations of the three unit cell parameters a, b and c, the corresponding x_{max} value is equal to 2.14 and 2.09 from the TUPD and TPPD solid solutions studies, respectively. It seems then possible to replace about 52–54 mol% of thorium by neptunium (IV) in the TPD lattice.

Table 3
Maximum substitution of thorium by neptunium (IV) (x_{max}) expected for $Th_{4-x}Np_x(PO_4)_4P_2O_7$

Unit cell parameter	x_{max} (I) [a]	x_{max} (II) [a]
a (Å)	2.14	2.39
b (Å)	2.01	1.87
c (Å)	1.95	2.16
V (Å^3)	2.14	2.09

[a] Calculated from the studies of TUPD (I) and TPPD (II) solid solutions.

3.2. The ThO_2–NpO_2–P_2O_5 system

As noticed previously, the $Th_{4-x}Np_x(PO_4)_4P_2O_7$ solid solutions were synthesized from a mixture of thorium and neptunium (IV) nitrate solutions and phosphoric acid. The corresponding X-ray diffraction patterns are presented in Fig. 2. It results from these diagrams that the system is single phase. Neither neptunium (IV) or thorium diphosphates (α-NpP_2O_7: JCPDS file number 35-0287 and β-ThP_2O_7: JCPDS file number 17-0576) nor neptunium (IV) or thorium oxides (NpO_2 or ThO_2: JCPDS files number 23-1269 and 42-1462, respectively) have been detected.

In order to study whether the substitution of thorium by neptunium (IV) in the TPD structure is experimentally obtained and to verify that the variations of the cell parameters and cell volume are in good agreement with those predicted from the studies of TUPD and TPPD, the cell parameters of $Th_{4-x}Np_x(PO_4)_4P_2O_7$

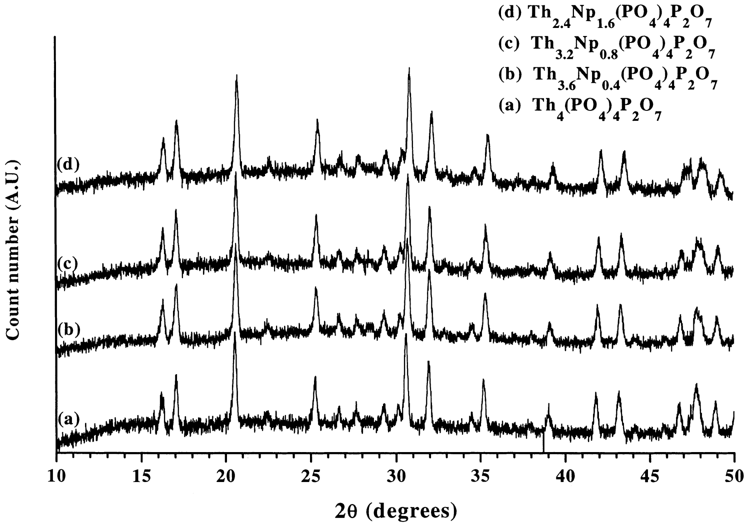

Fig. 2. X-ray powder diffraction of solid-solutions of thorium–neptunium (IV) phosphate–diphosphate.

were refined using the U-Fit program [9]. The main diffraction lines obtained for $Th_{3.6}Np_{0.4}(PO_4)_4P_2O_7$, $Th_{3.2}Np_{0.8}(PO_4)_4P_2O_7$ and $Th_{2.4}Np_{1.6}(PO_4)_4P_2O_7$ are listed in Table 4. The corresponding refined cell parameters are gathered in Table 5 while their variations in terms of x are shown in Fig. 3.

From this figure we can observe the decrease of all cell parameters when the x value increases (as for TUPD and TPPD solid solutions) which is in good agreement with the substitution of thorium by the smaller tetravalent neptunium ion. Moreover, the variation is linear from $x = 0$ up to 1.6 which confirms that solid solutions $Th_{4-x}Np_x(PO_4)_4P_2O_7$ are well formed and that neptunium (IV) actually replaced thorium in the TPD lattice. Thus, it remains tetravalent during the synthesis. The variation of the cell parameters were obtained by linear regression from experimental results. The equations obtained are consistent with those expected for neptunium (IV) from the studies of TUPD and TPPD solid solutions (Table 2).

