Inorg. Chem. **2007**, *46*, 10390–10399

Inorganic Chemistry
Article

Hydrothermal Method of Preparation of Actinide(IV) Phosphate Hydrogenphosphate Hydrates and Study of Their Conversion into Actinide(IV) Phosphate Diphosphate Solid Solutions

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Received July 2, 2007

Several compositions of $Th_{2-x/2}An^{IV}_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$ (An = U, Np, Pu) were prepared through hydrothermal precipitation from a mixture of nitric solutions containing cations and concentrated phosphoric acid. All the samples were fully characterized by X-ray diffraction, UV–vis, and infrared spectroscopies to check for the existence of thorium–actinide(IV) phosphate hydrogenphosphate hydrates solid solutions. Such compounds were obtained as single phases, up to $x = 4$ for uranium, $x = 2$ for neptunium, and $x < 4$ for plutonium, the cations being fully maintained in the tetravalent oxidation state. In a second step, the samples obtained after heating crystallized precursors at high temperature (1100 °C) were characterized. Single-phase thorium–actinide(IV) phosphate–diphosphate solid solutions were obtained up to $x = 0.8$ for Np(IV) and $x = 1.6$ for Pu(IV). For higher substitution rates, polyphase systems composed by β-TAnPD, $An_2O(PO_4)_2$, and/or α-AnP_2O_7 were formed. Finally, this hydrothermal route of preparation was applied successfully to the synthesis of an original phosphate-based compound incorporating simultaneously tetravalent uranium, neptunium and plutonium.

1. Introduction

In the framework of a 1991 French research law,[1] the immobilization of radionuclides in an underground repository can be considered one of the options for the management of long-lived and highly radioactive radionuclides. In this field, the french research group NOMADE (CNRS/CEA/AREVA/French Universities) was set up to study and propose several ceramics for the final disposal of minor actinides (Np, Am, Cm). Among them, three phosphate materials were chosen on the basis of several interesting properties such as high weight loadings in actinides and good resistance to aqueous alteration or to radiation damage. In this field, brabantites ($Ca_{0.5}M^{IV}_{0.5}PO_4$),[2−7] monazites ($M^{III}PO_4$),[8−10] or britholites ($Ca_9Nd_{1-x}M^{IV}_x(PO_4)_{5-y}(SiO_4)_{1+y}F_2$),[11−14] as their natural analogues, can incorporate large amounts of uranium and/or thorium (e.g., up to 30 wt % in ThO_2)[8,15] and usually appear to be well-crystallized even for high doses of irradiation. In the past decade, several studies were also dedicated to the thorium phosphate diphosphate (β-$Th_4(PO_4)_4P_2O_7$, called β-TPD),[16−21] as a promising ceramic for the specific im-

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10.1021/ic701297v CCC: $37.00 © 2007 American Chemical Society
Published on Web 11/01/2007

mobilization of tetravalent actinides since it allows the incorporation of large amounts of uranium (up to 47.6 wt %), neptunium (33.2 wt %), or plutonium (26.1 wt %) by substitution of thorium in its crystal structure.[19,20] Moreover, the resulting solid solutions with actinides, β-$Th_{4-x}An_x(PO_4)_4$-(P_2O_7) (β-TAnPD), and their association with monazites exhibit good sintering properties,[18,22,23] very slow normalized dissolution rates,[21,24−26] and good resistance to radiation damage.[27−30]

Several chemistry routes, including wet and dry methods, were already developed to perform the preparation of β-TPD and associated solid solutions with tetravalent actinides.[17] The process based on the evaporation of a mixture of acidic solutions containing cations and concentrated phosphoric acid led to single phase but heterogeneous solids (especially in terms of the cation distribution inside the prepared ceramics) after heating at high temperature. Consequently, the synthesis of crystallized precursors of β-TPD and β-TUPD solid solutions, i.e., thorium phosphate hydrogenphosphate hydrate (TPHPH)[31] and related TUPHPH solid solutions ($Th_{2-x/2}U_{x/2}$-$(PO_4)_2(HPO_4)\cdot H_2O$),[32,33] respectively, was developed to get dense and homogeneous samples after heating at high temperature.

This paper reports the first attempts to incorporate tetravalent neptunium or plutonium in the β-TPD structure through the initial preparation of new TNpPHPH ($Th_{2-x/2}Np_{x/2}$-$(PO_4)_2(HPO_4)\cdot H_2O$) and TPuPHPH ($Th_{2-x/2}Pu_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$) solid solutions. The preparation of such compounds was performed with nitric media due to its predominance in the nuclear fuel cycle, particularly during the reprocessing of spent fuels.[34] The preparation of several compounds with various compositions, including the Pu and Np end-members, was thus envisaged, and the unit cell parameters were refined from X-ray diffraction (XRD) data reported for pure TPHPH.[35] Finally, the transformation of such low-temperature crystallized precursors into high-temperature β-TPuPD and β-TNpPD solid solutions was investigated to examine the range of composition allowing the preparation of homogeneous and single-phase powdered samples.

2. Experimental Section

2.1. Chemicals. The usual reagents used for the syntheses and the analyses were supplied by Prolabo and were of “pro-analysis” grade. All acidic solutions containing actinides were homemade at the Atalante facility of CEA-Valrhô. The nitric solution of uranium(IV) was obtained after purification by chromatography of a stock solution of uranium nitrate provided by AREVA NC, then the associated concentrations of uranium(IV) and uranium(VI) were determined by spectrophotometry. The concentration was fixed to 100 $g\cdot L^{-1}$ (i.e., 0.42 M), and the tetravalent oxidation state of uranium was stabilized by adding 0.07 M of hydrazinium ions ($N_2H_5^-$, NH) as an anti-nitrous reagent. Nevertheless, at least 10% of the total uranium was found in the uranyl form.

The neptunium(IV) solution was prepared from two purified liquors. The concentrations of hydronium, hydrazinium, and hydroxylammonium (NH_3OH^-, NHA) ions (these two last being added to prevent any oxidation of Np(IV) into Np(V)) were set to 1, 0.5, and 0.5 M, respectively. The final neptunium concentration was evaluated to 0.18 ± 0.02 M while that of its daughter product, i.e., ^{233}Pa ($T_{1/2} = 27$ days), present in secular equilibrium with ^{237}Np, reached about 10^{-9} M and was consequently neglected in the mass balance during the synthesis.

Finally, the plutonium(IV) solution was obtained through the digestion of plutonium oxalate in hot concentrated nitric acid (5 M HNO_3, $T = 70$ °C). The tetravalent oxidation state was adjusted by adding hydrogen peroxide when necessary.

