Investigations of systems ThO_2–MO_2–P_2O_5 (M = U, Ce, Zr, Pu). Solid solutions of thorium–uranium (IV) and thorium–plutonium (IV) phosphate–diphosphates

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Abstract

In the framework of nuclear waste management aiming at the research of a storage matrix, the chemistry of thorium phosphates has been completely re-examined. In the ThO_2–P_2O_5 system a new compound thorium phosphate–diphosphate $Th_4(PO_4)_4P_2O_7$ has been synthesized. The replacement of Th^{4+} by a smaller cation like U^{4+} and Pu^{4+} in the thorium phosphate–diphosphate (TPD) lattice has been achieved. $Th_{4-x}U_x(PO_4)_4P_2O_7$ and $Th_{4-x}Pu_x(PO_4)_4P_2O_7$ solid solutions have been synthesized through wet and dry processes with $0 < x < 3.0$ for uranium and $0 < x < 1.0$ for plutonium. From the variation of the unit cell parameters, an upper x value equal to 1.67 has been estimated for the thorium–plutonium (IV) phosphate–diphosphate solid solutions. Two other tetravalent cations, Ce^{4+} and Zr^{4+}, cannot be incorporated in the TPD lattice: cerium (IV) because of its reduction into Ce (III) at high temperature, and zirconium probably because of its too small radius compared to thorium. © 1998 Elsevier Science B.V.

1. Introduction

At the present time, nuclear fuel wastes are conditioned for storage in borosilicate glasses. However, other matrices like monazites [1] or Synroc [2] have been proposed. Among the general problem of radioactive waste, plutonium is a special one. It is produced in a nuclear reactor by several ways and for different purposes. Currently, part of the plutonium is mixed with uranium for the production of new kinds of fuels. After several cycles in the nuclear reactor, the used fuel produced contains uranium and plutonium isotopes. Furthermore, in weight, the most important plutonium isotope produced is ^{239}Pu. This fissile nuclide is also an α emitter and has a long decay period ($T_{1/2} = 24\,500$ yr) leading to ^{235}U (α, $T_{1/2} = 7 \times 10^8$ yr), the latter also being fissile. Thus, it is necessary to think about the immobilization of both actinides and to perform the final disposal of the excess plutonium from dismantled nuclear weapons. This long-term storage requires a material able to immobilize both plutonium and uranium for a long time (10^6 yr at least). Some silicates or phosphates, like zircon: $ZrSiO_4$, $Ca_2La_8(SiO_4)_6O_2$ or $Ca_{10}(PO_4)_6F_2$, have been already proposed as hosts for plutonium [3–5] but these matrices are not very resistant to heavy particle irradiation. With the same objective, thorium phosphate–diphosphate $Th_4(PO_4)_4P_2O_7$ (TPD) [6] which solubility is very low [7] could be an alternative compound [8].

In order to study the incorporation of foreign ions into a matrix, it is necessary to investigate the conditions of the solid solution formation. Solid solutions are formed when the ionic radii of the host and the inserted ions are close and when the crystal structure of the host material is conserved. This is the case of diphosphates of tetravalent elements. Indeed, α-MP_2O_7 (M = Th, U, Pu, Zr and Ce) have the same crystal structure [9,10] and solid solutions of thorium–uranium (IV) diphosphates were synthesized many years ago [11]. Double salts $M'M_2(PO_4)_3$ (M' = Li, Na, K, Rb and Cs; M = Th, U, Pu and Zr) are also isostructural [12–14]. These facts suggest that solid solutions based on thorium phosphate–diphosphate could be

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obtained. In fact, the ionic radii of U (IV), Ce (IV) and Pu (IV) for the eightfold coordination number are close to thorium [15]:

$$^{[8]}r_{Th} = 1.05 \text{ Å} > {}^{[8]}r_U = 1.00 \text{ Å} > {}^{[8]}r_{Ce}$$

$$= 0.97 \text{ Å} > {}^{[8]}r_{Pu} = 0.96 \text{ Å}$$

while that of zirconium is smaller: $^{[8]}r_{Zr} = 0.84$ Å.

In previous publications we have presented the methods of synthesis [6,16,17] and the results of leaching tests of TPD, uranium phosphates and thorium–uranium (IV) phosphate–diphosphate (TUPD) [17,18]. The resistance to water or acidic solutions of such a solid $Th_{4-x}U_x(PO_4)_4P_2O_7$ was found to be very good [17].

In this work we reported the results of investigation on the systems ThO_2–MO_2–P_2O_5, where M is uranium, plutonium, cerium and zirconium.

