

Synthesis and characterization of uranium (IV) phosphate-hydrogenphosphate hydrate and cerium (IV) phosphate-hydrogenphosphate hydrate

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Received 17 October 2004; received in revised form 3 January 2005; accepted 8 January 2005

Abstract

A new uranium (IV) phosphate of proposed formula $U_2(PO_4)_2HPO_4 \cdot H_2O$, i.e. uranium phosphate-hydrogenphosphate hydrate (UPHPH), was synthesized in autoclave and/or in polytetrafluoroethylene closed containers at 150 °C by three ways: from uranium (IV) hydrochloric solution and phosphoric acid, from uranium dioxide and phosphoric acid and by transformation of the uranium hydrogenphosphate hydrate $U(HPO_4)_2 \cdot nH_2O$. The new product appears similar to the previously published thorium phosphate-hydrogenphosphate hydrate $Th_2(PO_4)_2HPO_4 \cdot H_2O$ (TPHPH). From preliminary studies, it was found that UPHPH crystallizes in monoclinic system ($a = 2.1148(7)$ nm, $b = 0.6611(2)$ nm, $c = 0.6990(3)$ nm, $\beta = 91.67(3)^\circ$ and $V = 0.9768(10)$ nm³). Heated under inert atmosphere, this compound is decomposed above 400 °C into uranium phosphate-triphosphate $U_2(PO_4)P_3O_{10}$, uranium diphosphate α - UP_2O_7 and diuranium oxide phosphate $U_2O(PO_4)_2$.

Crystallized cerium (IV) phosphate-hydrogenphosphate hydrate $Ce_2(PO_4)_2HPO_4 \cdot H_2O$ (CePHPH) was also synthesized from $(NH_4)_2Ce(NO_3)_6$ and phosphoric acid solutions by the same method (monoclinic system: $a = 2.1045(5)$ nm, $b = 0.6561(2)$ nm, $c = 0.6949(2)$ nm, $\beta = 91.98(1)^\circ$ and $V = 0.9588(9)$ nm³). When heating above 600 °C, cerium (IV) is reduced into Ce (III) and forms a mixture of $CePO_4$ (monazite structure) and CeP_3O_9 .

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Keywords: Uranium (IV); Cerium (IV); Phosphate; Hydrogenphosphate

1. Introduction

Tetravalent uranium phosphates were extensively studied in the past [1–11]. However, their chemistry required to be revised since the general physico-chemical properties of these solids (and especially their low solubility) appear of particular interest for their potential use as conditioning matrices for radioactive waste. Syntheses of several new compounds were reported in the last decade [12–19]. With the same aim, the chemistry of other tetravalent actinide phosphates [20–22], especially that of thorium, was also

reexamined [20]. Among the new solids, thorium phosphate-diphosphate β - $Th_4(PO_4)_4P_2O_7$ (β -TPD) was found to be a very stable matrix in the field of the immobilization of radionuclides for an underground repository (thermal stability, high resistance to aqueous alteration) [20–22]. It allows the incorporation of large amounts of other tetravalent actinides leading to the preparation of solid solutions of general formula β - $Th_{4-x}M_x(PO_4)_4P_2O_7$ ($M = U, Np, Pu$) with $x \leq 3.0$ for uranium, $x \leq 2.1$ for neptunium and $x \leq 1.6$ for plutonium [21–23]. Taking into account these properties, β -TPD was proposed for the long-term storage of these elements [24–26]. This compound or associated solid solutions was obtained by mixing concentrated aqueous solutions of actinide chloride, nitrate, etc. (for uranium chloride only) with phosphoric acid. The mixture was

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evaporated, the residue was ground, pressed at room temperature then fired at 1200–1250 °C to obtain the final ceramics [27]. In order to avoid the evaporation of volatile products (such as HCl, NO, NO₂) during the heat treatment, another way of preparation of these ceramics was developed. This new method consists of the precipitation of thorium phosphate-hydrogenphosphate, amorphous Th₂(PO₄)₂HPO₄·*n*H₂O with *n* = 3–7 [28] or crystallized monohydrate (using hydrothermal conditions) Th₂(PO₄)₂HPO₄·H₂O [29] as precursors. The precipitate was filtered, washed then heated for dehydration (≈ 200 °C) and final transformation into β-TPD (950–1000 °C).

The main objective of the studies undertaken is to obtain solid solutions of thorium-actinide (IV) phosphate-hydrogenphosphate hydrate Th_{2-x/2}An_{x/2}(PO₄)₂HPO₄·H₂O (*An* = U, Np, Pu), using the same process. These solid solutions, obtained by precipitation, separation from the mother liquor then drying, will afterwards be heated at high temperature to prepare the thorium-actinide (IV) phosphate-diphosphate β-Th_{4-x}An_x(PO₄)₄P₂O₇ ceramics [30].

In this paper, the synthesis and the characterization of the pure crystallized uranium (IV) phosphate-hydrogenphosphate hydrate U₂(PO₄)₂HPO₄·H₂O (UPHPH) is described. Synthesis of cerium (IV) phosphate-hydrogenphosphate hydrate Ce₂(PO₄)₂HPO₄·H₂O (CePHPH) is also reported since Ce (IV) is often used as a surrogate for tetravalent plutonium.

2. Experimental

2.1. Chemicals and apparatus

All reagents, except uranium salt solution, were supplied by Aldrich-Fluka. Uranium metal chips were dissolved in 6 M hydrochloric acid [19] to obtain a 1 M final solution. Cerium-ammonium nitrate (NH₄)₂Ce(NO₃)₆ was also prepared as 1 M solution. All concentrations were determined by conventional analytical methods.

Syntheses were performed under hydrothermal conditions in Parr Instrument Company autoclaves supported with polytetrafluoroethylene (PTFE) containers (maximum volume of 23 mL). Samples were heated at 150 °C during one week to two months. Some syntheses were also carried out in closed PTFE recipients heated on a sand bath at 150 °C for 2–4 weeks. Heating treatments were performed in alumina boats in a Pyrox MDB15 or HM40 tubular furnaces under argon atmosphere (with a rate of 5 °C/min).