From these variations it is also possible to determine the x_{max} experimental value corresponding to the maximum substitution of thorium by neptunium (IV). It is equal to 2.20, 2.10, 1.86 from the variations of the a, b and c parameters, respectively while the average value is 2.08 from the decrease of the cell volume V. This value is

Table 4
X-ray powder diffraction pattern of $Th_{4-x}Np_x(PO_4)_4P_2O_7$

$h\ k\ l$	$Th_{3.6}Np_{0.4}(PO_4)_4P_2O_7$		$Th_{3.2}Np_{0.8}(PO_4)_4P_2O_7$		$Th_{2.4}Np_{1.6}(PO_4)_4P_2O_7$	
	$2\theta_{obs}$ (°)	$2\theta_{cal}$ (°)	$2\theta_{obs}$ (°)	$2\theta_{cal}$ (°)	$2\theta_{obs}$ (°)	$2\theta_{cal}$ (°)
2 1 0	16.189	16.220	16.265	16.254	16.293	16.312
0 2 0	16.993	17.007	17.059	17.047	17.088	17.106
2 1 1	20.542	20.562	20.611	20.602	20.664	20.680
0 0 2	25.244	25.259	25.304	25.301	25.387	25.407
1 3 0	26.569	26.570	26.631	26.633	26.722	26.726
1 1 2	27.590	27.596	27.647	27.644	27.786	27.757
2 3 0	29.212	29.222	29.283	29.289	29.390	29.393
2 1 2	30.144	30.165	30.212	30.219	30.331	30.341
4 0 1	30.624	30.610	30.681	30.668	30.781	30.791
0 2 2						
2 3 1	31.918	31.915	31.983	31.986	32.102	32.103
4 2 1	35.232	35.227	35.301	35.299	35.442	35.432
2 3 2	39.006	39.002	39.070	39.083	39.239	39.235
4 2 2	41.837	41.827	41.910	41.910	42.084	42.075
6 1 0	43.187	43.180	43.261	43.268	43.446	43.433
4 4 1	46.714	46.710	46.818	46.816	46.979	46.993
2 3 3	48.901	48.883	48.975	48.979	49.183	49.182

Table 5
Unit cell parameters of solid solutions $Th_{4-x}Np_x(PO_4)_4P_2O_7$

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
$Th_4(PO_4)_4P_2O_7$ [1]	12.8646(9)	10.4374(8)	7.0676(5)	949.0(1)
$Th_{3.6}Np_{0.4}(PO_4)_4P_2O_7$	12.822(4)	10.419(3)	7.046(2)	941.3(9)
$Th_{3.2}Np_{0.8}(PO_4)_4P_2O_7$	12.797(2)	10.394(2)	7.034(1)	935.7(4)
$Th_{2.4}Np_{1.6}(PO_4)_4P_2O_7$	12.751(3)	10.359(3)	7.006(2)	925.4(8)

in very good accordance with those reported from the application of the results obtained for TUPD ($x_{max} = 2.14$) and TPPD ($x_{max} = 2.09$) solid solutions to neptunium (IV). Thereby, it should be possible to synthesize the solid solution $Th_{1.92}Np_{2.08}(PO_4)_4P_2O_7$. This compound corresponds to the replacement of 52 mol% of thorium by neptunium (IV) in the TPD structure.