2.2. Hydrothermal Precipitation of the Precursors. The preparation of tetravalent actinide phosphate hydrogenphosphate hydrates (An = Th, U, Np, Pu) was based on the method previously developed when studying the precipitation of $Th_2(PO_4)_2(HPO_4)\cdot H_2O$[31] and associated solid solutions with uranium(IV).[32,33] Concentrated phosphoric acid (5 M H_3PO_4) was added dropwise to a mixture of nitric solutions containing cations ($\Sigma C_{An} = 0.15$ M). Stoichiometric proportions ($\Sigma An/PO_4 = {}^2/_3$) were considered, but a small excess of phosphate (of about 2%) was introduced to ensure the quantitative precipitation of tetravalent cations. Moreover, solutions of 0.2 M hydrazinium and hydroxylammonium were used as anti-nitrous reagents to keep uranium and neptunium in their

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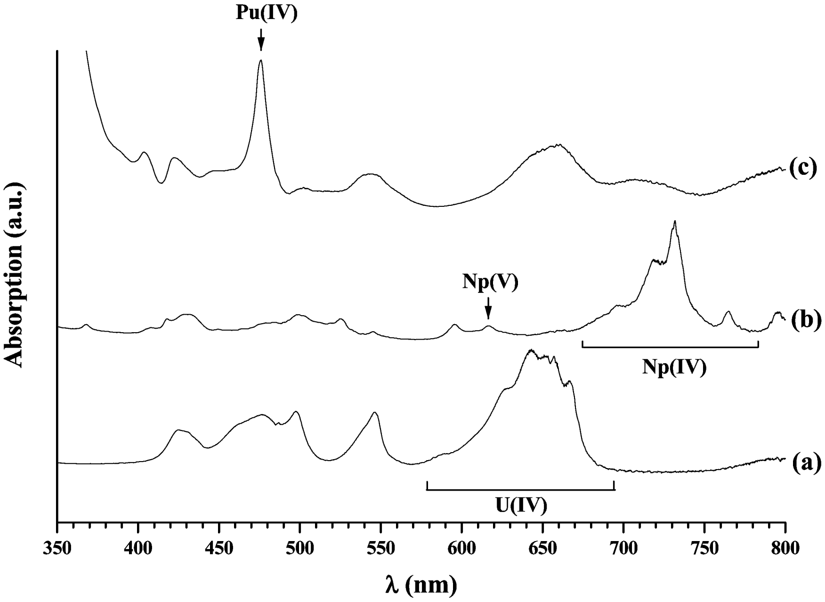

Figure 1. UV−vis absorption spectra of gelatinous phases obtained from phosphoric acid and 0.12 M Th + 0.03 M U(IV); (a) 0.135 M Th + 0.015 M Np(IV); (b) 0.135 M Th + 0.015 M Pu(IV); (c) with a mole ratio $An^{IV}/PO_4 = {}^2/_3$.

tetravalent oxidation state during the hydrothermal treatment. We checked that both compounds slowly decomposed in hot nitric media.[36,37]

The gelatinous compounds initially formed when mixing the solutions progressively turned into well-crystallized precipitates by heating at 130 °C for several weeks: the PTFE vials containing the gels were placed in a Parr acid digestion bomb (model no. 4749), then set in an oven specially designed for this purpose. After heating, the precipitates were separated by filtration, washed several times with ethanol, and then finally dried at room temperature. Different powder colors were observed depending on the actinide considered: white for the well-known thorium compound, green for uranium and neptunium, and pink for plutonium ones (all agreed well with that expected in phosphoric media for the tetravalent oxidation state of such actinides[38,39]).

Finally, the compounds were heated up to 1100 °C in air or under an inert atmosphere (Ar) to study their conversion into the final thorium−actinide phosphate diphosphate compounds. Due to the high specific activity of such samples, all the chemical steps were carried out in a glovebox, and only small quantities of compounds were prepared.

2.3. Characterization of the Powders. The oxidation states of uranium and plutonium, on the one hand, and of neptunium, on the other hand, were checked by UV−vis absorption spectrometry using the GBC UV/VIS 920 and Shimadzu UV-3101PC double-beam apparatus, respectively. Infrared absorption spectra were recorded from 400 to 4000 cm^{-1} using cylindrical pellets of about 1−3 wt % of powder dispersed in KBr with a Nicolet Magna IR 550 Série II spectrophotometer.

The XRD diagrams were collected with a Inel diffractometer equipped with a CPS 120 curve detector using the Cu $K\alpha_1$ ray ($\lambda = 1.54056$ Å). The analyzed samples were mixed with a resin of low diffusion, then set on a platelike sample holder. After drying and checking for the absence of contamination, the plate was transferred outside the glovebox, placed in a boat, and covered with Kapton. This protocol, related to the confinement of α-radioactive materials, could explain the important background observed on the XRD diagrams. The precise peak positions were determined using the fitting program *EVA*, available in the software package *Diffrac-AT*, version 3.0, purchased by Socabim and supplied by Siemens. Finally, the unit cell parameters were refined using the *U-Fit* software.[40]

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) experiments were carried out on a Netzsch STA 409C apparatus equipped with a furnace operating up to 1500 °C and using alumina boats. After each measurement, the powder was carefully characterized by XRD.

3. Results and Discussion

3.1. Characterization of the Initial Crystallized Precursors. 3.1.1. UV−Vis Absorption Spectroscopy.

UV−vis absorption spectra were recorded for the gelatinous phases formed after mixing the actinide solutions with concentrated phosphoric acid (Figure 1).

The positions of the absorption bands for each actinide appear close to those previously observed in the initial solutions. Only a small shift in the position was detected due to the complexing of actinides by phosphate species. Moreover, the spectra of tetravalent neptunium- and plutonium-bearing samples evidenced a weak oxidation of plutonium(IV) into plutonium(VI) (characteristic absorption band around 830 nm) as well as the minor presence of neptunium(V) (around 616 nm). In this last case, Np(V) was already present in the initial solution due to the difficulty in fully stabilizing neptunium in its tetravalent oxidation state. Moreover, the peak positions of uranium(IV) and uranium(VI) appeared consistent with those obtained for several