X-ray powder diffraction (XRD) data were collected with a Philips PW 1050/70 or a BRUKER-AXS D8 Advance diffractometer using the monochromatic CuKα radiation (λ = 0.15418 nm) and a nickel filter. Patterns

were recorded from 5 to 60° (2θ with a step of 0.01°). High-temperature XRD data (HT-XRD) were recorded with a Philips X'PERT PRO—PW 3040/60 apparatus using an HTK 1200 furnace from Anton Parr Instrument Company.

The infrared (IR) spectra were recorded from 4000 to 400 cm⁻¹ with a Hitachi I-2001 spectrophotometer. Samples of 1–1.5 wt% of the solids were prepared in KBr pellets. The UV-visible absorption spectrum of the obtained products was recorded by means of a Varian DMS 300 spectrophotometer.

The Raman spectra were recorded using a Labram (Dilor-Jobin Yvon) microspectrometer with an argon laser working at 514.5 nm and equipped by a Notch filter. The power varied from 50 to 100 mW and the laser beam was focused on the sample with an Olympus microscope.

Thermal gravimetric analysis (TGA) was performed in argon flow up to 1000 °C by means of a SETARAM TG-DTA92 apparatus.

Electron probe microanalyses (EPMA) were carried out by means of a CAMECA SX 50 apparatus working with a 15 kV voltage and a 10 nA current beam. Uranium dioxide UO₂ (*Mβ* ray of uranium), KTi₂(PO₄)₃ or SmPO₄ (*Kα* ray of phosphorus) and CePO₄ (*Lα* ray of cerium) were used as calibration monitors.

The observations of the powders were carried out with a HITACHI S 2500 scanning electron microscope (SEM).

2.2. Samples preparation

Crystallized uranium (IV) phosphate-hydrogenphosphate hydrate was obtained using three ways:

- By direct mixture of uranium (IV) hydrochloric solution and phosphoric acid in the mole ratio P/U = 3/2 with 2% excess of 5 M H₃PO₄, either in autoclave or in closed PTFE containers heated on a sand bath (150 °C). The gel initially formed was transformed into a precipitate after one day. Crystallized powder was obtained after one week.
- By mixing uranium dioxide UO₂ with phosphoric acid (5% of excess) in the same initial mole ratio. This synthesis was performed in autoclave (150 °C) during several weeks.
- By heating the amorphous uranium (IV) hydrogenphosphate hydrate U(HPO₄)₂·*n*H₂O in autoclave (150 °C). Instead of the expected crystals of U(HPO₄)₂·2H₂O, the solid revealed the same XRD lines and IR spectrum as those prepared by the first two ways.

Cerium (IV) phosphate-hydrogenphosphate hydrate was obtained in autoclave from a mixture of cerium

ammonium nitrate and 5 M H_3PO_4 in 2 M HNO_3 solution.

Whatever the method considered, the crystallized products were filtered, washed with de-ionized water and ethanol, dried at 120 °C then finally stored in a desiccator. In order to study the behavior of the obtained products during the heating treatment, the samples were fired (under argon atmosphere for uranium samples) from room temperature up to 1000–1100 °C with heating steps of 100 °C and heating times of 1 hour (HT-XRD experiments) or 14 hours (room temperature XRD experiments).

3. Results and discussion

3.1. Uranium phosphate-hydrogenphosphate hydrate

The results of EPMA are gathered in Table 1. The P/U mole ratios were found to be equal to 3/2 whatever the method of preparation applied.

As it can be seen on the SEM micrograph in Fig. 1a, the crystals do not exceed 2 μm in length and appear as layered bars. Fig. 1b exhibits bigger aggregates (up to 20 μm) composed of these small crystals. The observations performed on the same type of aggregates in thorium-uranium (IV) phosphate-hydrogenphosphate hydrate (TUPHPH) solid solutions revealed spherulitic texture with an empty core [30].

The final uranium (IV) phosphate sample exhibited a similar XRD diagram (Fig. 2b) as thorium phosphate-hydrogenphosphate hydrate (TPHPH) (Fig. 2a). The corresponding XRD data are listed in Table 2. The morphology of the samples leads to preferential orientations for (00) peaks, which is clearly observed in the figure. From preliminary studies, it was found that uranium (IV) phosphate-hydrogenphosphate hydrate (UPHPH) crystallizes in the monoclinic system with

$a = 2.1148(7) \text{ nm}$, $b = 0.6611(2) \text{ nm}$, $c = 0.6990(3) \text{ nm}$ and $\beta = 91.67(3)^\circ$ (calculated density of 5.31) (Table 3). Taking into account the similarities between the XRD diagrams of UPHPH and TPHPH, recently described as an orthorhombic compound with $a = 2.1368(2) \text{ nm}$, $b = 0.6695(1) \text{ nm}$, $c = 0.7023(1) \text{ nm}$ (calculated density of 5.08) [31,32], it can be accepted that the structures of both compounds are similar. However, a slight distortion of the unit cell is observed between both solids due to the weak difference of the ionic radii ($^{\text{VII}}r_{\text{Th}^{4+}} = 0.100 \text{ nm}$ and $^{\text{VII}}r_{\text{U}^{4+}} = 0.095 \text{ nm}$) leading to a monoclinic system with $\beta = 91.67^\circ$ [32]. The comparison of the refined unit cell parameters exhibits a contraction of only 2.8% in volume from TPHPH to UPHPH, which appears in good agreement with the small difference between the ionic radii of Th^{4+} and U^{4+} .

Since uranium (IV) can be easily oxidized into the molecular uranyl ion UO_2^{2+} , UV-visible spectrum was recorded in order to check that uranium was only present in the tetrapositive oxidation state in the obtained phosphate. All the bands were assigned to the transition levels of the tetravalent uranium [33]: $^3\text{P}_1$ multiplets (500–560 nm), $^1\text{G}_4$, $^1\text{D}_2$, $^3\text{P}_0$ mixed levels (650–750 nm) and $^3\text{H}_6$ level (800 nm). No absorption band characteristic of the uranyl ion [34] was evidenced between 400 and 440 nm.