2. Experimental procedures

2.1. Syntheses

Uranium (IV) chloride solution was prepared by dissolving uranium metal chips in concentrated hydrochloric acid. Thorium chloride solution as well as thorium nitrate pentahydrate were obtained from Rhône-Poulenc. Plutonium nitrate solution was prepared by dissolving plutonium dioxide in concentrated nitric acid. Other chemicals used for syntheses, i.e. phosphoric and nitric acids, cerium–ammonium nitrate and zirconyl chloride were obtained from Fluka or Merck. Uranium (IV) diphosphate α-UP_2O_7, used for dry syntheses, was prepared by wet chemistry from a mixture of uranium (IV) chloride solution and phosphoric acid, under the conditions of the mole ratio $Th/PO_4 = \frac{1}{2}$ [17].

Previous works concerning thorium phosphate chemistry [6] have shown that when the mole ratio $r = Th/PO_4$ is in the range $0.5 < r < 1$, only the thorium phosphate–diphosphate ($r = \frac{2}{3}$) is well defined at high temperature ($\theta = 1250°C$). For other r values, polyphase systems composed of thorium phosphate–diphosphate and thorium diphosphate (for $\frac{1}{2} < r < \frac{2}{3}$) or thorium oxide (for $\frac{2}{3} < r < 1$) have been obtained. For this reason, all systems ThO_2–MO_2–P_2O_5 (M = U, Pu, Ce and Zr) were studied using the mole ratio $(Th + M)/(PO_4) = \frac{2}{3}$.

Solid solutions of thorium–uranium (IV) phosphate–diphosphate were synthesized by wet and dry methods of chemistry [16,17]. For dry ways of synthesis, α-UP_2O_7 and $Th_4(PO_4)_4P_2O_7$ were ground and then heated in argon atmosphere between 1270°C and 1320°C for 17–34 h (the higher the temperature of heating, the shorter the time required). Before each treatment, the samples were reground several times in order to get homogeneous powders.
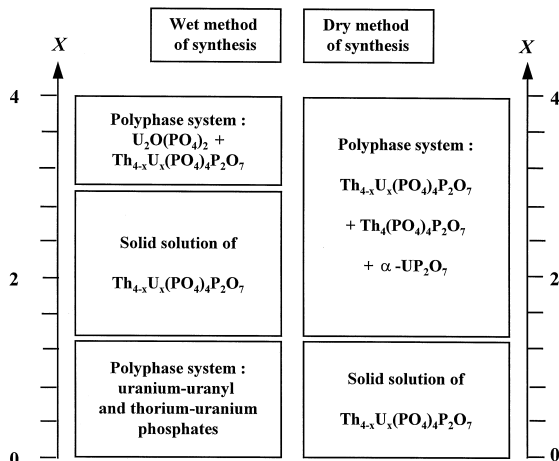

Fig. 1. Field of existence of solid solutions of $Th_{4-x}U_x(PO_4)_4P_2O_7$ as a function of x.

In the soft chemistry method, 1.6 M U (IV) and 1 M thorium hydrochloric solutions were mixed with 15 M phosphoric acid. From the gelatinous precipitate obtained, water and HCl were evaporated at 140°C, ground and heated in argon, first at 400–500°C for 2 h to eliminate the remaining volatile species, then at 1050–1250°C for 10 h at least. From either way of synthesis, solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ were obtained with mole ratios Th/U from 39 ($x = 0.1$) to 0.33 ($x = 3.0$) as shown in Fig. 1.

Thorium phosphate–diphosphate samples containing different mol% of cerium (IV) or zirconium (IV) were prepared starting from mixtures of 1 M solutions of $Th(NO_3)_4$, $(NH_4)_2Ce(NO_3)_6$ or $ZrOCl_2$ with concentrated phosphoric acid. The same evaporation procedure as for the thorium–uranium phosphate system was applied.

Thorium–plutonium (IV) phosphate–diphosphate (TPPD) solid solutions were synthesized by the wet method. Thorium nitrate solution was prepared by the dissolution of $Th(NO_3)_4 \cdot 5H_2O$ in 1 M nitric acid. The determination of the thorium concentration was performed using two methods: a complexometric titration with EDTA and an α liquid scintillation method (PERALS®) using an $ALPHAEX_\alpha$™ scintillating extractor (HDEHP extractive molecule) [19]. Both methods led to similar results: 1.49 M (complexometry) and 1.52 M (α liquid scintillation). The average concentration was found to be equal to 1.51 ± 0.02 M.

The initial solution of plutonium (IV) was prepared by dissolving PuO_2 in concentrated nitric acid in the presence of 0.05 M hydrofluoric acid to induce the complete dissolution of the powder. The resulting solution was evaporated in order to get a more concentrated solution and to eliminate the remaining HF. The final concentration of plutonium in 4 M HNO_3, determined by a conventional α-spectrometric method, was equal to 0.528(1) M (e.g. 126.1 ± 0.1 g l^{-1}). Only plutonium (IV), which is the only

oxidation state stable in these conditions, was found in the dark green–brown solution. The presence of ^{241}Am in this solution (about 320 ppm) is due to the decay of ^{241}Pu (β^-, $T_{1/2} = 14.4$ yr). Studies concerning ^{241}Am have been performed and will be published soon.

