

Chemistry of tetravalent actinide phosphates—Part II

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Abstract

The chemistry and crystal structure of tetravalent cation phosphates, including that of actinides was reviewed several times until 1985. Later, new compounds were synthesized and characterized. In more recent studies it was found that some of previously reported phases, especially those of thorium, uranium, and neptunium, were wrongly identified. In the light of these new facts, an update review and classification of tetravalent actinides phosphates is proposed in this two-part paper. Their crystal structure and some chemical properties are compared to non-actinide cation phosphates.

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1. Introduction

The phosphates of some tetravalent cations like Th^{4+} , U^{4+} , Sn^{4+} , Ti^{4+} , or Zr^{4+} were synthesized in the end of the 19th century. Nevertheless, the real interest in this subject began since the 1950s. Reviews concerning the chemistry of this kind of phosphates were published by several authors: a phosphates chemistry by Averbuch-Pouchot and Durif [1], chemistry of tetravalent element phosphates by Tananaev [2], and the chemistry of actinide phosphates by Keller [3] and Bamberger [4].

In this article, the chemistry of phosphates of tetravalent actinides (Th, Pa, U, Np, Pu) and non-actinide elements (Si, Sn, Pb, Ti, Zr, Hf, Ce) is reviewed up to 2004. A systematic, based on a general framework $[(M^h)_m(A^q)_p]^k$ (where $k = hm + pq$), is proposed. For tetravalent cations, where $h = 4$, and various phosphate anions, where $A^q = \text{H}_2\text{PO}_4^-$, HPO_4^{2-} , PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$, PO_3^- ,

the framework formula takes the $[\text{M}_m(\text{A}^q)_p]^k$ form with $k = 4m + pq$ and considering the following (combined) parameters:

$$q = -1 \text{ to } -4, \quad m = 1 \text{ to } 4, \quad p = 1 \text{ to } 6.$$

Three main families of derivatives result from this formula:

- uncharged compounds for $k = 0$,
- cationic framework if $k > 0$, the charge must be compensated by an anion $[(A^z)_y]^{yz}$,
- anionic framework if $k < 0$, the charge must be compensated by a monovalent or divalent cation $[(M^n)_x]^{nx}$ with the following parameters: $n = 1, 2$, $x = 1 \text{ to } 14$; $y = 1, 2$, and $z \neq -3$.

The three families of tetravalent cation phosphates with $k = 0$ were described in the first part of this article [5]. Phases with $k < 0$ and $k > 0$ are considered in this second part. In mixed phosphates, monovalent ($n = 1$) or divalent ($n = 2$) cations M as well as anions A with $z = -1, -2$, and -4 guarantee the charge compensation. Mixed actinide(IV) phosphates with $n = 4$ or $z = -3$ were not reported in the literature.

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2. Phosphates of positive framework: $k > 0$, $[M_m(A^q)_p]^k$

To this family belong as well few crystallized two-anion thorium and uranium hydrogenphosphates ($q = -1$, $p = 2$ and $q = -2$, $p = 1$) of unknown structure as a large group of two-anion phosphates ($q = -3$) with $m = p$ [5].

D'Ans and Dawihl [6] reported two thorium hydrogenphosphates: $\text{Th}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Th}(\text{HPO}_4)\text{SO}_4 \cdot 4\text{H}_2\text{O}$. For uranium(IV), the XRD data of $\text{U}(\text{H}_2\text{PO}_4)_2(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and the three forms of $\text{U}(\text{H}_2\text{PO}_4)_2(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (unknown system and structure) were published by Dunn [7]. The formula of the hydrogen phosphate $\text{U}(\text{HPO}_4)_2 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ published by Schreyer [8] can also be written $\text{U}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ which appears similar to the thorium compound.