On the TGA curve (Fig. 3), four steps are observed up to 540 °C. The substantial weight loss of about 2.5% occurs at 200 °C, corresponding to about 1.1 molecule of water per unit formula. Thus, as it was observed for TPHPH [29,31], it can be accepted that UPHPH is monohydrated from room temperature to about 150 °C and fully dehydrated at about 200 °C.

The IR and Raman spectra of the synthesized uranium compound are presented in Figs. 4a and 5a, respectively. All the bands of UPHPH (Table 4) were assigned to the vibrations of the bonds in phosphate,

Table 1
Results obtained from EPMA for uranium (IV) and cerium (IV) phosphate-hydrogenphosphates

Synthesized solid and ways of synthesis	Ce (wt%)	U (wt%)	P (wt%)	O (wt%) ^b	Ratio P/M
$\text{U}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	—	61.0 ^a	11.9 ^a	26.7 ^a	1.50 ^a
$\text{UO}_2 + \text{H}_3\text{PO}_4$	—	61.5 ± 0.4	12.0 ± 0.1	26.5 ± 0.4	1.50 ± 0.01
$\text{UCl}_4 + \text{H}_3\text{PO}_4$	—	61.6 ± 0.3	11.9 ± 0.3	26.5 ± 0.8	1.49 ± 0.04
$\text{U}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ (hydrolysis)	—	61.4 ± 0.6	12.1 ± 0.2	25.8 ± 0.7	1.52 ± 0.04
$\alpha\text{-U}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$	—	63.2 ^a	12.4 ^a	24.4 ^a	1.50 ^a
Heating at 250 °C	—	62.7 ± 0.3	12.6 ± 0.2	24.7 ± 0.5	1.54 ± 0.01
$\text{U}(\text{UO}_2)(\text{PO}_4)_2$	—	68.2 ^a	8.9 ^a	22.9 ^a	1.00 ^a
Heating at 1200 °C (in air)	—	69.8 ± 0.4	9.1 ± 0.2	21.1 ± 0.6	1.00 ± 0.03
$\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	47.9 ^a	—	15.9 ^a	35.6 ^a	1.50 ^a
$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 + \text{H}_3\text{PO}_4$	48.7 ± 0.5	—	16.2 ± 0.3	35.1 ± 1.0	1.51 ± 0.04

^aCalculated.

^bIncluding oxygen from water molecules.

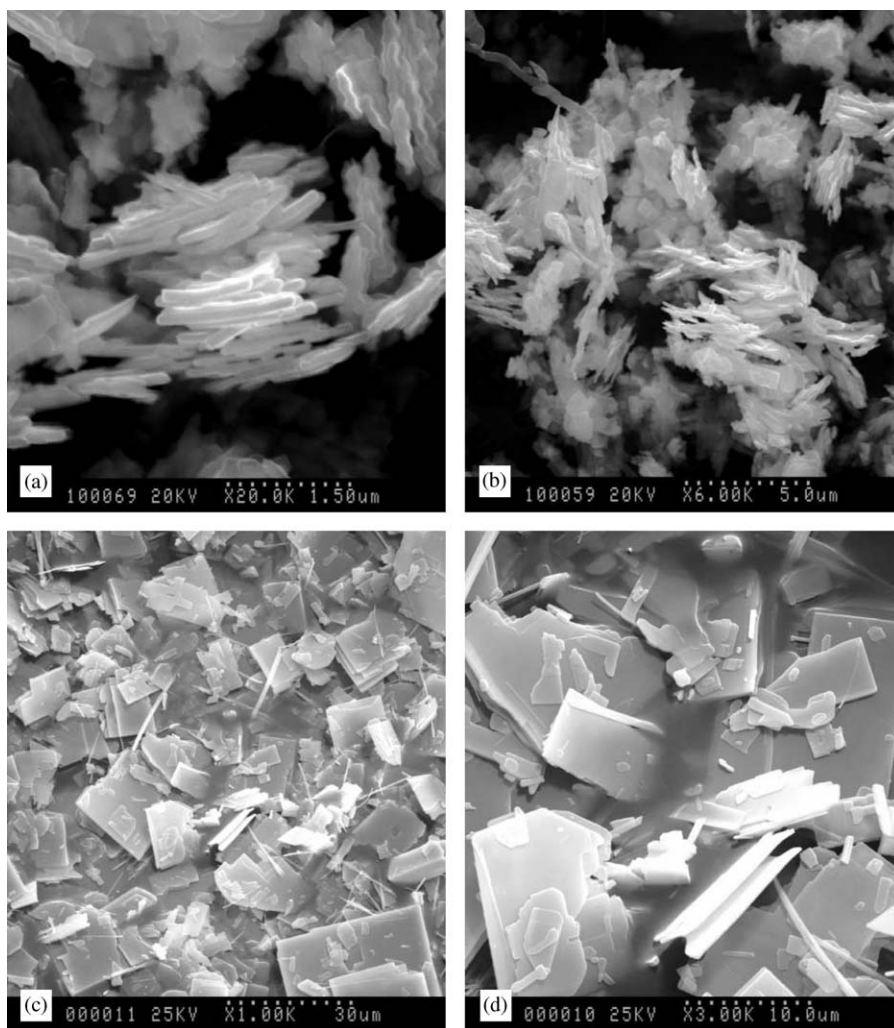


Fig. 1. SEM micrographs of UPPHP (a, b) and CePPHP (c, d).