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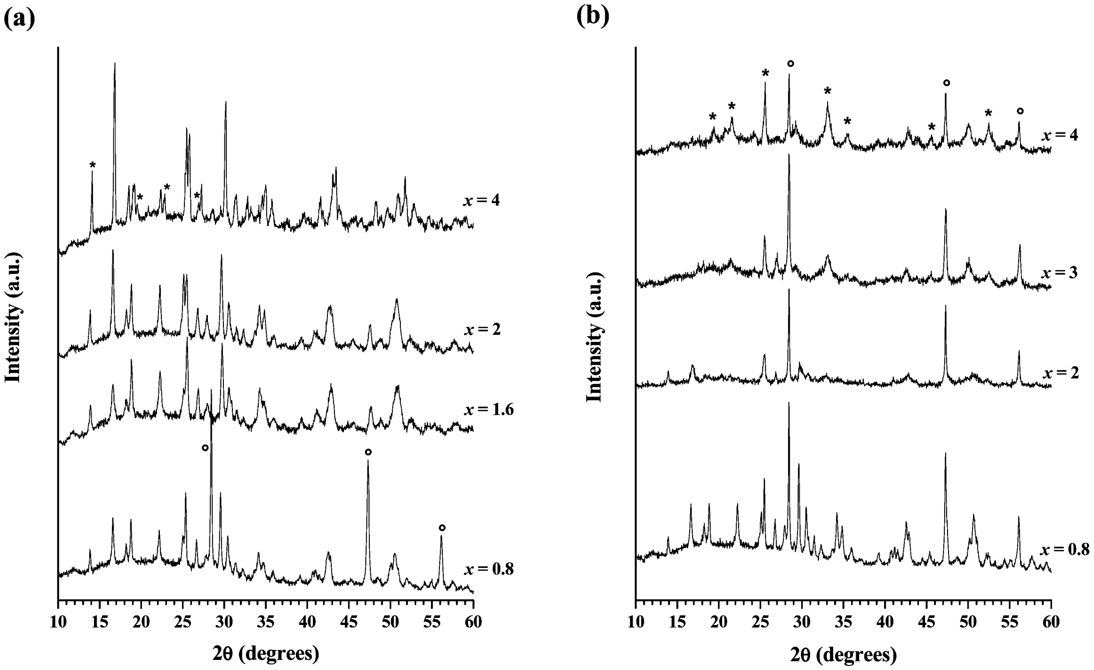

Figure 2. XRD diagrams of TPuPHPH (a) and TNpPHPH (b) solid solutions. The XRD lines of Si used as internal reference are indicated by ° while those of additional $Pu(OH)PO_4$ or $Np(OH)PO_4$ phases are marked by *.

uranium(IV) and uranium(VI) phosphate compounds such as $U(UO_2)(PO_4)_2$, α-UP_2O_7, and $U_2O(PO_4)_2$.[41−44]

3.1.2. X-ray Diffraction. In order to check the effective incorporation of tetravalent actinides in the TPHPH structure, several compositions were considered: $Th_{2-x/2}U_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$ ($x = 0.8$), $Th_{2-x/2}Np_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$ ($x =$ 0.8, 2.0, 3.0, and 4.0), and $Th_{2-x/2}Pu_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$ (x = 0.8, 1.6, 2.0, and 4.0). XRD diagrams recorded for TPuPHPH and TNpPHPH samples are gathered in Figure 2. For plutonium-based compounds, XRD patterns always appear consistent with those reported for pure TPHPH.[35] Nevertheless, attempts to prepare pure and single-phase PuPHPH (i.e., $Pu_2(PO_4)_2(HPO_4)\cdot H_2O$) remained unfruitful since additional XRD lines indicated the presence of the secondary phase. On the basis of the data reported for $U(OH)PO_4\cdot 2H_2O$,[45] $U(OH)PO_4$, or $Th(OH)PO_4$,[31,46] these XRD lines were assigned to the hydrated plutonium hydroxide phosphate $Pu(OH)PO_4\cdot nH_2O$. The same isomorphic Np compound was also systematically obtained as part of a polyphase system when trying to prepare TNpPHPH solid solutions with Np/Th mole ratios higher than 1. The expected TNpPHPH single phase was only prepared for Np/Th = 1:4 and 1:1.

For all the TAnPHPH solids prepared, the unit cell parameters were refined considering the orthorhombic system (*Cmcm* space group) reported for TPHPH[35] or the slightly distorted monoclinic unit cell (*Cc* space group) evidenced on several TUPHPH solid solutions and UPHPH and CePHPH compounds (Table 1).[33,48,49]

Their variation versus the average cationic radius in the eight-fold coordination (${}^{[VIII]}r_{Th} = 1.05$ Å; ${}^{[VIII]}r_{U} = 1.00$ Å; ${}^{[VIII]}r_{Np} = 0.98$ Å; ${}^{[VIII]}r_{Pu} = 0.96$ Å[47]) is plotted in Figure 3 while the associated equations are gathered in Table 2. The data collected in this work were analyzed by the method previously reported for TUPHPH,[33] UPHPH,[33,48] and CePHPH.[49] The linear variation of the lattice parameters confirms the existence of a unique AnPHPH structure between both the Th and Pu end-members. Indeed, even for the ${}^{[VIII]}r_{cat}$ values leading to a monoclinic cell, the angle remains close to 90° and the structure could be considered as a slight distortion of the initial orthorhombic lattice, as already described for TUPHPH.[33] Moreover, the contraction of the cell between Th and Pu end-members appears limited: only 1.9% along *a*, 1.7% along *b*, and 1.6% along *c*, i.e., 5.1% along the unit cell volume, *V*.

Tetravalent plutonium and cerium are the smallest tetravalent cations involved in the formation of $M(PO_4)_2(HPO_4)\cdot H_2O$ compounds. Indeed, this structure was not obtained for tetravalent zirconium (${}^{[VIII]}r_{Zr} = 0.84$ Å), hafnium (${}^{[VIII]}r_{Hf} = 0.83$ Å), and tin (${}^{[VIII]}r_{Sn} = 0.81$ Å).[50] On the basis of steric considerations, TNpPHPH compounds should have been obtained whatever the composition examined. The main factor driving the obtention of polyphase systems should thus be the operating conditions rather than the steric constraints.

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Table 1. Unit Cell Parameters of Actinide(IV) Phosphate Hydrogenphosphate Hydrates Solid Solutions