Thorium and plutonium (IV) nitrate solutions were mixed with 5 M phosphoric acid under the conditions of the following mole ratios: Th/Pu = 9, Th/Pu = 3 and Th/Pu = 0 in order to obtain solid solutions Th$_{4-x}$Pu$_x$(PO$_4$)$_4$P$_2$O$_7$ with $x = 0.4$, 1.0 and 4.0 respectively. At this stage, the color of the solution changed (from green–brown in the nitric medium to wine-coloured in the presence of phosphate ions) which is an evidence of the formation of plutonium (IV) phosphate complexes [20]. Moreover, no precipitation nor gelation step was observed during this process. These mixtures were slowly evaporated at 160°C for 6 h in porcelain crucibles. The resulting amorphous residues were ground and heated at 300°C for 2 h in alumina nacelles (aiming at the elimination of water and nitric acid). At this stage of the synthesis, the solid is still amorphous. After the second grinding step, the powders were heated at 1000–1050°C for 18 h in air with a rate of 5°C min^{-1}. No secondary surface reactions were observed. After heating, the samples were pink-coloured (for $x = 0.4$ and 1.0) which is characteristic of tetravalent plutonium in phosphate matrices while the blue coloured powder obtained for $x = 4.0$ seems to indicate that a part of plutonium (IV) has been reduced into the trivalent state during the heating (this has been confirmed during the analysis of the samples, as mentioned in the last part of this work). Indeed, according to literature, plutonium (VI) phosphates seem to be unstable at high temperature. Moreover, plutonium (IV) phosphates are often white or pink coloured while plutonium (III) phosphates (for instance monazite structure or plutonium (III) metaphosphate) are always dark blue coloured [20].

2.2. Apparatus and methods of characterization

A high temperature treatment was performed with a Pyrox MDB15 and an Adamel (for thorium–plutonium phosphates in a glove box) furnaces. X-ray powder diffraction diagrams of thorium–uranium (IV), thorium–cerium (IV) and thorium–zirconium phosphate–diphosphate systems were obtained with a Philips PW 1050/70 diffrac-

tometer using Cu K$_\alpha$ radiation and a Ni filter. XRD data for thorium–plutonium (IV) phosphate–diphosphate solid solutions were collected with a Jobin-Yvon CGR apparatus using Cu K$_\alpha$ rays in a glove box. In all cases silicon (JCPDS file 27-1402), as an internal reference, was added to samples in order to calibrate the peak positions. Patterns were scanned using the following conditions: 0.01° step^{-1} and 1.2 s step^{-1} from 10 to 50° (2θ).

As the crystal structure of thorium phosphate–diphosphate is now well known [6], it is possible to evidence the deformation of the unit cell when thorium is substituted by a smaller tetravalent cation M^{4+}. The refinement of the cell parameters has been obtained using the U-fit program [21].

Electron probe microanalyses (EPMA) of the solids were carried out with a CAMECA SX 50 apparatus using an acceleration voltage of 15 kV and a current of 10 nA. The diameter of the analytical spot was about 1 μm. The following calibration standards were used: ThO$_2$ (M$_\alpha$ ray of thorium), ZrO$_2$ (L$_\alpha$ ray of zirconium), CeRuGe$_2$ (L$_\alpha$ ray of Ce), UO$_2$ (M$_\beta$ ray of uranium) and Ca$_5$(PO$_4$)$_3$OH (K$_\alpha$ ray of phosphorus).

3. Results and discusion

3.1. The ThO$_2$–UO$_2$–P$_2$O$_5$ system

The X-ray powder diffraction pattern obtained for solid solutions Th$_{4-x}$U$_x$(PO$_4$)$_4$P$_2$O$_7$ is the same as for the pure thorium phosphate–diphosphate. Nevertheless, this result cannot give precise information about the homogeneity of the synthesized products. Thus, we have used an electron probe to verify whether the solids are single phase or polyphase.

The results obtained from electron probe microanalysis on Th$_{4-x}$U$_x$(PO$_4$)$_4$P$_2$O$_7$ are collected in Table 1. The weight percentages obtained for uranium, thorium, phosphorus and oxygen are in good agreement with the calculated values taking into account the general formula proposed, as seen from this table. The experimental mole ratios Th/U and (U + Th)/(PO$_4$) are quite good too. Furthermore, no evidence for a polyphase system has been seen; for all samples ($0 < x < 3.0$) the system is then single phase.