3.3. The ThO_2–UO_2–NpO_2–PuO_2–P_2O_5 system

From the studies described above, it seems possible to predict the field of existence of solid solutions $Th_{4-x_U-x_{Np}-x_{Pu}}U_{x_U}Np_{x_{Np}}Pu_{x_{Pu}}(PO_4)4P_2O_7$ (TUNPPD) making the assumption that no more redox reactions occur between uranium (IV), neptunium (IV) and plutonium (IV) during the synthesis in phosphoric medium. In these conditions, Eq. (1) becomes

$$ {}^{[8]}r_{\mathrm{cat}} = \Big((4 - x_{\mathrm{U}} - x_{\mathrm{Np}} - x_{\mathrm{Pu}})\ {}^{[8]}r_{\mathrm{Th}} + x_{\mathrm{U}}\ {}^{[8]}r_{\mathrm{U}} + x_{\mathrm{Np}}\ {}^{[8]}r_{\mathrm{Np}} + x_{\mathrm{Pu}}\ {}^{[8]}r_{\mathrm{Pu}}\Big)\Big/4. \qquad (11) $$

Thus, it is possible to describe the field of existence of solid solutions. As instance, from the variation of the *a* parameter, Eq. (2) becomes

$$ 12.705 = \Big(4.4[(4 - x_{\mathrm{U}} - x_{\mathrm{Np}} - x_{\mathrm{Pu}})\ {}^{[8]}r_{\mathrm{Th}} + x_{\mathrm{U}}\ {}^{[8]}r_{\mathrm{U}} + x_{\mathrm{Np}}\ {}^{[8]}r_{\mathrm{Np}} + x_{\mathrm{Pu}}\ {}^{[8]}r_{\mathrm{Pu}}]\Big)\Big/4 + 8.250. \qquad (12) $$

Solid solutions could then be synthesized for

$$ 12.705 \leqslant \Big(4.4[(4 - x_{\mathrm{U}} - x_{\mathrm{Np}} - x_{\mathrm{Pu}})\ {}^{[8]}r_{\mathrm{Th}} + x_{\mathrm{U}}\ {}^{[8]}r_{\mathrm{U}} + x_{\mathrm{Np}}\ {}^{[8]}r_{\mathrm{Np}} + x_{\mathrm{Pu}}\ {}^{[8]}r_{\mathrm{Pu}}]\Big)\Big/4 + 8.250, \qquad (13) $$

which leads to

$$ 5x_{\mathrm{U}} + 7x_{\mathrm{Np}} + 9x_{\mathrm{Pu}} \leqslant 15. \qquad (14) $$

The representation of the field of existence of such solid solutions is presented in Fig. 4. The maximum substitution of thorium by the three other tetravalent

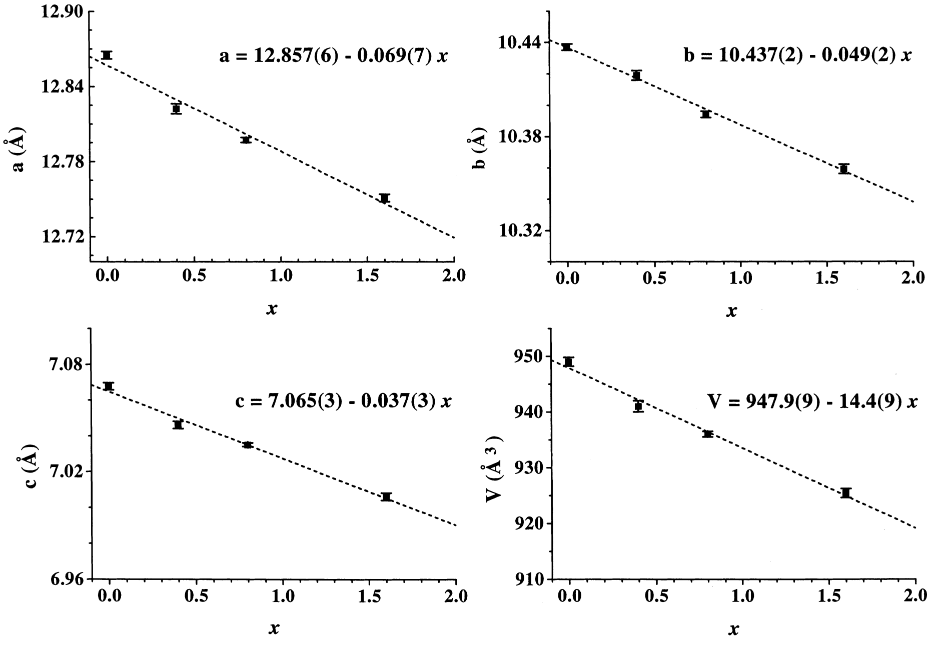

Fig. 3. Variation of the unit cell parameters and cell volume of thorium–neptunium (IV) phosphate–diphosphate as a function of *x*.