composition[a]	average $^{[VIII]}r_{cat}$	a (Å)	b (Å)	c (Å)	β (deg)	V (Å^3)
$Th_2(PO_4)_2(HPO_4)\cdot H_2O$	1.050	21.368(2)	6.695(1)	7.023(1)	90	1004.8(4)
$Th_{1.92}U_{0.08}(PO_4)_2(HPO_4)\cdot H_2O$	1.048	21.384(4)	6.690(2)	7.027(1)	90	1005.3(6)
$Th_{1.84}U_{0.16}(PO_4)_2(HPO_4)\cdot H_2O$	1.046	21.363(3)	6.689(2)	7.023(1)	90	1003.6(6)
$Th_{1.63}U_{0.37}(PO_4)_2(HPO_4)\cdot H_2O$	1.041	21.347(7)	6.684(3)	7.021(2)	90	1001.8(10)
$Th_{1.6}Np_{0.4}(PO_4)_2(HPO_4)\cdot H_2O$	1.036	21.228(8)	6.651(3)	6.982(3)	90	985.7(10)
$Th_{1.6}Pu_{0.4}(PO_4)_2(HPO_4)\cdot H_2O$	1.032	21.282(6)	6.670(2)	6.996(2)	90	993.1(10)
$Th_{1.34}Np_{0.22}Pu_{0.22}U_{0.22}(PO_4)_2(HPO_4)\cdot H_2O$	1.027	21.346(9)	6.676(4)	7.024(4)	90	985.7(10)
$ThU(PO_4)_2(HPO_4)\cdot H_2O$	1.025	21.263(8)	6.640(3)	7.008(2)	90	989.5(10)
$Th_{0.88}U_{1.12}(PO_4)_2(HPO_4)\cdot H_2O$	1.022	21.234(9)	6.633(3)	7.010(3)	91.13(4)	987.1(20)
$Th_{0.75}U_{1.25}(PO_4)_2(HPO_4)\cdot H_2O$	1.019	21.236(12)	6.627(3)	7.011(4)	91.16(4)	986.5(20)
$Th_{1.2}Np_{0.4}Pu_{0.4}(PO_4)_2(HPO_4)\cdot H_2O$	1.018	21.203(8)	6.637(2)	6.969(3)	90	980.9(10)
$Th_{1.32}Pu_{0.68}(PO_4)_2(HPO_4)\cdot H_2O$	1.014	21.311(10)	6.648(4)	6.982(4)	90.28(10)	983.5(30)
$Th_{0.44}U_{1.56}(PO_4)_2(HPO_4)\cdot H_2O$	1.011	21.182(11)	6.622(4)	7.000(4)	91.39(4)	981.6(20)
$ThPu(PO_4)_2(HPO_4)\cdot H_2O$	1.005	21.122(7)	6.603(2)	6.977(3)	90.92(7)	972.9(20)
$U_2(PO_4)_2(HPO_4)\cdot H_2O$	1.000	21.148(7)	6.611(2)	6.990(3)	91.67(3)	976.8(10)
$Ce_2(PO_4)_2(HPO_4)\cdot H_2O$	0.970	21.0142(3)	6.55082(7)	6.94382(6)	91.983(1)	955.32(2)
$Pu_2(PO_4)_2(HPO_4)\cdot H_2O$	0.960	20.968(15)	6.583(3)	6.911(5)	91.93(10)	953.4(50)

[a] Determined on the basis of the analytical balance and/or from electron probe microanalysis experiments.

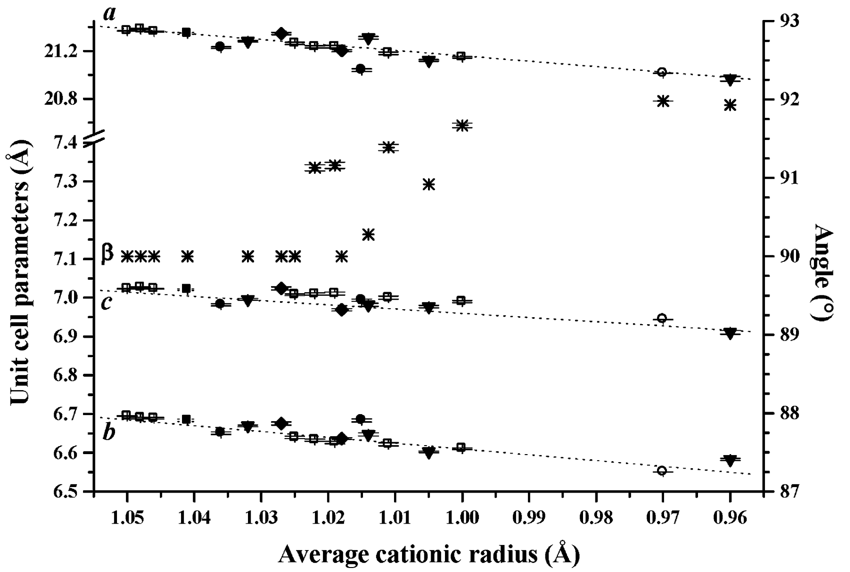

Figure 3. Variation of the unit cell parameters of the actinide(IV) phosphate hydrogenphosphate hydrates versus the average ionic radius. Key: □, TUPHPH;[33] ■, TUPHPH (this work); ▼, TPuPHPH; ●, TNpPHPH; ♦, TPuNpUPHPH; ○, CePHPH.[49]

Table 2. Variation of the Unit Cell Parameters and Associated Volume of $An(PO_4)_2(HPO_4)\cdot H_2O$ versus the Average Cationic Radius $^{[VIII]}r_{cat}$

a (Å)	$16.6(4) + 4.5(4)\times {}^{[VIII]}r_{cat}$
b (Å)	$5.9(1) + 1.1(1) \times {}^{[VIII]}r_{cat}$
c (Å)	$5.1(2) + 1.5(2) \times {}^{[VIII]}r_{cat}$
V (Å^3)	$390(35) + 585(35) \times {}^{[VIII]}r_{cat}$

3.1.3. **IR Spectroscopy.** The IR spectra of Np- and Pu-based samples were recorded to confirm the purity of AnPHPH compounds (Figure 4 and Table 3). Although the solids were washed several times with ethanol after their preparation under hydrothermal conditions, some nitrate groups absorbed at the surface of the solids were responsible for the band usually located at around 1385 cm^{-1} (stretching vibration of the N−O bond).

As expected from the XRD data, the TNpPHPH and TPuPHPH solid solutions were obtained as single phases only for $x_{Np} < 2$ and $x_{Pu} < 4$, respectively. For these substitution values, all the IR spectra recorded match well with that obtained for pure TPHPH.[35] The vibration modes of the P−O bonds are observed from 490 to 660 cm^{-1} (δ_{as}), from 930 to 980 cm^{-1} (ν_s), and from 980 to 1190 cm^{-1} (ν_{as})[51−54] while the bands associated with δ_s(P−O), usually observed below 450 cm^{-1}, are not observed in the IR spectra presented. Moreover, the presence of hydrogenphosphate entities is evidenced by the observation of two shoulders at about 3200 and 2400 cm^{-1} (stretching modes) and of two bands located at 1240 and 880−940 cm^{-1} (deformation in the plane and out of the plane, respectively).[55−59] Finally, the large band