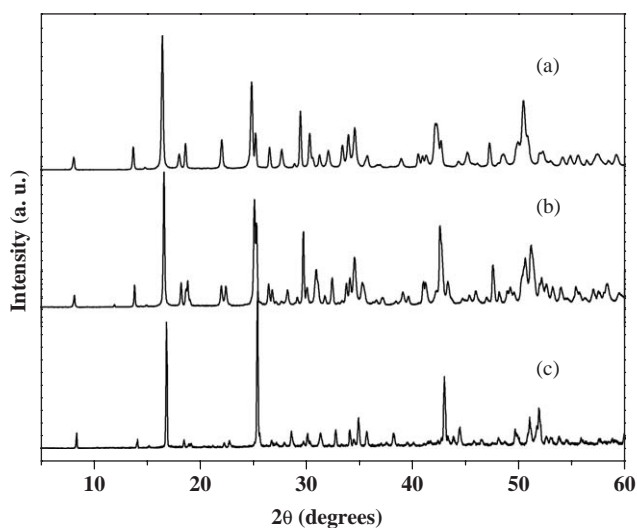
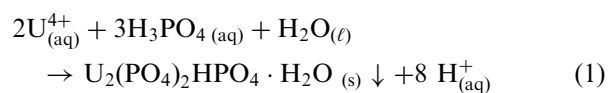


Fig. 2. XRD diagrams of TPHPH (a), UPPHP (b) and CePPHP (c).

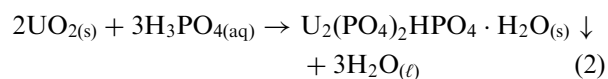
hydrogenphosphate and OH groups as well as in water molecule according to the data reported in the literature [35–40].

As a summary, all the results presented confirm the formula proposed for UPPHP, i.e. $U_2(PO_4)_2HPO_4 \cdot H_2O$. The reactions involved can thus be written as follows:

- from uranium (IV) in hydrochloric solution



- from uranium dioxide



- from amorphous uranium hydrogenphosphate

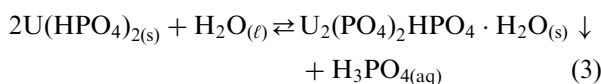


Table 2
XRD data of powdered UPHPH

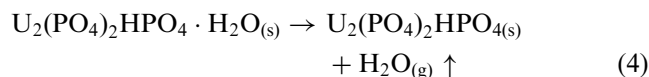
$2\theta_{\text{calc}}(^{\circ})$	$2\theta_{\text{exp}}(^{\circ})$	$d_{\text{exp}}(\text{nm})$	I/I_0
8.35	8.37	1.058	9
14.04	14.02	0.632	17
16.78	16.79	0.528	100
18.40	18.39	0.482	19
19.03	19.01	0.467	20
22.62	22.61	0.393	16
25.28	25.30	0.352	80
25.50	25.48	0.350	63
26.64	26.64	0.335	18
26.98	26.97	0.331	14
28.40	28.40	0.314	13
29.33	29.33	0.304	8
29.90	29.90	0.299	56
30.25	30.24	0.295	15
31.10	31.09	0.288	28
31.32	31.32	0.286	17
31.94	31.93	0.280	9
32.60	32.60	0.275	22
33.93	33.94	0.264	18
34.29	34.29	0.262	22
34.67	34.72	0.258	37
35.43	35.45	0.253	19
36.46	36.47	0.246	4
36.75	36.76	0.244	6
37.30	37.35	0.241	8
38.62	38.62	0.233	5
39.29	39.27	0.229	11
39.80	39.77	0.227	9
41.19	41.18	0.219	19
41.27	41.42	0.218	18
42.40	42.41	0.213	13
42.77	42.67	0.211	61
43.49	43.50	0.208	19
44.90	44.88	0.202	7
45.54	45.52	0.199	9
46.14	46.12	0.197	12
47.14	47.14	0.193	8
47.77	47.74	0.191	32
48.37	48.33	0.188	12
49.00	49.09	0.186	13
49.39	49.37	0.185	15
49.76	49.72	0.183	11

Table 3
Unit cell parameters of TPHPH [31], UPHPH and CePHPH [32]

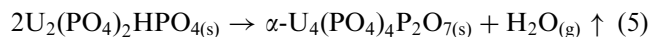
Compound	a (nm)	b (nm)	c (nm)	β ($^{\circ}$)	V (nm ³)
$\text{Th}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	2.1368(2)	0.6695(1)	0.7023(1)	—	1.0048
$\text{U}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	2.1148(7)	0.6611(2)	0.6990(3)	91.67(3)	0.9768
$\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$	2.1045(5)	0.6561(2)	0.6949(2)	91.98(1)	0.9588

Eq. (3) is written after King [41] who observed the conversion of hydrated plutonium (IV) hydrogenphosphate $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$, PuHP, into a plutonium phosphate that formula was presumed as $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$. It was not specified whether the process is a real equilibrium. However, PuHP was only stable with large excess of phosphoric acid.

When heating above 200 °C, UPHPH is fully dehydrated and forms UPHP according to



As it was already observed for TPHPH, the condensation of HPO_4 groups occurs above 200 °C, leading to P_2O_7 entities with loss of one additional water molecule for two formula units [31]. For UPHPH, the band located at 1235 cm^{-1} associated with the δ (P–O–H) vibration disappears progressively in the IR spectrum (Fig. 6) with the temperature rise. Simultaneously, a band located at 752 cm^{-1} (IR, $\theta \approx 400$ °C, Fig. 6) and at 760 cm^{-1} (Raman, $\theta \approx 250$ °C, Fig. 7) associated with the ν_s (P–O–P) vibration is observed [35,39]. This fact suggests the conversion of UPHPH into α -UPD, analogous to α -TPD (low-temperature form of TPD) [31] as follows:



Nevertheless, the band associated with the H_2O bending mode at 1622 cm^{-1} remains present even after

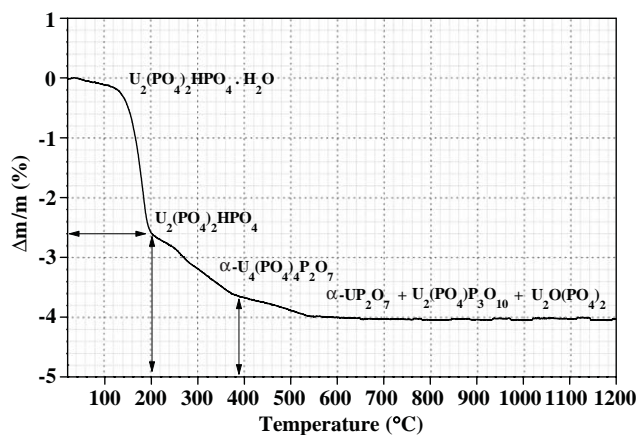


Fig. 3. Results of TGA obtained for UPHPH.