For compounds where $m = p$, the positive charge of the framework $[\text{M}_m(\text{PO}_4)_m]^{m+}$ is compensated by an anion A^z with $z = -1, -2, -4$. This group includes halogenide phosphates, hydroxide phosphates. It should also include the zirconium and hafnium phosphate–dihydrogenphosphates: $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (JCPDS File No. 83-0176) and $\text{Hf}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ (JCPDS File No. 89-1244) indexed in the monoclinic system. The presentation of such formulae including a phosphate and dihydrogenphosphate grouping in the same compound was never reported before for other compounds. Furthermore, their chemical formula can also be written as $\text{M}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$. In fact, there is no difference between the XRD data and the unit-cell parameters of $\text{Zr}(\text{PO}_4)\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Zr}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS File No. 45-0068).

2.1. Halogenide phosphates $\text{MXPO}_4 \cdot n\text{H}_2\text{O}$ ($q = -3$, $p = 1$, $m = 1$)

Few compounds of the formula MXPO_4 and $\text{MXPO}_4 \cdot n\text{H}_2\text{O}$ ($n = 1, 2$) belong to this group. Among all tetravalent cation phosphates, only thorium and uranium fluoride, chloride, and bromide phosphates were reported.

Crystals of thorium and uranium(IV) chloride phosphates MClPO_4 ($\text{M} = \text{Th}, \text{U}$) were obtained by heating a mixture of anhydrous polytrioxophosphates $\text{M}(\text{PO}_3)_4$ and tetrachloride MCl_4 [2]. Thorium bromide phosphate, $\text{Th}_{10}\text{Br}_4(\text{PO}_4)_{12}$, was also synthesized in similar conditions [2]. Thorium fluoride phosphate $\text{ThFPO}_4 \cdot \text{H}_2\text{O}$ was obtained as a crystallized powder using hydrothermal synthesis from a mixture of thorium chloride, hydrofluoric acid, and phosphoric acid solutions [9]. Its XRD diagram was similar to that of $\text{UFPO}_4 \cdot \text{H}_2\text{O}$ [7].

In the 1950s, Dunn [7] reported the X-ray diffraction data for uranium fluoride phosphate $\text{UFPO}_4 \cdot \text{H}_2\text{O}$, but neither unit cell parameters nor symmetry were determined.

Crystallized precipitate was obtained by reaction between uranium(IV) hydrochloric solution and phosphoric acid [10]. A similar product was precipitated in hydrobromic medium [11]. Both compounds were identified as hydrated $\text{UXPO}_4 \cdot 2\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}$) crystallizing in tetragonal system (unit-cell parameters presented in Table 1). Their structure (Fig. 1) is built on the UXO_6 polyhedron linked by PO_4 tetrahedra [12]. Uranium(IV) is coordinated by two oxygen atoms of water molecules, four oxygen atoms of the phosphate

Table 1
Crystallographic data of halogenide phosphates and hydroxide phosphates^a

Compound	System	S. G.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg)	Refs.
$\text{UClPO}_4 \cdot 2\text{H}_2\text{O}$	Tetragonal	<i>I4/m</i>	14.631	6.662			[12]
$\text{UBrPO}_4 \cdot 2\text{H}_2\text{O}$	Tetragonal	<i>I4/m</i>	14.748	6.681			[12]
$\text{Th}(\text{OH})\text{PO}_4$	Orthorhombic	<i>C</i>	7.139	9.258	12.522		[14]
$\text{U}(\text{OH})\text{PO}_4 \cdot \text{H}_2\text{O}$	Orthorhombic	<i>P2_12_12_1</i>	9.72	18.89	10.13		^b
$\text{U}(\text{OH})\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Orthorhombic	<i>C*<i>c</i>*</i>	6.96	9.10	12.38		^c
$\text{Np}(\text{OH})\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Orthorhombic	n.d.	6.967	9.09	12.37		[15]
$\text{Ti}(\text{OH})\text{PO}_4$	Monoclinic	<i>C</i>	7.393	7.071	7.401	117.77	[18]
α - $\text{Zr}(\text{OH})\text{PO}_4$	n.d.						[19,20]
β - $\text{Zr}(\text{OH})\text{PO}_4$	Orthorhombic	<i>C*<i>ca</i></i>	6.607	8.657	11.718		[19]
$\text{Hf}(\text{OH})\text{PO}_4$	n.d.						[20]
$\text{Ge}(\text{OH})\text{PO}_4$	Orthorhombic	<i>Bmam</i>	12.25	7.01	7.16		[16]
	Monoclinic	<i>C2/c</i>	7.09	7.01	7.16	120.3	[16]
			7.11	7.00	7.07	119.5	^d
$\text{Sn}(\text{OH})\text{PO}_4$	Monoclinic	<i>C2/c</i>	7.567	7.252	7.512	118.93	[17]