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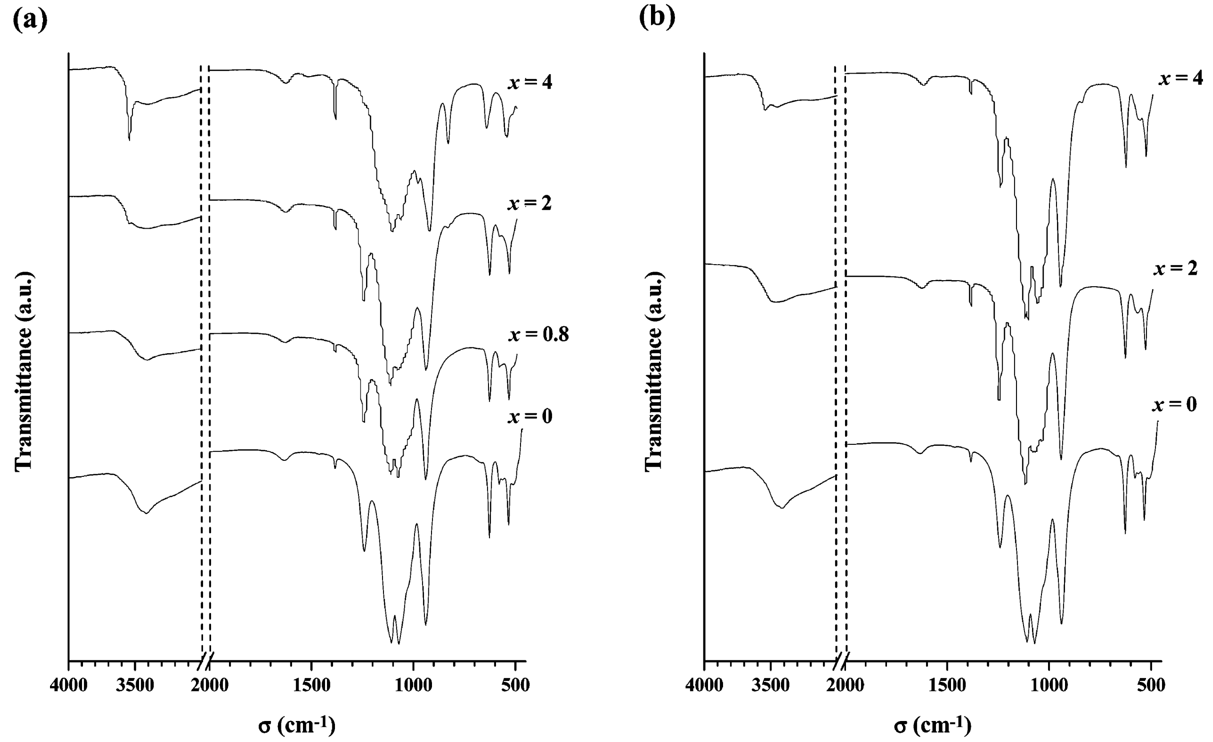

Figure 4. IR spectra of TNpPHPH (a) and TPuPHPH (b) solid solutions.

Table 3. Assignment of the IR Bands (cm^{-1}) Observed on the Spectra of TNpPHPH and TPuPHPH Solid Solutions. Comparison with the Data Obtained for Pure TPHPH[35]

	δ_{as}(P−O)	ν_s(P−O)	ν_{as}(P−O)	δ_{ip}(P−(O−H))	δ_{op}(P−(O−H))	ν(An^{IV}−O)	ν(An^{IV}−(O−H))
TPHPH[35]							
	500−625	962	1005−1105	934	1251		
TNpPHPH							
$x = 0.8$	500−640	940	990−1190	N.O.	1240	N.O.	N.O.
$x = 2$	500−650	930	990−1180	N.O.	1240	827	3540
$x = 4$	500−660	915	970−1180	N.O.	N.O.	829	3540
TPuPHPH							
$x = 2$	500−660	940	980−1180	N.O.	1250	N.O.	N.O.
$x = 4$	500−660	945	970−1170	N.O.	1240	837	3550

at 3400 cm^{-1} (O−H stretching vibrations) and the small one at 1630 cm^{-1} (bending mode of H_2O) confirm the presence of structural water in the samples.

The spectra recorded from the compounds precipitated for $x_{Np} > 2$ or $x_{Pu} = 4$ agree well with the presence of tetravalent actinide hydroxide phosphate, $An(OH)PO_4 \cdot xH_2O$, in the samples prepared. The apparition of a narrow absorption band near 830 cm^{-1} could be assigned to the An−O bond while that located at 3540 cm^{-1} was correlated to the vibration of a terminal hydroxide group (An−O−H bond), as reported in several compounds such as magnesium hydroxide phosphate or kaolinite[52,60,61] and more recently in the Raman spectrum of $Th(OH)PO_4$.[46] All the other absorption bands match well with those reported by Brandel et al. for homogeneous and single-phase $Th(OH)PO_4$.[31]

3.2. Thermal Behavior and Characterization of the Systems Obtained by Heating.

3.2.1. Thorium−Neptunium-Based Compounds. In order to study the thermal behavior of the initial precursors precipitated in hydrothermal conditions, the samples were heated at 400 °C for 1 h and then up to 1100 °C for 1 h in air or under an argon atmosphere. After the first heating step, the XRD diagrams recorded for all the samples matched well with that of pure α-TPD[62] and indicated the existence of a complete α-TNpPD solid solution. On the contrary, β-TNpPD solid solutions were only obtained for Np/Th mole ratios lower than 1 after heating at 1100 °C (Figure 5a), which agrees well with the data reported for other samples prepared through the wet chemistry method of reference (i.e., direct evaporation of the initial mixture). The substitution of thorium by tetravalent neptunium was shown possible for Np/Th ≤ 1.08.[20]

For higher substitution rate (Np/Th > 1), polyphase systems were systematically prepared, as described in Table 4.

A mixture of β-TNpPD solid solution and small amounts of $Np_2O(PO_4)_2$ and α-NpP_2O_7 was obtained in either air or

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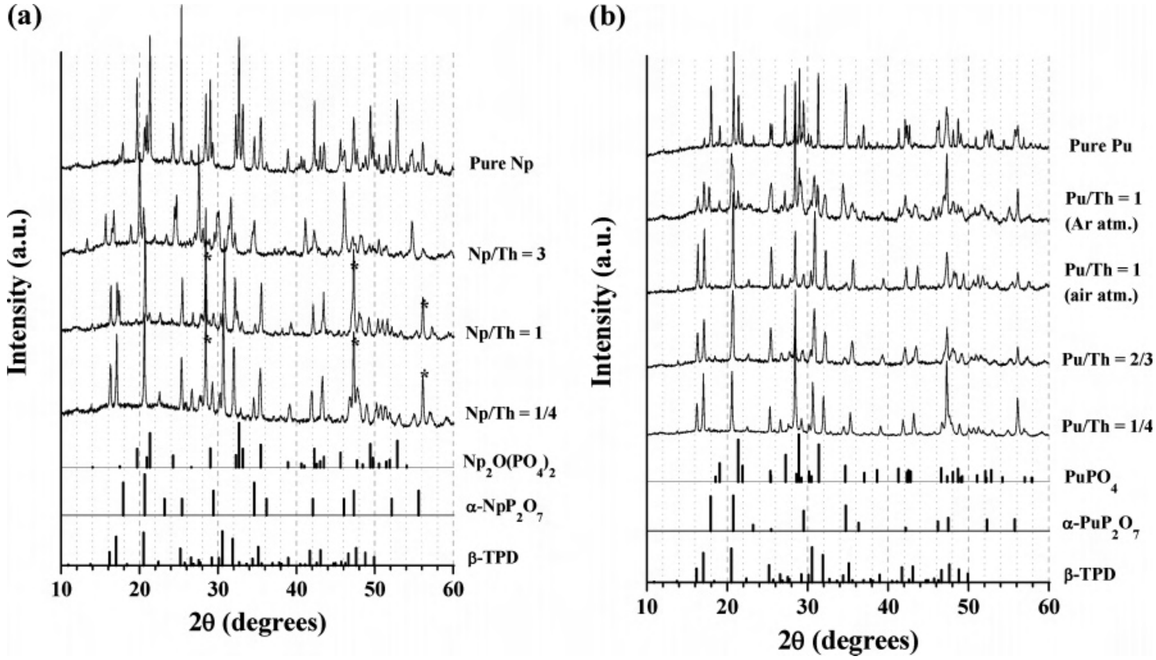

Figure 5. XRD diagrams of (a) Np- and (b) Pu-bearing samples ($T = 1100$ °C, $t = 1$ h). XRD lines of silicon used as internal reference are marked by *.