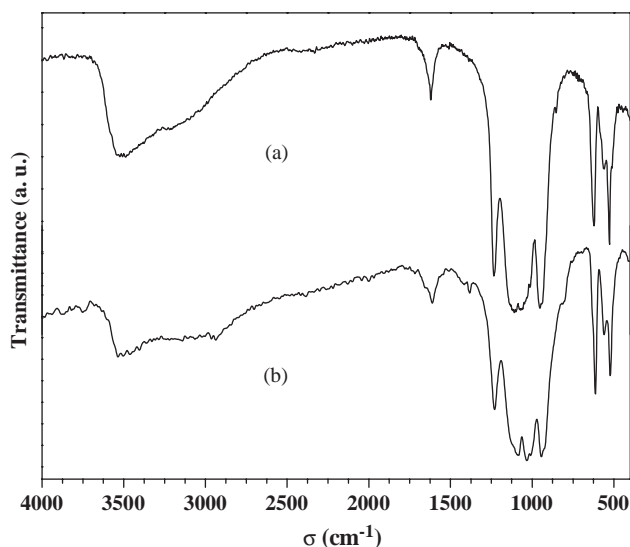


Fig. 4. IR spectra of UPHPH (a) and CePHPH (b).

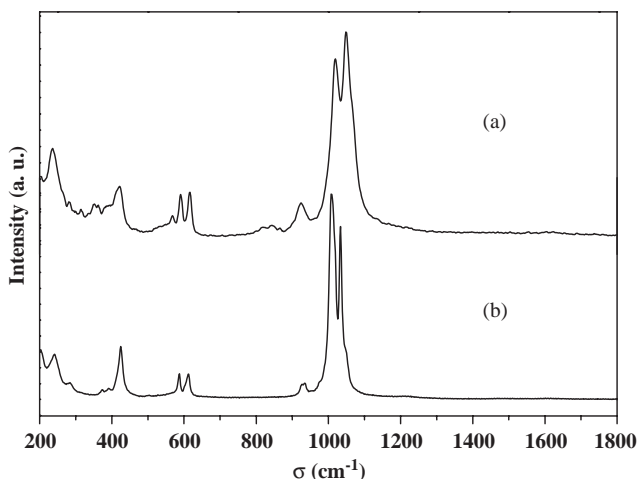
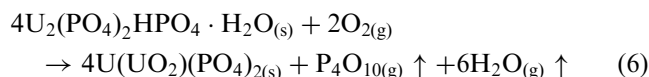


Fig. 5. Raman spectra of UPHPH (a) and CePHPH (b).

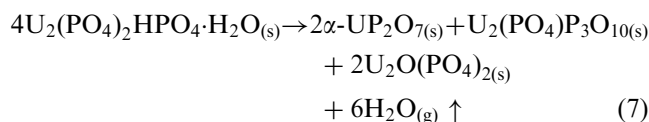
heating the sample at 400–600 °C, which is probably due to the hygroscopic behavior of the product(s) formed above 200 °C.

As it was already described for TPHPH and α -TPD [31], the XRD diagrams of UPHPH and α -UPD remain almost unchanged compared to that of UPHPH showing that these compounds are isostructural. When heated under argon atmosphere at 400 °C, α -UPD is decomposed into other uranium compounds as it can be observed on the XRD diagram (see below in the following section). On this basis, the band located at 1308 cm^{-1} in the IR spectrum (Fig. 6c) can be attributed to a polyphosphate grouping [35] and that at 752 cm^{-1} to the ν_s (P–O–P) of α -UP₂O₇ and/or of α -UPD. Moreover, a weak band located at 872 cm^{-1} is observed in the IR spectrum obtained for 800–1000 °C (Fig. 6d). Two other weak bands appear in the Raman spectrum at 865 and at 877 cm^{-1} for $\theta = 250$ and 1200 °C,

respectively (Fig. 7). According to Grending et al. [42], these frequencies can be assigned to ν_1 (U=O) bond in the UO_2^{2+} ion. The oxidation process of U^{4+} , probably due to the presence of small amounts of oxygen (or air) in argon, seems to take place at the surface of the grains during the heat treatment. Another experiment, performed in air atmosphere at 1200 °C revealed a band of very high intensity at 877 cm^{-1} (Fig. 7) as previously observed in the Raman spectrum of $\text{U}(\text{UO}_2)(\text{PO}_4)_2$ [11]. Thus, UPHPH was transformed into $\text{U}(\text{UO}_2)(\text{PO}_4)_2$ in air at 1200 °C (which was also confirmed from the results of EPMA, Table 1):



In the XRD diagram (Fig. 8), the lines of uranium (IV) phosphate-triphosphate (UPTP) $\text{U}_2(\text{PO}_4)_3\text{O}_{10}$ [43] (formerly known as β -UP₂O₇) appear above 400 °C. Its transformation into the more stable α -UP₂O₇ is observed at higher temperature (800–1000 °C). Simultaneously, the diffraction lines of $\text{U}_2\text{O}(\text{PO}_4)_2$ also appear. The decomposition of UPHPH (in argon atmosphere) may be approximately written as



In these conditions, a β -UPD compound analogous to β -TPD [20] was not obtained at high temperature as already described for the other ways of synthesis [21,22]. Finally, α -UP₂O₇ was transformed into $\text{U}_2\text{O}(\text{PO}_4)_2$ when heating at higher temperature (about 1250 °C) and/or when extending the heating time [15].

3.2. Cerium phosphate-hydrogenphosphate hydrate

Several cerium (IV) phosphates were mentioned in the literature. King [41] reported the preparation of $\text{Ce}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ from a Ce (IV) salt and sodium phosphate in acidic solution. However, no XRD data or any other result were published for this compound that formula may be also written as $\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot y\text{H}_2\text{O}$.