^aSix-fold coordination for orthorhombic and monoclinic $\text{M}(\text{OH})(\text{PO}_4)$ and seven-fold coordination for $\text{UXPO}_4 \cdot 2\text{H}_2\text{O}$.

^bJCPDS File No. 41-1399.

^cJCPDS File No. 38-0397.

^dJCPDS File No. 37-0141.

n.d., not determined.

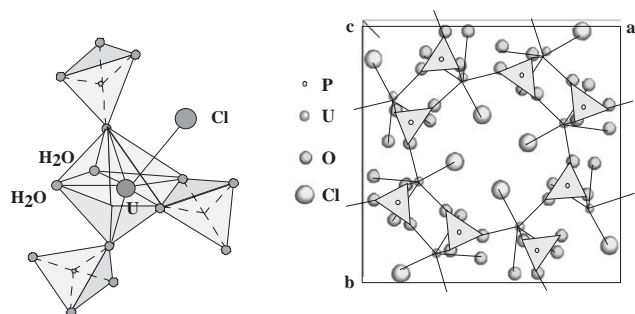


Fig. 1. Coordination polyhedron of uranium(IV) and representation of the $UXPO_4 \cdot 2H_2O$ structure [11].

tetrahedron, and one halogenide anion in a pentagonal bipyramid. Contrarily to these compounds, the preparation of $UIPO_4 \cdot 2H_2O$ was unsuccessful [11].

2.2. Hydroxide phosphates $M(OH)PO_4$ ($q=-3$, $p=1$, $m=1$)

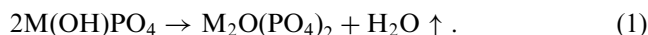
Two uranium hydroxide phosphates crystallizing in orthorhombic system (Table 1) are known as minerals: lermontovite $U(OH)PO_4 \cdot H_2O$ (JCPDS File No. 41-1399) and vyacheslavite $U(OH)PO_4 \cdot 2H_2O$ (JCPDS File No. 38-0397). Nevertheless, their structures were not determined. An amorphous uranium hydroxide phosphate of the formula $U(OH)PO_4 \cdot 6H_2O$ was also obtained by hydrolysis from uranium chloride or bromide phosphate [10,11]. In hydrothermal conditions, it is transformed into crystallized $U(OH)PO_4 \cdot 2H_2O$ [11] which XRD patterns agrees well with that of vyacheslavite. Uranium(IV) hydroxide phosphate is the only anion exchanger reported up to present. In contact with hydrochloric or hydrobromic solution, it is converted into $UClPO_4 \cdot 4H_2O$ and $UBrPO_4 \cdot 5H_2O$.

Thorium hydroxide phosphate $Th(OH)PO_4$, which XRD pattern is similar to that of $U(OH)PO_4 \cdot 2H_2O$ was also obtained using hydrothermal synthesis [13]. It was indexed in the orthorhombic system [14]. In this compound the hydroxide ion cannot be exchanged by a halogenide. Recently, $Np(OH)PO_4$ and $Np(OH)PO_4 \cdot 2H_2O$ were synthesized in similar conditions, while $Pu(OH)PO_4$ seems to co-precipitate with $Th(OH)PO_4$ as minor phase [15].