Table 4. Description of the Systems Obtained After Heat-Treatment of TNpPHPH Solid Solutions

Np/Th mole ratio	$x_{Np, calc}$ in β-TNpPD	initial precipitate	system obtained after heating at 1100 °C: air	system obtained after heating at 1100 °C: argon	$x_{Np, exp}$ in β-TNpPD
0.25	0.8	TNpPHPH	β-TNpPD		0.8
1	2	TNpPHPH + ϵ $Np(OH)PO_4$ + unidentified phase[a]	**β-TNpPD** + ϵ $Np_2O(PO_4)_2$ + ϵ α-NpP_2O_7		1.8
3	2.1	$An(OH)PO_4$ + unidentified phase[a]	**β-TNpPD** + $Np_2O(PO_4)_2$+ α-NpP_2O_7	$An_2O(PO_4)_2$ + α-AnP_2O_7	2.3
1/0		$An(OH)PO_4$ + unidentified phase[a]	$Np_2O(PO_4)_2$ + α-NpP_2O_7		

[a] Unidentified phase introduced to maintain the $An/PO_4 = {}^2/_3$ mole ratio. It could probably be amorphous $AnP_2O_7{\cdot}nH_2O$ or $An(HPO_4)_2{\cdot}nH_2O$.

argon atmosphere for Np/Th = 1. The composition of the final β-TNpPD compound, determined from the refined unit cell parameters, was evaluated to β-$Th_{2.2}Np_{1.8}(PO_4)_4P_2O_7$ (i.e., Np/Th = 0.82), which appears in good agreement with the presence of Np-enriched phases ($Np_2O(PO_4)_2$ and α-NpP_2O_7) in the final mixture prepared. Since the Np/Th mole ratio is close to the limit of incorporation of Np in the β-TPD structure, the formation of such phases could be explained by the presence of local small heterogeneities in the initial cation distribution even if this method of preparation leads to a significant improvement of this parameter compared with direct evaporation methods.

For Np-enriched materials (e.g., Np/Th = 3) and pure neptunium compound, the mixture was always composed by diactinide oxide phosphate $Th_{2-x}Np_xO(PO_4)_2$ and actinide diphosphate α-$Th_{1-y}Np_yP_2O_7$ solid solutions. When heating in air the initial mixture obtained and considering an initial mole ratio Np/Th equal to 3, the composition of the β-TNpPD-type solid solution was evaluated to $x_{Np} = 2.3$ (i.e., Np/Th = 1.35). Finally, when heating neptunium phosphate hydrogenphosphate hydrate at 1100 °C, the XRD diagram of the final sample confirmed the presence of significant amounts of $Np_2O(PO_4)_2$ (orthorhombic, *Cmca*, $a = 7.038(1)$ Å, $b = 9.015(2)$ Å, $c = 12.603(3)$ Å), isotypic of $U_2O(PO_4)_2$,[44] and of α-NpP_2O_7 (cubic, *Pa*3, $a = 8.591(4)$ Å).

Whatever the composition and the operating conditions considered, it is worth noting that neptunium was kept in the tetravalent oxidation state during the heating treatment, which was confirmed by the broad band lying between 650 and 750 nm in the UV-vis spectra and by the deep green color of the samples. Moreover, no absorption band was detected near 400 nm, excluding the presence of Np(VI) in the solids.

3.2.2. Thorium−Plutonium-Based Compounds. The same study was devoted to the thermal behavior of thorium−plutonium(IV) phosphate hydrogenphosphate hydrate samples. The incorporation of tetravalent plutonium in the samples prepared by heating at 1100 °C was checked by XRD (Figure 5b), leading to the evaluation of the limit of incorporation of plutonium(IV) in the β-TPD structure. Indeed, for Pu/Th mole ratios lower than ${}^2/_3$, the heating treatment performed at 1100 °C on the initial crystallized precursors, i.e., TPuPHPH, was always sufficient to prepare pure and single-phase β-TPuPD solid solutions, whatever the atmosphere considered. The total weight loss of about 4%, observed in the TGA curve between 100 and 600 °C agrees well with the departure of water molecules associated with the dehydration of TPuPHPH solid solutions then with the condensation of hydrogenphosphate groups into diphosphate entities, as already described for pure TPHPH.[35] The variations of the associated refined unit cell parameters match well with those reported in the literature when studying their variation versus the average ionic radius (Table 5).[19] β-TPuPD solid solutions were prepared in air for Pu/Th mole

Table 5. Variation of the Unit Cell Parameters and Associated Volume of β-TAnPD Solid Solutions versus the Average Cationic Radius $^{[VIII]}r_{cat}$

composition[a]	average $^{[VIII]}r_{cat}$	a (Å)	b (Å)	c (Å)	V (Å^3)
$Th_{3.2}U_{0.8}(PO_4)_4P_2O_7$	1.040	12.829(4)	10.409(4)	7.052(3)	941(1)
$Th_{3.2}Np_{0.8}(PO_4)_4P_2O_7$	1.036	12.802(4)	10.398(4)	7.035(3)	936(1)
$Th_{2.2}Np_{1.8}(PO_4)_4P_2O_7$	1.019	12.733(6)	10.349(5)	6.998(6)	922(2)
$Th_{3.2}Pu_{0.8}(PO_4)_4P_2O_7$[b]	1.032	12.83(1)	10.42(1)	7.053(8)	944(3)
$Th_{2.4}Pu_{1.6}(PO_4)_4P_2O_7$[b]	1.014	12.81(2)	10.39(1)	7.033(9)	936(4)
$Th_{2.4}Np_{0.8}Pu_{0.8}(PO_4)_4P_2O_7$[c]	1.018	12.783(6)	10.370(5)	7.016(4)	930(1)
$Th_{2.4}U_{0.8}Np_{0.4}Pu_{0.4}(PO_4)_4P_2O_7$	1.024	12.810(4)	10.401(3)	7.035(5)	937(1)

[a] Calculated. [b] Important uncertainties due to the use of Si as internal monitor. [c] Presence of $PuPO_4$ and α-$Th_{0.3}Pu_{0.7}P_2O_7$ as minor phases.