Table 1
Results of electron probe microanalysis for Th$_{4-x}$U$_x$(PO$_4$)$_4$P$_2$O$_7$

Compound	U (%)		Th (%)		P (%)		O (%)		Th/U		(U + Th)/PO$_4$	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
Th$_4$(PO$_4$)$_4$P$_2$O$_7$	–	–	62.7	62.6	12.5	12.6	24.8	24.8	–	–	0.67	0.67
Th$_{3.6}$U$_{0.4}$(PO$_4$)$_4$P$_2$O$_7$	6.5	6.4	57.3	56.3	12.0	12.5	24.2	24.8	9.04	9.00	0.70	0.67
Th$_3$U(PO$_4$)$_4$P$_2$O$_7$	15.8	16.0	47.8	46.8	12.1	12.5	24.3	24.7	3.10	3.00	0.69	0.67
ThU$_3$(PO$_4$)$_4$P$_2$O$_7$	47.8	47.6	15.2	15.4	12.4	12.4	24.6	24.6	0.33	0.33	0.66	0.67

Table 2
Unit cell parameters of $Th_{4-x}U_x(PO_4)_4P_2O_7$

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)
$Th_4(PO_4)_4P_2O_7$ [6]	12.865(9)	10.437(8)	7.068(5)	949(9)
$Th_{3.6}U_{0.4}(PO_4)_4P_2O_7$	12.851(3)	10.410(3)	7.061(2)	944(7)
$Th_3U(PO_4)_4P_2O_7$	12.816(4)	10.400(2)	7.043(2)	939(8)
$Th_2U_2(PO_4)_4P_2O_7$	12.772(4)	10.366(3)	7.016(3)	929(10)
$Th_{1.6}U_{2.4}(PO_4)_4P_2O_7$	12.758(6)	10.373(8)	6.998(4)	926(2)
$ThU_3(PO_4)_4P_2O_7$	12.705(3)	10.334(5)	6.996(3)	918(2)

In order to verify that uranium (IV) takes the place of thorium in the thorium phosphate–diphosphate structure, the unit cell parameters of several solid solutions were refined in the space group Pcam. The results are shown in Table 2. Their variations in terms of x are presented in Fig. 2. These results show that for $x = 3.0$, the thorium phosphate–diphosphate lattice deformation is respectively equal to $\approx 1.3\%$ along the a axis, 1.07% along the b axis and 1.1% along the c axis. The contraction of the cell volume is thus about 3.35%.

If thorium is replaced by another tetravalent cation, the variations of the unit cell parameters and cell volume in solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ can be formulated as a function of the radius of the incorporated cation, as follows:

$$a = 4.400 \times {}^{[8]}r_{cat} + 8.2500, \tag{1}$$

$$b = 2.448 \times {}^{[8]}r_{cat} + 7.8597, \tag{2}$$

$$c = 2.112 \times {}^{[8]}r_{cat} + 4.8506, \tag{3}$$

$$V = 820.72 \times {}^{[8]}r_{cat} + 87.044, \tag{4}$$

where ${}^{[8]}r_{cat}$ is the average cation radius, e.g.:

$$ {}^{[8]}r_{cat} = \frac{(4-x)^{[8]}r_{Th} + x \times {}^{[8]}r_U}{4} \tag{5}$$

when, for example, x atoms of thorium are replaced by uranium (IV): $Th_{4-x}U_x(PO_4)_4P_2O_7$. The maximum substitution of uranium in the thorium phosphate–diphosphate is obtained for $x \geq 3.0$. This value ($x \geq 3.0$) corresponds to the following unit cell parameters set $\{a = 12.705(3)$ Å, $b = 10.334(5)$ Å, $c = 6.996(3)$ Å$\}$, Table 2. If we consider that these parameters correspond to the maximum deformation of the thorium phosphate–diphosphate unit cell, then the maximum x values (x_{max}) for other tetravalent