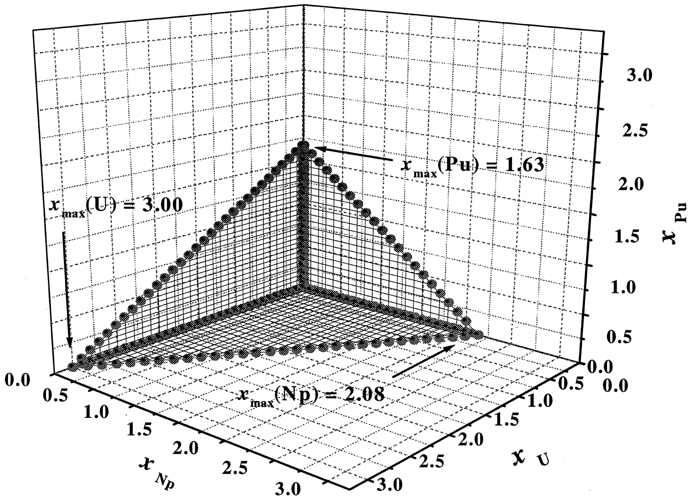

Fig. 4. Field of existence of TUNPPD solid solutions.

actinides (uranium, neptunium or plutonium) could be described by the following plane:

$$5x_{\mathrm{U}} + 7x_{\mathrm{Np}} + 9x_{\mathrm{Pu}} = 15. \quad (15)$$

Similar equations can be obtained from Eqs. (3)–(9).

These solid solutions of thorium–uranium (IV)–neptunium (IV)–plutonium (IV) phosphate diphosphates (TUNPPD) could be synthesized by dry chemical processes. For wet ways of synthesis, the use of nitrate solutions is not possible because of the oxidation of tetravalent uranium into uranyl UO_2^{2+} in solution [2,10]. Moreover, the heating treatment should be performed under inert conditions as for TUPD solid solutions in order to avoid the formation of $U_{1-x}Th_x(UO_2)(PO_4)_2$ in air as reported in our published works [2,10].

3.4. The NpO_2–P_2O_5 system

In our investigation, we also studied the NpO_2–P_2O_5 system in order to verify whether $Np_4(PO_4)_4P_2O_7$ (NPD) could be synthesized. The literature concerning the chemistry of neptunium phosphates is rather poor. Indeed, only few solids were synthesized then characterized from a crystallographic point of view since the last forty years [11–15]. Moreover, from the literature it appears that only neptunium (IV) phosphates can be synthesized in the NpO_2–P_2O_5 system at high temperature [11–15]. Attempts to prepare the Np(III) phosphate: $NpPO_4$ (analogous for the $PuPO_4$ monazite structure) were unsuccessful by dry chemical processes like the reaction by decomposition of neptunium (IV) diphosphate NpP_2O_7 in Ar–4% H_2 at 1000°C [11,12] or by wet processes as its preparation by phosphate precipitation from a neptunium (III) solution [13]. Moreover, no information concerning pentavalent or hexavalent neptunium phosphates at high temperature has been found in the literature [11]. The neptunyl (VI) phosphates concern mainly double salts. As instance we can report the compounds of general formula $M(NpO_2)PO_4 \cdot xH_2O$ ($M^{I} = H$, NH_4, Li, Na and K with $x = 3$ or 4) and $M(NpO_2)_2(PO_4)_2 \cdot y\ H_2O$ ($M^{II} =$ Mg, Ca, Sr or Ba with $y = 6$ or 9) [16]. Two neptunyl (VI) phosphates were also mentioned: $(NpO_2)HPO_4 \cdot 4.5\ H_2O$ and $(NpO_2)_3(PO_4)_2 \cdot 5\ H_2O$ [17]. All these solids have been prepared at room temperature (or heated at low temperature).