Table 6. Description of the Systems Obtained After Heat-Treatment of TPuPHPH Solid Solutions

Pu/Th mole ratio	expected x_{Pu} in β-TPuPD	initial precipitate	system obtained after heating at 1100 °C		obtained x_{Pu} value in β-TPuPD
			air	argon	
1/4	0.8	TPuPHPH	**β-TPuPD**		0.8
2/3	1.6	TPuPHPH	**β-TPuPD**		1.6
1	2	TPuPHPH	**β-TPuPD**	**β-TPuPD** + $PuPO_4$ + α-$Th_{1-y}Pu_yP_2O_7$	1.88 (air) 1.68 (Ar)
1/0		PuPHPH + $Pu(OH)PO_4$	$PuPO_4$ + α-PuP_2O_7		

ratios lower than 1. On the contrary, polyphase systems were prepared for a mole ratio of Pu/Th = 1 under argon atmosphere and for a pure Pu end-member (Table 6). In the first case, the anoxic atmosphere leads to the partial reduction of Pu(IV) into Pu(III) and thus to the formation of $PuPO_4$ monazite as a secondary phase. This was accompanied by the formation of α-$Th_{1-y}Pu_yP_2O_7$ solid solutions to counterbalance the (Th + Pu)/PO_4 mole ratio. The associated refined unit cell parameters led to a limit of incorporation of tetravalent plutonium near 47% in air and 42% when firing under an inert atmosphere, which appears to be consistent with that reported when synthesizing the samples through the direct evaporation of the initial mixture (i.e., 41% − x_{Pu} = 1.63).[19]

For the pure plutonium samples, a mixture of $PuPO_4$ monazite (monoclinic, $P_{21/n}$, $a = 6.747(2)$ Å, $b = 6.974(2)$ Å, $c = 6.438(3)$ Å, and $\beta = 103.68(3)°$) and of α-PuP_2O_7 (cubic, $Pa3$, $a = 8.554(2)$ Å) was systematically obtained after heating at 1100 °C, whatever the operating conditions during the heating treatment (air or argon atmosphere). All the unit cell parameters are close to those already reported by Björklund in the literature.[63]

3.3. Thorium−Uranium−Neptunium−Plutonium-Based Compounds. On the basis of the good results obtained for β-TNpPD and β-TPuPD solid solutions, several attempts were undertaken to simultaneously incorporate all the tetravalent actinides considered, i.e., Th, U(IV), Np(IV), and Pu(IV) in a β-TPD-type compound. Two nitric solutions containing tetravalent actinides were prepared by considering a mole ratio of U/Np/Pu/Th = 2/1/1/6 while the concentration of hydrazinium and hydroxylammonium varied between 0.02 and 0.2 M (Table 7).

Table 7. Concentrations of Tetravalent Actinides and Anti-Nitrous Reagents in the Initial Th/U/Np/Pu Nitric Solution

sample	I	II
[Th] M	0.061(2)	0.061(2)
[U(IV)] M	0.021(1)	0.021(1)
[Np(IV)] M	0.010(1)	0.010(1)
[Pu(IV] M	0.0100(6)	0.0100(6)
[NH] M	0.021(5)	0.21(5)
[NHA] M	0.021(5)	0.21(5)

During the preparation of solutions containing cations, the corresponding UV−vis spectra did not appear significantly modified by the amount of anti-nitrous reagent. In both cases, the characteristic bands of Np(IV) and Pu(III) in nitric medium are detected, showing that plutonium was reduced and stabilized in its trivalent oxidation state (Figure 6a). Indeed, Pu(IV) and U(IV) react together in nitric media leading to the quantitative formation of Pu(III) and U(VI). In these conditions, about 50% of the initial amount of tetravalent uranium was oxidized, the U(VI) absorption bands being partly hidden by tetravalent neptunium.

Depending on their oxidation state, actinide species presented different behaviors when adding phosphoric acid (Figure 6b). On the one hand, thorium and the remaining U(IV) and Np(IV) were complexed by the phosphate species to give an initial gelatinous phosphate phase. In these conditions, uranium(VI) and some neptunium(V), coming from the initial Np solution, were not precipitated in this gel and thus quantitatively remain in the supernatant whatever the amount of NH/NHA considered. On the other hand, Pu(III) was first stabilized in the gelatinous phase by the anti-nitrous reagents, then slowly turned into Pu(IV) during their decomposition, leading to the incorporation of plutonium in the crystallized phosphate phase. Simultaneously, uranium(IV) was quickly incorporated in the gel and then into the crystallized precipitate. In these conditions, the concentrations in hydrazinium and hydroxylammonium must be low enough to allow the progressive oxidation of Pu(III) into Pu(IV) (keeping in mind that it could not be equal to zero in order to stabilize uranium in the tetrapositive state). Meanwhile, a low concentration in NH/NHA could be responsible for the formation of additional Np(V) in the solution,[64] related to the soluble character of Np(V) phosphates in acidic media. In these conditions, complementary studies are in progress to determine the optimal concentra-

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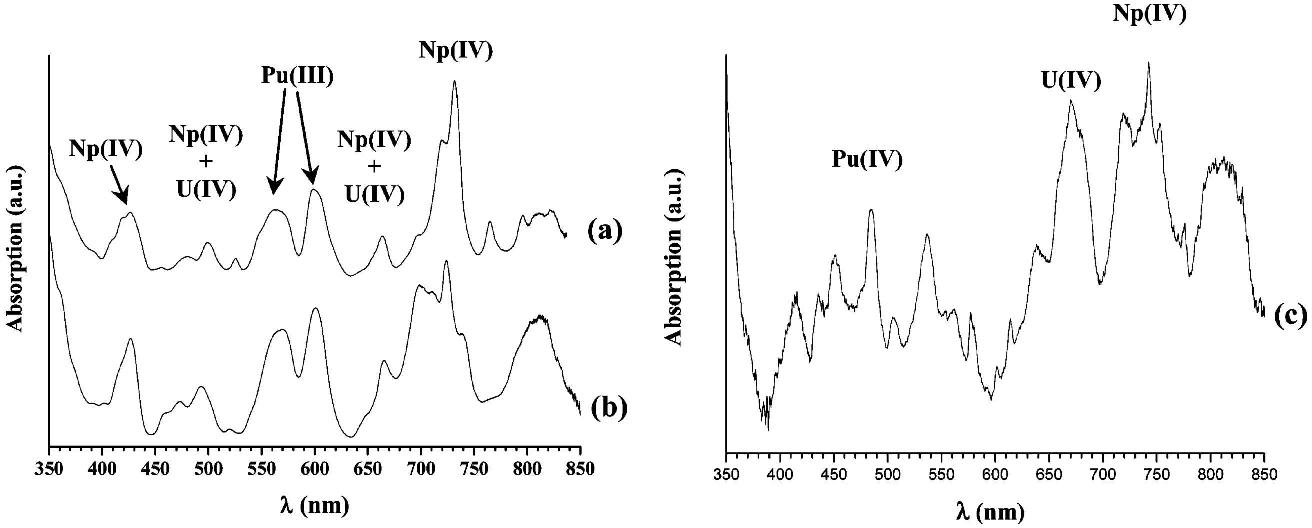

Figure 6. UV−vis absorption spectra of a mixture of nitric acidic solutions containing Th, U(IV), Np(IV), and Pu(IV) (a); of a gelatinous phase obtained after adding phosphoric acid (b); and of the final β-actinide(IV) phosphate−diphosphate solid solution (c).