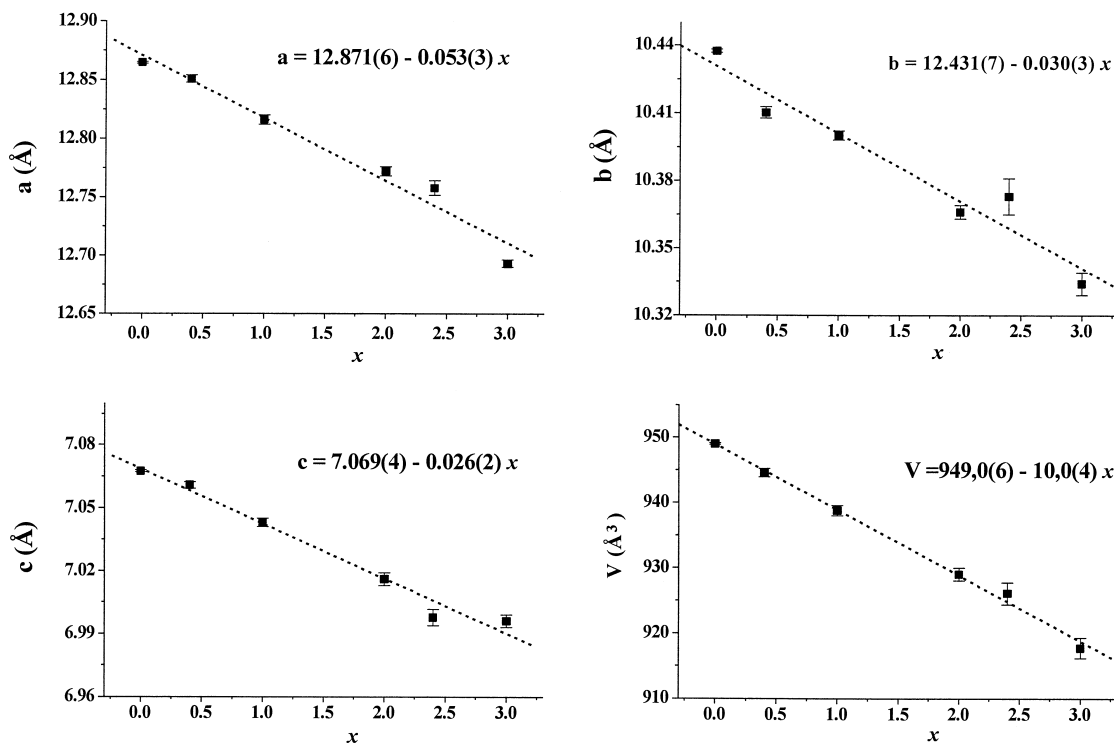

Fig. 2. Variation of the unit cell parameters and cell volume of thorium–uranium (IV) phosphate–diphosphate as a function of x.
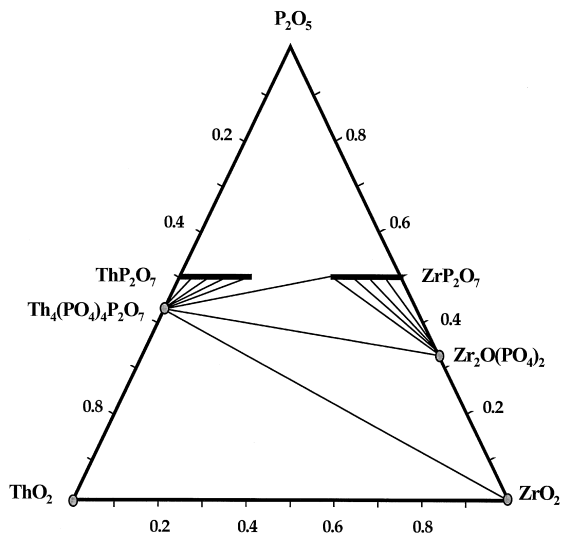
Fig. 3. Phase diagram of the system ThO_2–ZrO_2–P_2O_5 at 1200°C. (○) Defined compound, (black horizontal bar) solid solution, (———) equilibrium line.

cations (ionic radius r) can be calculated (for example in the case of the a parameter) as follows:

$$12.705 = 4.4 \times {}^{[8]}r_{cat} + 8.250, \qquad (6)$$

$$12.705 = \frac{\left[4.4(4 - x_{max}) \times {}^{[8]}r_{Th} + x_{max} \times r\right]}{4} + 8.250. \qquad (7)$$
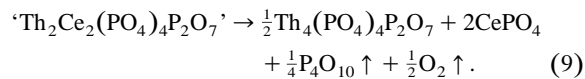
Finally

$$x_{max} = \frac{0.15}{1.05 - r}. \qquad (8)$$

The same relation can be obtained considering the variation of the b and c parameters and the cell volume V. The

maximum x values calculated from Eq. (8) for the systems studied are the following: 1.86 for cerium, 1.67 for plutonium, and 0.71 for zirconium.

The smallest x_{max} value is obtained for zirconium, which is the smallest cation among the four studied.

3.2. The ThO_2–CeO_2–P_2O_5 system

Several samples of the composition $Th_{4-x}Ce_x(PO_4)_4P_2O_7$ for $0 < x < 4.0$ were synthesized by mixing solutions prepared from $Th(NO_3)_4 \cdot 5H_2O$ and $(NH_4)_2Ce(NO_3)_6$. After evaporation and calcination, the X-ray powder diffraction diagrams show that the final products are heterogeneous, composed of $Th_4(PO_4)_4P_2O_7$ and $CePO_4$ (monazite structure) which indicates that cerium (IV) has been reduced during the heat treatment. Simultaneously, we observed a great change in the colour of the powdered samples (from yellow for cerium (IV) it becomes colourless for cerium (III)). The TPD lattice is not deformed which means that thorium is not replaced by cerium (IV) or cerium (III). To get a better understanding of the reaction mechanism, samples of the hypothetical '$Th_2Ce_2(PO_4)_4P_2O_7$' were prepared and then heated. At room temperature these solids are amorphous. Heated to 650°C, the system is partly crystallized. At 850°C, intermediate solid solutions $Th_{1-x}Ce_xP_2O_7$ (based on α and β forms of thorium diphosphate) appear. Between 1050°C and 1250°C, they are decomposed into TPD and $CePO_4$, even in an oxygen atmosphere. The reaction involved can be described as follows:

$$'Th_2Ce_2(PO_4)_4P_2O_7' \rightarrow \tfrac{1}{2}Th_4(PO_4)_4P_2O_7 + 2CePO_4$$
$$+ \tfrac{1}{4}P_4O_{10} \uparrow + \tfrac{1}{2}O_2 \uparrow. \qquad (9)$$