Syntheses of germanium [16], tin [17], titanium [18], zirconium [19,20], and hafnium [20] hydroxide phosphates, crystallizing in monoclinic and/or orthorhombic system (Table 1), were also described by several authors. The structure of $Ge(OH)PO_4$ and $Sn(OH)PO_4$ is built by octahedral MO_4OH group surrounded by PO_4 tetrahedra and linked through M–O–M chains.

The thermal condensation (dehydration) of the $M(OH)PO_4$ compounds leads generally to the formation

of oxide phosphates as follows:



This kind of reaction was observed for temperatures above $1000^\circ C$ [18,21] except for $Th(OH)PO_4$, which was converted into $Th_2O(PO_4)_2$ at $650\text{--}700^\circ C$. At higher temperatures the dithorium oxide phosphate was decomposed into ThO_2 and orthorhombic thorium phosphate–diphosphate (TPD) $Th_4(PO_4)_4P_2O_7$ [13]. The dehydration of $Sn(OH)PO_4$ is also an exception to Reaction (1), since it is decomposed into SnO_2 and SnP_2O_7 [16] at about $900^\circ C$.

2.3. Oxide phosphates $M_2O(PO_4)_2$ ($q=-3$, $p=2$, $m=2$)

This group of compounds is given by some authors in an empirical formula $M_2P_2O_9$, as diphosphate $(MO)_2P_2O_7$ by others, and finally as oxide phosphate forms $M_2O(PO_4)_2$. These compounds were often obtained by heating MO_2 with phosphorous(V) oxide. Some of them were formed by decomposition of M(IV) diphosphate at high temperature [5] or by condensation of hydroxide phosphates (Reaction (1)).

Among the tetravalent actinides, the uranium compound is the most investigated up to now. The XRD pattern of the “uranyl(IV)” diphosphate $(UO)_2P_2O_7$ was published for the first time by Dunn [7]. Then, other authors [22–24] mentioned the same formula. Single crystals of $U_2O(PO_4)_2$ were obtained by chemical vapor transport from 800 to $900^\circ C$ from reaction of $U(PO_3)_4$ with UP_2 and iodine in an evacuated, sealed silica tube in a two-zone furnace [25]. In the same time, a crystallized powder of this compound was obtained by heating under inert atmosphere either uranium halogenide phosphate or uranium hydroxide phosphate [10,11,21] between 1200 and $1350^\circ C$. The structure of $U_2O(PO_4)_2$ (Fig. 2) was determined as well from single crystal [25] as from powder diffraction [26]. The pentagonal bipyramid UO_7 is linked through linear U–O–U arrangements and bidentate phosphate tetrahedra. The $U_2O(PO_4)_2$ structure (orthorhombic symmetry) belongs the same type than the dizirconium oxide phosphate $Zr_2O(PO_4)_2$ [27]. Their unit-cell parameters are given in Table 2. The XRD patterns of both $U_2O(PO_4)_2$ [26] and $(UO)_2P_2O_7$ [22] are similar. Nevertheless, the structure of $U_2O(PO_4)_2$ and IR/Raman spectroscopy excluded the presence of diphosphate entities. The vibration modes of the linear U–O–U ($D_{\infty h}$ symmetry) active in Raman and IR spectra could be predicted from the group theory [28]: ν_s and δ_s in the region $200\text{--}150\text{ cm}^{-1}$ and ν_{as} in the region $800\text{--}700\text{ cm}^{-1}$ (medium intensity at 756 cm^{-1} and strong at 706 , 203 , and 175 cm^{-1}). The frequencies of the Th–O–Th bond in $Th_2O(PO_4)_2$ was interpreted in the same way [13]. Moreover, in the Raman spectrum of the $(NpO)_2P_2O_7$ [23], the weak band at about 790 cm^{-1} may be assigned

to the Np–O–Np, which leads to the re-definition of its formula. Mal'shikov and Bondar' [29] synthesized a compound “(HfO)₂P₂O₇” and suggested this formula basing on a weak band at 747 cm⁻¹ in the IR spectrum. However, it can be also attributed to the Hf–O–Hf bond. Furthermore, the comparison to the XRD data of “(HfO)₂P₂O₇” to that published earlier by Chernorukov et al. [20] lead to the conclusion that “(HfO)₂P₂O₇” is a mixture of α-Hf₂O(PO₄)₂ (system not determined) and its orthorhombic form. In the light of spectroscopic