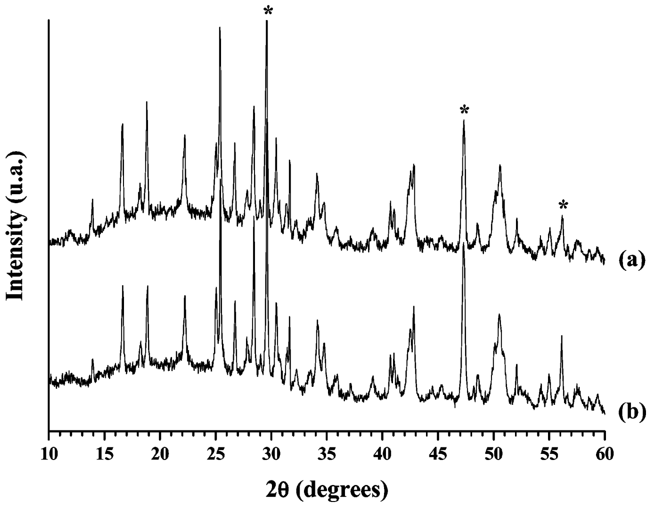

Figure 7. XRD diagrams of TUNpPuPHPH solid solutions prepared with [NH] + [NHA] = 0.4 M (a) and 0.04 M (b). XRD lines of silicon used as internal reference are marked by *.

tions of hydrazinium and hydroxylammonium required to ensure the quantitative precipitation of tetravalent actinides.

After heating at 130 °C for 6 weeks, the XRD pattern of the final precipitates (Figure 7) matched well with that of TPHPH. The refined unit cell parameters were found as $a = 21.346(9)$ Å, $b = 6.676(4)$ Å, $c = 7.024(4)$ Å, and $V = 985.7(10)$ Å^3 (Table 1). The heat-treatment of the crystallized precursors containing both tetravalent thorium, uranium, neptunium, and plutonium was performed in air or under an argon atmosphere at 1100 °C. Whatever the atmosphere considered, a single-phase β-TPD-type solid solution was evidenced by XRD. The determination of the refined unit cell parameters yielded $a = 12.810(4)$ Å, $b = 10.401(3)$ Å, $c = 7.035(3)$ Å, and $V = 937(1)$ Å^3 for [NH] + [NHA] = 0.04 M and $a = 12.805(4)$ Å, $b = 10.391(3)$ Å, $c = 7.034(3)$ Å, and $V = 935.9(9)$ Å^3 for [NH] + [NHA] = 0.4 M. These results appear in good agreement with those expected for the ionic radius but did not allow for the evaluation of the elementary composition of the solids.

Finally, the tetravalent oxidation state of the actinides was confirmed by UV−vis spectroscopy. Moreover, no significant amounts of U(VI), Np(V), or Pu(III) were detected (Figure 6c). This result appears as the only known example of a phosphate-based compound simultaneously containing thorium, uranium, neptunium, and plutonium in the tetravalent oxidation state and thus confirms that the stabilization of tetravalent actinides in an unique β-TPD ceramic matrix can be efficiently performed through the initial precipitation of actinide(IV) phosphate hydrogenphophate hydrate. This new way of preparation of β-TPD samples from low-temperature crystallized precursors appears to be of strong interest in the field of decontamination of high-level radioactive liquid waste. The results describing the efficient recovery yield of radionuclides from the liquid phase will be published in a forthcoming paper.

4. Conclusion

The tetravalent oxidation state of actinides (Th, U, Np, Pu) was stabilized in phosphate-based gels obtained from the mixture of acidic solutions containing cations and phosphoric acid. The heat-treatment of such gelatinous phases under hydrothermal conditions led to the formation of crystallized compounds identified as that of actinide phosphate hydrogenphosphate hydrate $Th_{2-x/2}An_{x/2}(PO_4)_2(HPO_4)\cdot H_2O$. UV−vis and IR spectra confirmed that the actinides were stabilized in their tetravalent oxidation state in the samples. Moreover, these solids were always found to be single phase for An/Th ≤ 1 while several secondary phases such as $PuPO_4\cdot{}^1/_2H_2O$, $Pu(OH)PO_4\cdot nH_2O$, or $Np(OH)PO_4\cdot nH_2O$ were formed for higher mole ratios with An = Np or Pu. In these conditions, the formation of a complete solid solution between TPHPH and PuPHPH was evidenced from the linear variation of the unit cell parameters versus the average ionic radius. The orthorhombic structure (or slightly distorded monoclinic cell) appears characteristic of large tetravalent cations and was not observed for tin, zirconium, or hafnium.

The thermal behavior of the crystallized precursors was then studied after heating the powders at 1100 °C under an air or argon atmosphere. As expected from the results obtained with the former method of preparation based on the direct evaporation of a mixture of solutions, single-phase β-TAnPD solid solutions were prepared up to $x = 1.6$ for Np and $x = 0.8$ for Pu. For higher substitution rates, several secondary phases such as $An_2O(PO_4)_2$, α-AnP_2O_7, or $PuPO_4$ monazite were formed depending on the cation and the atmosphere employed. Finally, this method of preparation was applied with success to the preparation of actinide phosphate hydrogenphosphate hydrates then to actinide phosphate diphosphate solid solutions simultaneously incorporating all the tetravalent actinides. The amount of anti-nitrous reagents, introduced to keep the tetravalent oxidation state, was adjusted to maximize the precipitation yield.

This result appears very promising for the field of the decontamination of high-level liquid radioactive waste. Indeed, the precipitation of TAnPHPH could be efficiently applied to the separation of tetravalent actinides from other elements in a nitric medium. The evaluation of the associated decontamination factors, along with their comparison to other methods, will be published soon.

Acknowledgment. This work was supported by the French research group “Nouveaux Matériaux pour les Dechets” (NOMADE, GdR 2023, CNRS/CEA/EDF/AREVA). The authors would like to thank Gilles Wallez and Michel Quarton from the University Pierre & Marie Curie, Paris VI, for their help in the refinement of the XRD patterns.

IC701297V