All syntheses led to the same conclusion. Thus, cerium (IV) phosphates are not stable at high temperatures, even

(d) $Th_3Pu(PO_4)_4P_2O_7$ (I) + Si
(c) $Th_3Pu(PO_4)_4P_2O_7$ (II)
(b) $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$
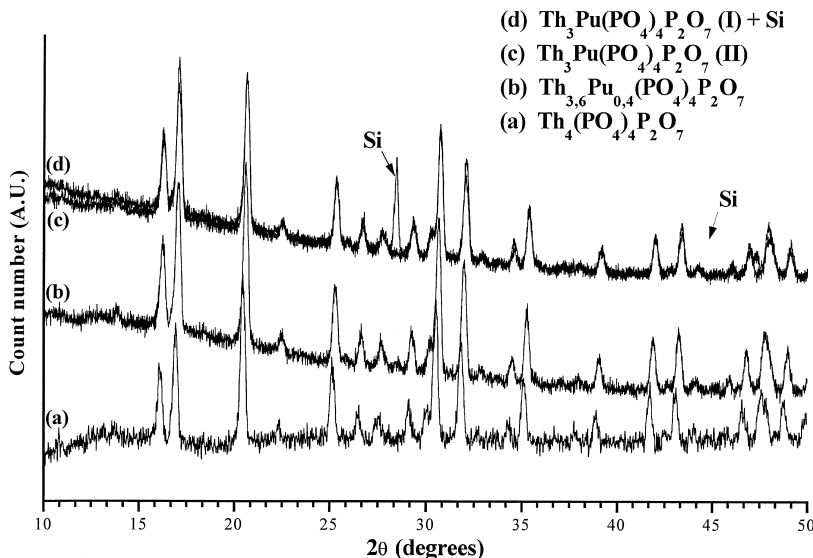(a) $Th_4(PO_4)_4P_2O_7$

Fig. 4. X-ray powder diagram of solid solutions of thorium–plutonium (IV) phosphate–diphosphate.

Table 3
Unit cell parameters of solid solutions $Th_{4-x}Pu_x(PO_4)_4P_2O_7$

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)
$Th_4(PO_4)_4P_2O_7$ [6]	12.865(9)	10.437(8)	7.068(5)	949(9)
$Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$	12.829(5)	10.410(4)	7.049(3)	941(1)
$Th_3Pu(PO_4)_4P_2O_7$ (I)	12.779(6)	10.365(3)	7.027(3)	930(1)
$Th_3Pu(PO_4)_4P_2O_7$ (II)	12.779(5)	10.367(5)	7.024(3)	930(1)

in the presence of thorium; solid solutions of $Th_{4-x}Ce_x(PO_4)_4P_2O_7$ cannot be obtained in these conditions. These results are in good agreement with other published works in which several authors have shown the decomposition of cerium (IV) and plutonium (IV) diphosphates in $CePO_4$ [22,23] and $PuPO_4$ [10,24], respectively, at high temperature. Moreover, the study of the ThO_2–La_2O_3–P_2O_5 system (where lanthanum can be only trivalent) leads to the same polyphase system as for cerium, which confirms that cerium is reduced at the trivalent state during the synthesis.

3.3. The ThO_2–ZrO_2–P_2O_5 system

The same kind of investigations has been performed for thorium–zirconium phosphates. XRD patterns were used to make the scheme of the ThO_2–ZrO_2–P_2O_5 system. All attempts to replace thorium by zirconium in the TPD structure were unsuccessful. The electron probe microanalysis has shown that the system is always polyphase after heating at 1250°C. Three polyphase systems can be obtained:

$$Th_4(PO_4)_4P_2O_7\text{–}Zr_{0.7}Th_{0.3}P_2O_7\text{–}Zr_2O(PO_4)_2,$$

$$Th_4(PO_4)_4P_2O_7\text{–}Zr_2O(PO_4)_2\text{–}ZrO_2,$$

$$Th_4(PO_4)_4P_2O_7\text{–}ZrO_2\text{–}ThO_2.$$
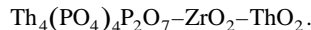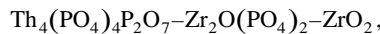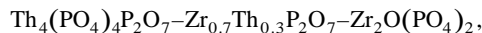
As shown in Fig. 3, solid solutions have been obtained only for thorium–zirconium diphosphates. For all other phases, thorium cannot be replaced by zirconium in thorium phosphates and inversely in zirconium phosphates. This is probably due to the difference between the ionic radii of zirconium ($^{[8]}r_{Zr} = 0.84$ Å) and thorium ($^{[8]}r_{Th} = 1.05$ Å) being too great.