Among the neptunium (IV) phosphates reported in the literature, the diphosphate α-NpP_2O_7 which crystallizes in the cubic symmetry (JCPDS file number 35-0287) was synthesized using dry ways of synthesis and characterized by X-ray diffraction. It was obtained from a mixture of neptunium oxide NpO_2 and ammonium hydrogenphosphate $(NH_4)_2HPO_4$ [14] or by reaction between NpO_2 and BPO_4 [12] after heating at 1000°C and 1100°C respectively.

Three polymorphous forms were reported for the neptunium (IV) polytrioxophosphate (metaphosphate). α-$Np(PO_3)_4$ (tetragonal system), β-$Np(PO_3)_4$ (triclinic system) and γ-$Np(PO_3)_4$ (orthorhombic system, JCPDS file number 35-0288) were obtained after heating at 800°C, 900°C and 950°C considering the mole ratio $Np/PO_4 = \frac{1}{4}$ [14].

The last neptunium (IV) phosphate reported in the literature was tentatively identified as $(NpO)_2P_2O_7$ [11,12]. Indeed, similarities were evidenced with the unassigned diffraction lines of $(UO)_2P_2O_7$ mentioned in literature [18]. Moreover, the Raman spectra of both $(UO)_2P_2O_7$ and $(NpO)_2P_2O_7$ are close similar [11]. Nevertheless, we have proved recently that the reported $(UO)_2P_2O_7$ must be formulated as $U_2O(PO_4)_2$ which does not correspond to the uranium oxide diphosphate but to the diuranium oxide phosphate [19]. Its structure has been solved ab initio from X-ray and neutron

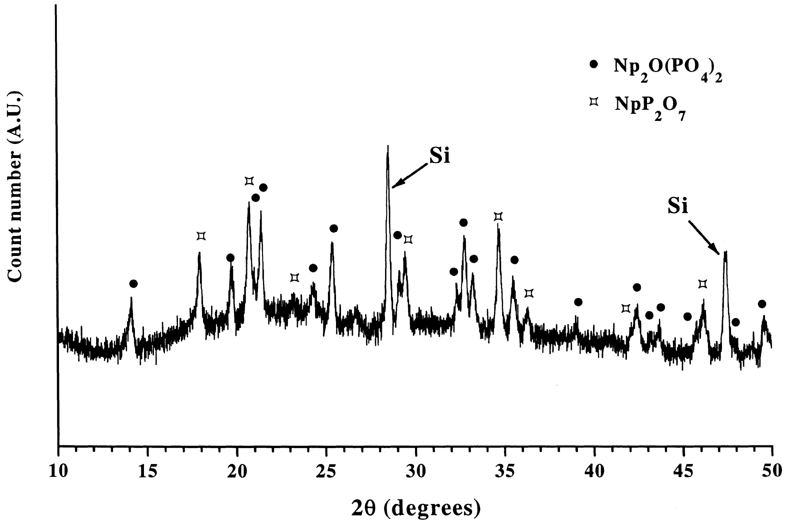

Fig. 5. The NpO_2–P_2O_5 system: X-ray powder diagram obtained for $Np/PO_4 = \frac{2}{3}$.

powder diffraction (JCPDS file number 47-0889). Its symmetry is orthorhombic (*Cmca*) with the following cell parameters: $a = 7.0878(5)$ Å, $b = 9.0362(8)$ Å, $c = 12.702(1)$ Å. The structure is built from edge-sharing pentagonal bipyramids UO_7 within zigzag chains along [1 0 0] which are cross-linked into sheets parallel to (0 0 1) through the linear (U–O–U) arrangements and bidentate phosphate groups. Chemical analyses, reaction schemes, electron probe microanalysis, XPS and UV–Visible spectra were already reported [19].