König and Meyn [44] precipitated a crystallized cerium (IV) phosphate with mole ratio P/Ce ≈ 1.5 from cerium sulfate and phosphoric acid solutions. These authors proposed the $(\text{Ce-O-Ce})(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$ formula based on the known $(\text{Ce-O-Ce})^{6+}$ ion in aqueous solution. They also postulated that this compound was transformed into $(\text{Ce-O-Ce})(\text{P}_2\text{O}_7)_3$ by condensation of HPO_4 entities when heating above 900 °C. However, the initial $(\text{Ce-O-Ce})(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$ can be also written as $\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (without excluding the presence of the P_2O_7 entity after heating). Furthermore, the temperature of condensation, mentioned by the authors,

Table 4
Assignment of frequencies in the IR and Raman spectra of MPPHP compounds

	Frequencies (cm ⁻¹)		Assignment	Refs.
	UPHPH	CePHPH		
IR	3700–2600	3640–2930	ν (O–H), ν ((P)–O–H)	[35]
	1622	1615	δ (H–O–H)	[35]
	1235	1232	δ_{ip} (P–O–H) ^a	[37]
	1100, 1072, 1014	1088, 1034	ν_{as} (P–O)	[35,36]
	950	944	ν_s (P–O)	[35,36]
	854	812 sh	ν_s (P–O) and/or δ_{op} (P–O–(H)) ^b	[35–38]
	620, 560, 520	612, 560, 512	δ_{as} (P–O)	[35–39]
	444	–	δ_s (P–O)	[35–39]
Raman	236	241	External modes and/or ν (U–O), ν (Ce–O)	[36,39]
	280	284	External modes	[36]
	314–421	373, 391, 424	δ_s (P–O)	[35–39]
	568, 591, 617	587, 612	δ_{as} (P–O)	[35–39]
	820–865	–	ν_s (P–O) and/or δ_{op} (P–O–(H)) ^b	[35–39]
	925	927, 935	ν_s (P–O)	[35–39]
	1019, 1049	1008, 1034	ν_{as} (P–O)	[35–39]

^aIn the plane deformation, which could also include the hydrogen bond deformation P–O–H...O–H (40) or P–O–H...O–P– [36]

^bOut of the plane deformation, which could also include the hydrogen bond deformation P–O–H...O–H (40) or P–O–H...O–P– [36]

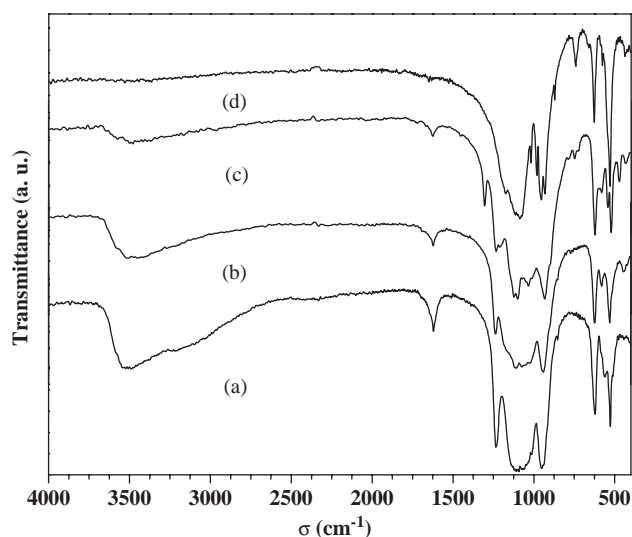


Fig. 6. Variation of the IR spectrum of UPPHP in terms of heating temperature: (a) initial solid, (b) heated at 200 °C, (c) heated at 400–600 °C, (d) heated at 800–1000 °C.

seems to be doubtful taking into account the behavior of tetravalent cerium at high temperature. Indeed, when heating α -CeP₂O₇ at 900 °C, Botto and Baran [45] observed the complete reduction of cerium (IV) into Cerium (III), leading to the formation of CePO₄ (monazite structure).

Alberti et al. [46] synthesized a cerium (IV) phosphate with a mole ratio PO₄/Ce equal to 1.55, but its chemical formula was not suggested. Nevertheless, the XRD data of this product (with estimated intensities) are similar to that of König and Meyn's [44].

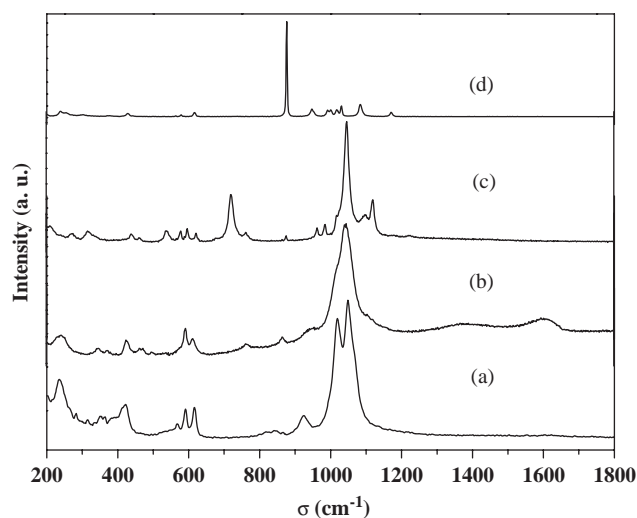


Fig. 7. Variation of the Raman spectrum of UPPHP in terms of heating temperature: (a) initial solid, (b) heated at 180 °C, (c) heated at 1200 °C under Ar-atmosphere (d) heated at 1200 °C in air.