3.4. The ThO_2–PuO_2–P_2O_5 system

Two kinds of mixtures of initial composition $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$ and $Th_3Pu(PO_4)_4P_2O_7$ were heated in a glove box at 300°C for 2 h and then at 1050°C for 18 h. From X-ray powder diffraction, the system is single phase: evidence for the presence of plutonium (IV) or thorium diphosphates, $PuPO_4$ (monazite structure), plutonium (IV) or thorium oxides has not been found. Moreover, for both pink-coloured powders, we observed a shift
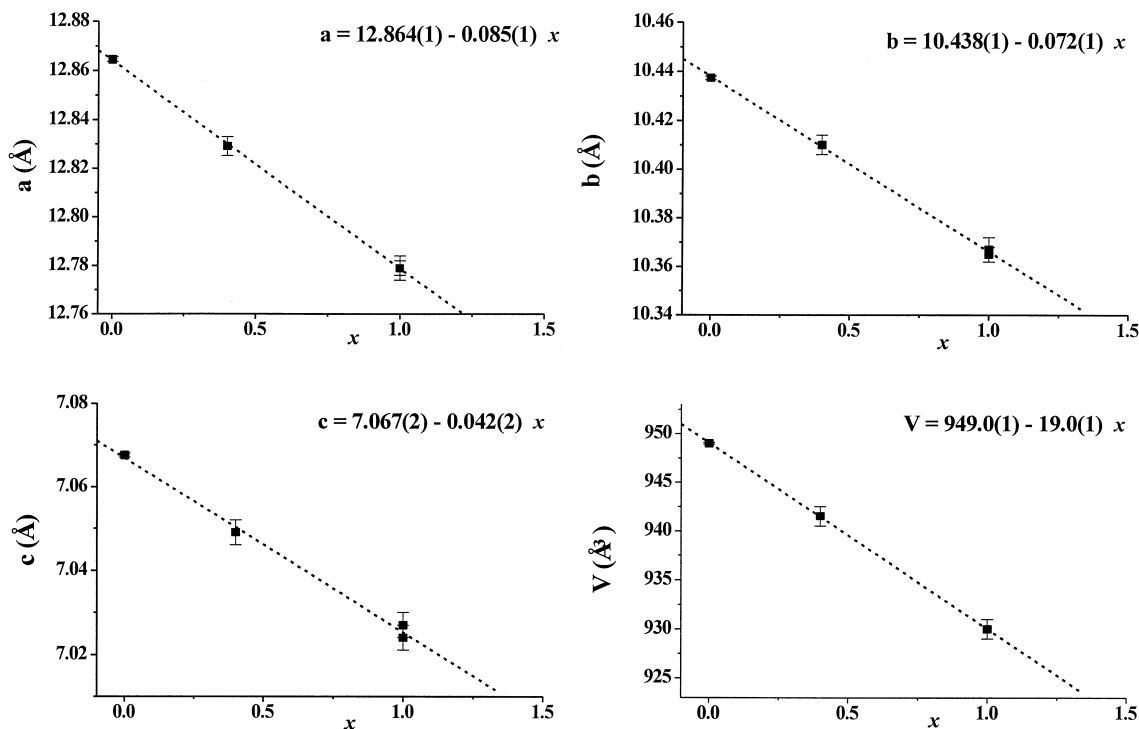

Fig. 5. Variation of the unit cell parameters and cell volume of thorium–plutonium (IV) phosphate–diphosphate as a function of x.
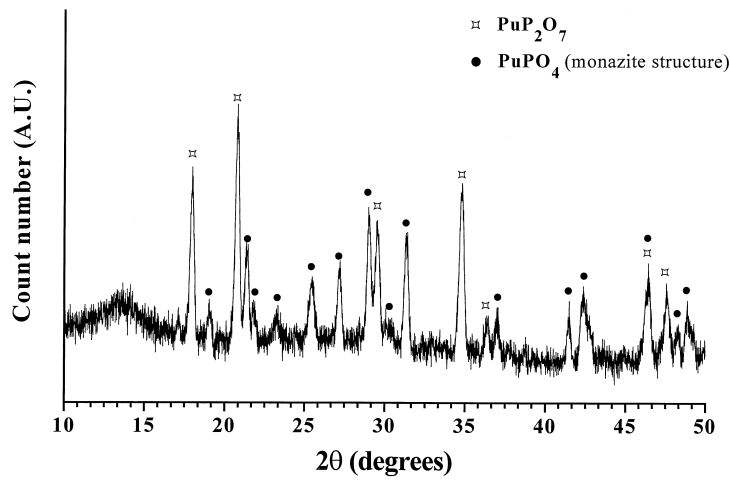
Fig. 6. The PuO_2–P_2O_5 system: X-ray powder diagram obtained for $Pu/PO_4 = \frac{2}{3}$.

of the peaks positions in the XRD diagram (compared to the TPD diagram) (Fig. 4). The higher the x value in $Th_{4-x}Pu_x(PO_4)_4P_2O_7$, the greater the shift observed, which is in good agreement with the substitution of thorium by another cation in the lattice.