As thorium can be replaced by neptunium (IV) in the thorium phosphate–diphosphate lattice, we attempted to synthesize the analogous neptunium (IV) phosphate–diphosphate $Np_4(PO_4)_4P_2O_7$ (NPD). Neptunium nitrate and phosphoric acid solutions were mixed considering the ratio $Np/PO_4 = \frac{2}{3}$. The greyish-green residue obtained after evaporation at 200°C was ground in water to get an homogeneous powder, evaporated and then heated at 1000°C for 14 h. The final powder, which is green colored, is a polyphase system as shown from Fig. 5. It is composed of neptunium (IV) diphosphate (JCPDS file number 35-0287) and of a second phase which can be identified as $Np_2O(PO_4)_2$ taking into account the similarities which exist with $U_2O(PO_4)_2$. As the crystal structure of $U_2O(PO_4)_2$ is now well known [19], it has been possible to refine the cell parameters using the U-Fit program [9] and assuming the same orthorhombic unit cell. In these conditions, the corresponding unit cell parameters set is $\{a = 7.033(2)$ Å, $b = 9.024(3)$ Å, $c = 12.587(6)$ Å$\}$ which leads to $V = 799(1)$ Å^3. The lattice deformation is respectively equal to 0.77% along the *a* axis, 0.13% along the *b* axis and 0.91% along the *c* axis. The contraction of the cell volume is thus about 1.78% in comparison to $U_2O(PO_4)_2$. The main diffraction lines of $Np_2O(PO_4)_2$ are listed and assigned in Table 6.

The same refinement was performed for the cubic α-NpP_2O_7. This refinement led to the lattice parameter $a = 8.586(1)$ Å which is consistent with those already reported: 8.593(2) Å [12], 8.565(10) Å [13] and 8.582(5) Å [14].

From all results obtained, the general reaction involved during the synthesis can be described as follows:

$$4Np(NO_3)_4 + 6H_3PO_4 \rightarrow 2\alpha\text{-}NpP_2O_7 + Np_2O(PO_4)_2 + 16HNO_3\uparrow + H_2O\uparrow . \quad (16)$$

Nevertheless, the diffraction lines of α-NpP_2O_7 are not so intense according to its cubic symmetry and the stoichiometric conditions. Thus, the neptunium diphosphate is probably decomposed into $Np_2O(PO_4)_2$ by heating as shown for uranium (IV) diphosphate [2,20] and mentioned in literature for the wrongly identified $(NpO)_2P_2O_7$ [12]. The corresponding reaction can be written

Table 6
X-ray powder diffraction pattern of $Np_2O(PO_4)_2$

h k l	$2\theta_{obs}$ (°)	$2\theta_{cal}$ (°)	d_{obs} (Å)	I/I_0
0 0 2	14.087	14.065	6.28	50
0 2 0	19.689	19.659	4.505	65
1 1 2	21.340	21.334	4.160	100
0 2 2	24.258	24.252	3.666	30
2 0 0	25.319	25.305	3.515	80
0 2 3	29.042	29.038	3.072	40
2 2 0	32.234	32.247	2.775	30
1 1 4	32.683	32.692	2.738	85
1 3 1	33.122	33.137	2.702	35
1 3 2	35.410	35.423	2.533	30
2 2 3	38.912	38.891	2.313	15
3 1 2	42.297	42.306	2.135	40
1 3 4	43.527	43.530	2.077	35

$$4\alpha\text{-}NpP_2O_7 \rightarrow 2Np_2O(PO_4)_2 + P_4O_{10}\uparrow . \quad (17)$$

In conclusion, the chemistry of neptunium (IV) phosphates at high temperature appears very close to the uranium (IV) one in inert atmosphere [2,20]. $Np_2O(PO_4)_2$ seems to be the only neptunium (IV) phosphate stable at high temperature. These results are in good agreement with those mentioned in literature from which the neptunium (IV) phosphate $Np_3(PO_4)_4$ cannot be synthesized while the neptunium (IV) diphosphate α-NpP_2O_7 slowly decomposes into $Np_2O(PO_4)_2$ [12].