In this study, the synthesis of cerium (IV) phosphate-hydrogenphosphate hydrate was undertaken in the same conditions as UPPHP using (NH₄)₂Ce(NO₃)₆ and H₃PO₄ solutions. For this sample, the EPMA results are given in Table 1 while the SEM micrographs are presented in Fig. 1c and d. The crystals present variable length up to 10 μm. Although the samples appear homogeneous and of the expected stoichiometry, some small impurities of CePO₄ (monazite structure), probably formed consequently to the reduction of small amounts of tetravalent cerium into trivalent cerium,

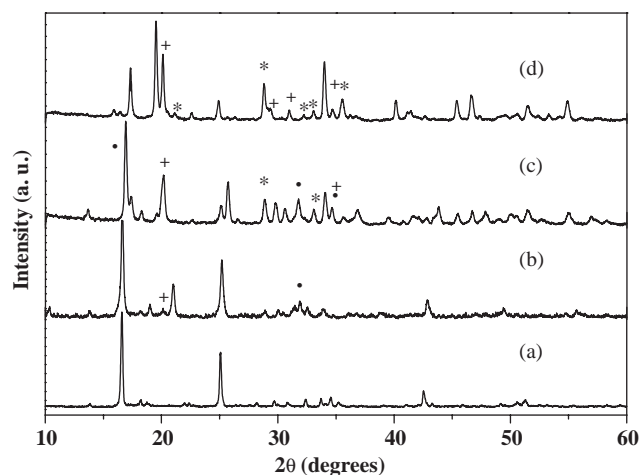


Fig. 8. Variation of XRD diagram versus heating temperature recorded for UPHPH: (a) initial product, (b) heated at 400 °C, (c) heated at 800 °C, (d) heated at 1000 °C. Diffraction lines of $U_2(PO_4)P_3O_{10}$ (o), $U_2O(PO_4)_2$ (*) and α - UP_2O_7 (+).

Table 5
XRD data of powdered CePHPH

$2\theta_{\text{calc}}(^{\circ})$	$2\theta_{\text{exp}}(^{\circ})$	$d_{\text{exp}}(\text{nm})$	I/I_0
8.41	8.41	1.052	10
14.14	14.12	0.626	6
16.86	16.86	0.526	81
18.98	18.98	0.468	3
19.18	19.18	0.463	4
22.30	22.29	0.399	4
22.80	22.80	0.390	5
25.41	25.41	0.350	100
27.95	27.96	0.319	4
28.63	28.62	0.312	11
30.13	30.14	0.296	10
31.36	31.35	0.285	10
34.10	34.11	0.263	12
34.91	34.93	0.257	20
35.69	35.71	0.252	11
37.07	37.06	0.243	3
37.55	37.56	0.239	4
39.51	39.51	0.228	4
40.11	40.09	0.225	4
43.00	43.01	0.210	46
43.34	43.34	0.209	8
43.84	43.85	0.206	8
47.55	47.54	0.191	4
48.68	48.67	0.187	5
49.66	49.67	0.183	13
49.91	49.89	0.183	9

were also found in the raw samples. The XRD data are listed in Table 5 and the diagram is drawn in Fig. 2c. The diffraction lines of the solid agree well with those observed for TPHPH and UPHPH allowing to propose the formula $Ce_2(PO_4)_2HPO_4 \cdot nH_2O$. The IR spectrum (Fig. 4b) of this solid, similar to that of UPHPH, can be interpreted in the same way (Table 4). The similarities

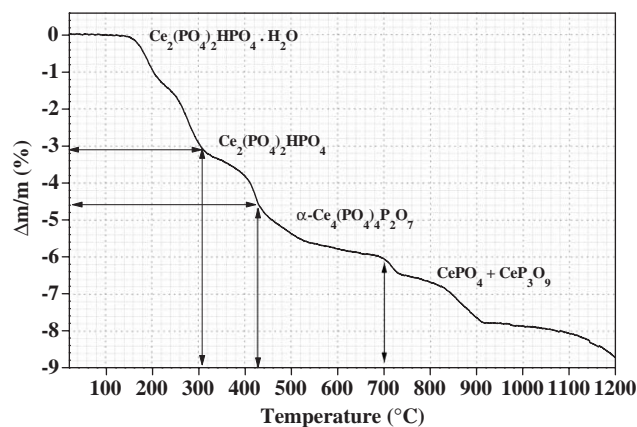


Fig. 9. Results of TGA obtained for CePHPH.

between UPHPH and CePHPH are also noted in the Raman spectrum (Fig. 5). Considering the similarities between the XRD patterns and IR spectra of UPHPH, TPHPH and the obtained cerium phosphate-hydrogenphosphate hydrate (CePHPH), the following formula: $Ce_2(PO_4)_2HPO_4 \cdot H_2O$ can be proposed. The refined unit cell parameters are presented in Table 3. As already described for uranium, a slight distortion of the unit cell resulting from the weak difference of the ionic radii ($^{VII}r_{Th^{4+}} = 0.100$ nm and $^{VII}r_{Ce^{4+}} = 0.092$ nm) leads to a monoclinic system with $\beta = 91.98^{\circ}$ instead of an orthorhombic one [32].

On the TGA curve (Fig. 9) several steps of weight loss are observed in the range of 160–1200 °C. Since no plateau was observed, it seems that the process was not complete even at 1200 °C. The first significant weight loss of 3.1% ($\theta \approx 300^{\circ}C$), corresponding to one molecule of water per unit formula, can be assigned to the complete dehydration of CePHPH leading to CePHP. An additional weight loss of 1.5% is observed at about 400 °C corresponding to 0.5 mole of H_2O per unit formula. Thus, the condensation reaction of HPO_4 group seems to take place leading to the formation of α - $Ce_4(PO_4)_4P_2O_7$ (α -CePD), analogous to α -TPD [31] and α -UPD. The XRD diagrams of CePHPH, CePHP and α -CePD are very close showing only small structure modifications during dehydration, then condensation of hydrogenphosphate groups which was already shown for TPHPH, TPHP and α -TPD [31].