The unit cell parameters and cell volume of thorium–plutonium (IV) phosphate–diphosphate, obtained by linear regression from the experimental data, can be described by the four following equations:

$$a = 12.864 - 0.085\,x, \tag{10}$$

$$b = 10.438 - 0.072\,x, \tag{11}$$

$$c = 7.067 - 0.042\,x, \tag{12}$$

$$V = 949.0 - 19.0\,x. \tag{13}$$

The values of the cell parameters and the cell volume are gathered in Table 3 for $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$ and $Th_3Pu(PO_4)_4P_2O_7$ while variations in terms of x are shown in Fig. 5.

The a, b, c and V values decrease with the increase of x because thorium is replaced by a smaller cation. Using the U-fit program [21], the approximate maximum x values for TPPD solid solutions have been calculated. They are equal to 1.81 from a, 1.38 from b, 1.86 from c and to 1.63 from the cell volume V. The last value is close to that calculated from Eq. (8): $x = 1.67$. Thus, the formula of the richer solid solution in plutonium could be considered approximately $Th_{2.4}Pu_{1.6}(PO_4)_4P_2O_7$ (40 mol% of thorium substituted by plutonium). The existence of such a compound needs to be verified experimentally.

With the aim of synthesizing the plutonium (IV) phosphate–diphosphate $Pu_4(PO_4)_4P_2O_7$, plutonium (IV) nitrate and phosphoric acid solutions were mixed with the ratio $Pu/PO_4 = \frac{2}{3}$. The residue obtained after evaporation (according to the same procedure as for solid solutions) is still amorphous. After heating at 1050°C for 18 h, the final

product is a polyphase system. It is composed of the plutonium (IV) diphosphate (JCPDS file number 43-1097) and plutonium (III) phosphate (monazite structure, JCPDS file number 43-1096) which are white and blue coloured respectively [20,24]. Both phases are pointed in the X-ray powder diffraction diagram in Fig. 6. Moreover, as mentioned in the literature [10,24], the plutonium diphosphate is certainly decomposed into $PuPO_4$ at temperature higher than 1050°C which leads to the non-existence of $Pu_4(PO_4)_4P_2O_7$ and to the decomposition of the phosphate excess.

4. Conclusions

Thorium–uranium solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ have been synthesized for x values up to $x = 3.0$. The ionic radius of uranium (IV) is very close to that of thorium. Thus, in the system ThO_2–UO_2–P_2O_5, up to 75 mol% of thorium can be substituted by uranium. Starting from these results, the unit cell parameters of the solid solutions based on TPD have been refined and their evolution as well as the evolution of the cell volume in terms of x value have been established. The maximum x value of thorium replaced by other tetravalent elements can be calculated by taking into account their ionic radii.

The Ce^{4+} radius (as well as that of U^{4+}) is close to thorium and then this cation could substitute thorium in TPD, but it is reduced into cerium (III), in the presence of phosphates when heated to high temperature. The system is always polyphase.

In the case of the ThO_2–ZrO_2–P_2O_5 system, thorium and zirconium phosphates form separated phases: no solid solutions based on TPD can be obtained. The zirconium ion is probably too small for the substitution of thorium in the TPD lattice and the crystal structure of thorium phos-

phate–diphosphate is certainly too rigid to allow the replacement of thorium by other cations of small ionic radii (10–15% relative to the thorium ion).

Thorium–plutonium phosphate–diphosphate solid solutions have been synthesized for $0 < x < 1.0$. In this case, the TPD lattice undergoes greater deformation than in the ThO_2–UO_2–P_2O_5 system which is in good agreement with the ionic radii of these cations. The calculated value is equal to 1.67 which suggests that solid solution of composition $Th_{2.4}Pu_{1.6}(PO_4)_4P_2O_7$ could be obtained.

It has not been possible to synthesize compounds $M_4(PO_4)_4P_2O_7$ (M = U, Pu) (analogous to TPD): the final systems are always polyphase (composed of α-UP_2O_7 and $U_2O(PO_4)_2$ for uranium and of α-PuP_2O_7 and $PuPO_4$ for plutonium).

The results obtained show that thorium phosphate–diphosphate may be used as a host matrix for large amounts of uranium and plutonium. Leaching tests of TPD and TUPD have been already published [17], while those of TPPD are in progress. Other results concerning the behaviour of ^{241}Am built within the TPD matrix by decrease of ^{241}Pu (which is also present in the plutonium (IV) solutions used) will be published soon. Irradiation effects on pure matrix and solid solutions are also under study.

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