4. Conclusions

In the ThO_2–NpO_2–P_2O_5 system, solid solutions of thorium–neptunium (IV) phosphate–diphosphate $Th_{4-x}Np_x(PO_4)_4P_2O_7$ were synthesized for x values equal to 0.4, 0.8 and 1.6 from a mixture of thorium and neptunium nitrates and phosphoric acid solutions. For all these turquoise colored solids, the X-ray powder diffraction showed that the system is single phase. The unit cell parameters were refined for each solid solution. The variations obtained for the a, b, c parameters and V in terms of the x value are linear from $x = 0$ up to $x = 1.6$. The equations obtained are consistent with those expected from the studies of $Th_{4-x}U_x(PO_4)_4P_2O_7$ and $Th_{4-x}Pu_x(PO_4)_4P_2O_7$ solid solutions. During the synthesis, the neptunium remains in the tetravalent state and takes the place of thorium in the TPD lattice. The maximum substitution of thorium by neptunium (IV) was evaluated considering the maximum deformation of the unit cell. The corresponding value is equal to 2.08 (from the variation of the cell volume V) which corresponds to $Th_{1.92}Np_{2.08}(PO_4)_4P_2O_7$ (i.e. about 52 mol% of thorium replaced by neptunium (IV) in the TPD structure). This value is in very good agreement with those calculated from the studies of TUPD and TPPD solid solutions.

Our investigation also dealt with the NpO_2–P_2O_5 system. The attempts to synthesize $Np_4(PO_4)_4P_2O_7$ were unsuccessful as expected from a crystallographic point of view. From the initial mole ratio Np/PO_4 equal to $\frac{2}{3}$, the system is polyphase, composed of neptunium (IV) diphosphate α-NpP_2O_7 and of dineptunium oxide phosphate $Np_2O(PO_4)_2$. For both solids, the unit cell parameters were refined. α-NpP_2O_7 crystallizes in the cubic system with $a = 8.586(1)$ Å while the unit cell obtained for $Np_2O(PO_4)_2$ is orthorhombic with $a = 7.033(2)$ Å, $b = 9.024(3)$ Å and $c = 12.587(6)$ Å. The corresponding unit cell volume is then equal to 799(1) Å^3. It appears that the reactions involved in the NpO_2–P_2O_5 system are quite similar to that observed in the UO_2–P_2O_5 system in inert atmosphere.

We proved that solid solutions can be synthesized by wet chemical processes for uranium (IV) (TUPD), neptunium (IV) (TNPD) and plutonium (IV) (TPPD). It could be also of interest to study the incorporation of protactinium (IV) in the TPD structure. Considering the ionic radius of the tetravalent protactinium for the eightfold coordination number ($^{[8]}r_{Pa} = 1.01$ Å), it should be possible to synthesize the solid solutions $Th_{4-x}Pa_x(PO_4)_4P_2O_7$ up to $x = 3.75$ (i.e. 94 mol% of thorium replaced by the protactinium (IV)). In this formula, the protactinium should be tetravalent while it is usually more stable in the pentavalent oxidation state. However, the protactinium (IV) polytrioxophosphate α-$Pa(PO_3)_4$ (orthorhombic system, JCPDS file number 33-1094), and the protactinium (IV) diphosphate α-PaP_2O_7 (cubic system) were already prepared by wet ways of synthesis after heating between 900°C and 1300°C in inert atmosphere [21,22]. For temperatures higher than 1300°C, α-PaP_2O_7 is decomposed into the protactinium (V) oxide diphosphate $(PaO)_4(P_2O_7)_3$ (monoclinic system, JCPDS file number 31-1154) [22].

Leaching tests on TPPD solid solutions in water or acidic solutions are under progress and will be published soon. They confirm the very low solubility of the TPD. The same leaching tests will be performed for TNPD solid solutions. The neptunium ^{237}Np activity released as well that of protactinium ^{233}Pa which is produced in situ in the solid by α decay will be determined in the same leachates by α liquid scintillation (PERALS) and γ spectrometry. The comparison of both activities should be of importance to evaluate the chemical fate of the recoil atoms.

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