Above 700 °C, the decomposition process begins (Fig. 10), which agrees well with the impossibility to prepare β -CePD, analogous to β -TPD, even in oxidizing conditions, as previously reported [21]. Plutonium (IV) phosphate in mole ratio $PO_4/Pu = 1.5$ behaves in the same way [21]. The diffraction lines of CeP_3O_9 and $CePO_4$ (monazite type) appear at 700 °C while $CePO_4$ seems to be the major phase at 900–1200 °C. Correlatively, the modification of the color of the sample (from dark yellow to light yellow then white) confirms the

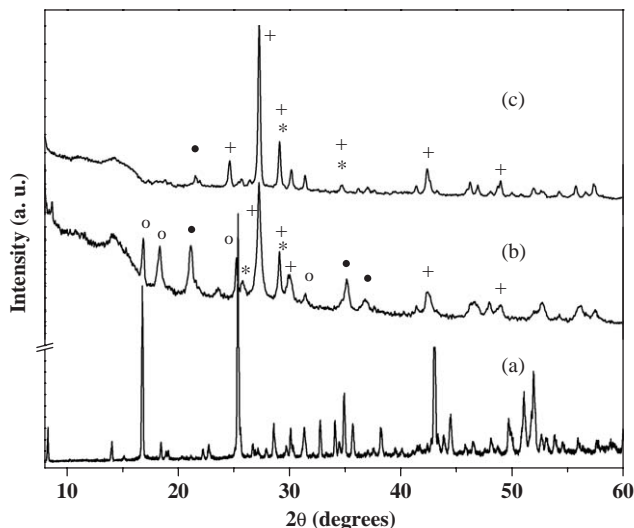
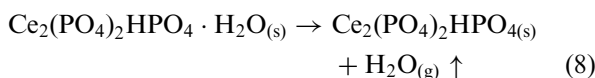


Fig. 10. Variation of XRD diagram versus heating temperature recorded for CePHPH: (a) heated at 600 °C, (b) heated at 700 °C, (c) heated at 900 °C and 1100 °C. Main diffraction lines of: α - $\text{Ce}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ (○), CeP_3O_9 (*), CePO_4 (+) and non-identified (●).

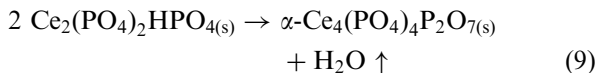
partial reduction of cerium (IV) into cerium (III). This reduction becomes quantitative by extending the heating time. No difference was observed between the XRD diagram recorded at 1100 °C and that obtained after cooling the sample to room temperature.

From the results obtained, the following chemical transformations can be suggested:

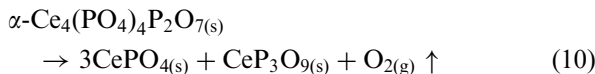
- progressive volatilization of water molecules starting from 160 °C leading first to the dehydration of the initial product:



- then condensation of HPO_4 groups:



- and finally, decomposition process, which can be written as follows:



4. Conclusion

Crystallized uranium phosphate-hydrogenphosphate hydrate (UPHPH) with the proposed chemical formula $\text{U}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$, was synthesized by mixing ura-

nium (IV) hydrochloric solution with phosphoric acid in autoclave or in PTFE closed containers at 150 °C. This product was also obtained in autoclave at 150 °C from uranium dioxide and phosphoric acid. In the same conditions, uranium hydrogenphosphate $\text{U}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ was converted into UPHPH. Cerium (IV) phosphate-hydrogenphosphate hydrate, $\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ (CePHPH) was also prepared from cerium (IV)—ammonium nitrate and phosphoric acid using the same procedure. The structures of both compounds seem to appear similar to that of the already described TPHPH, even though a slight distortion leads to a monoclinic unit cell (with β near to 90°) instead of the orthorhombic one [32]. When heating, both solids lead to dehydrated UPHPH and CePHPH, then to α -UPD and α -CePD (analogous to TPHP and α -TPD, respectively), which are rapidly decomposed when increasing the heating temperature. For the uranium compound, a mixture of $\text{U}_2(\text{PO}_4)_3\text{P}_3\text{O}_{10}$, α - UP_2O_7 and $\text{U}_2\text{O}(\text{PO}_4)_2$ is obtained in Ar-atmosphere. In air, uranium (IV) is oxidized leading to $\text{U}(\text{UO}_2)(\text{PO}_4)_2$. On the contrary, cerium (IV) is partly reduced to cerium (III) even in oxidizing conditions leading to CePO_4 (as one of the phases) and CeP_3O_9 . For both elements, neither the orthorhombic β -UPD nor β -CePD can be prepared, which agrees well with the results already reported in literature [21].

Taking into account these results, the crystallized thorium, plutonium (IV) and cerium (IV) phosphates (in nitric acid solutions) previously identified as $M_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}$ [41] should be certainly considered as $\text{Th}_2(\text{PO}_4)_2\text{HPO}_4 \cdot y\text{H}_2\text{O}$, $\text{Pu}_2(\text{PO}_4)_2\text{HPO}_4 \cdot y\text{H}_2\text{O}$ and $\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot y\text{H}_2\text{O}$, respectively.

The formation of $M_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ phosphates seems to be characteristic of M^{4+} ions with large ionic radii. Consequently, it should be also obtained for neptunium and plutonium which appears consistent with some recent results describing the preparation of $\text{Np}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Pu}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ in polyphase systems [47]. On the contrary, this phenomenon was not observed for smaller cations such as Hf^{4+} , Sn^{4+} , etc. For zirconium, some products of formulae $\text{H}_3\text{OZr}_2(\text{PO}_4)_3 \cdot 0.1\text{H}_2\text{O}$ (or rather $\text{Zr}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$) and $\text{HZr}_2(\text{PO}_4)_3$, both crystallized in the cubic system, were published by Ono and Yajima [48,49]. However, the results presented by these authors remain ambiguous and the existence of such compounds is rather doubtful.

Acknowledgments

The authors are very grateful to Dr. Renaud Podor, Alain Kohler and Lionel Aranda from the Laboratoire de Chimie du Solide Minéral, Université Henri Poincaré-Nancy I, for the EPMA results, TGA/DTA experiments

and SEM observations. They would like to thank Thérèse Lhomme from the CREGU (Université Henri Poincaré-Nancy I) for recording the Raman spectra. They also wish to express their gratitude to Prof. M. Quarton and Dr. G. Wallez from Université de Paris VI, Pierre et Marie Curie for their contribution in the determination of the unit cell parameters of TPHPH, UPHPH and CePHPH.

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