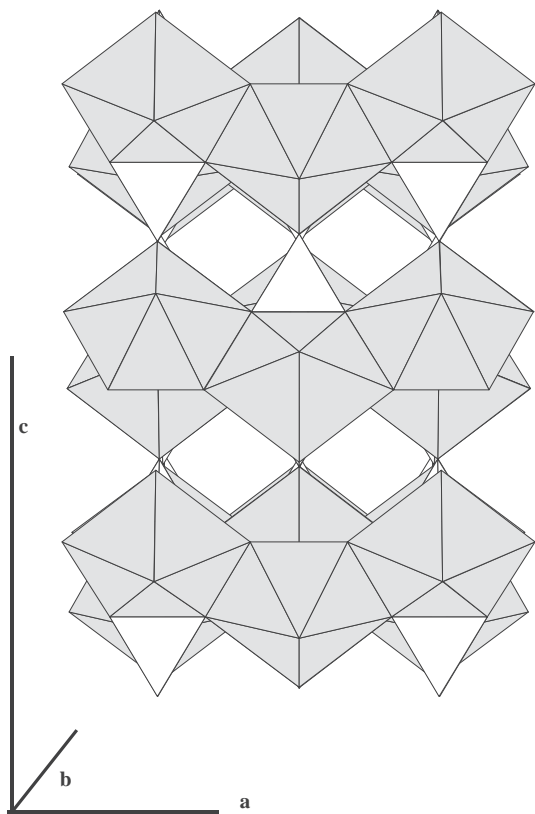


Fig. 2. Representation of the of U₂O(PO₄)₂ structure [26].

interpretation, all the (MO)₂P₂O₇ compounds should be written as M₂O(PO₄)₂.

The dineptunium oxide phosphate Np₂O(PO₄)₂ [15,30] and dithorium oxide phosphate Th₂O(PO₄)₂ [13] are isostructural to U₂O(PO₄)₂ (Table 2). Solid solutions Th_{2-x}Np_xO(PO₄)₂ were also reported [15]. No reference for Pu₂O(PO₄)₂, Ce₂O(PO₄)₂, and Pb₂O(PO₄)₂ was found in the literature, probably due to the reduction of the tetravalent cation to a lower oxidation state during the heat treatment.

As for U₂O(PO₄)₂, the chemical formulae of titanium ([17], JCPDS File No. 39-0207), zirconium [19,20,27,31,32], and hafnium [19,29] oxide phosphates were also presented in the literature in three forms. Gebert and Tillmanns [27] wrote for the first time the formula Zr₂O(PO₄)₂. Its crystal structure is built on a slightly distorted pentagonal bipyramid ZrO₇ [27]. Two modifications of this compound are reported. The unit-cell parameters of the orthorhombic form called β-Zr₂O(PO₄)₂ are given in Table 2. The crystal system of the α-form was not determined. Two similar forms of Hf₂O(PO₄)₂ were also reported [20].

The XRD patterns of Ti₂O(PO₄)₂ [18] and (TiO)₂P₂O₇ (JCPDS File No. 39-0207) are similar and seem to correspond to the same compound. They are also close to that of β-Zr₂O(PO₄)₂. Consequently, the right formula of the titanium compound should be written Ti₂O(PO₄)₂ and its crystal system should be orthorhombic. The relation of the unit-cell volume versus the ionic radii of the tetravalent cations is shown in Fig. 3. The Ti₂O(PO₄)₂ unit-cell parameters, calculated from the linear regression, are given in Table 2.

Silicon and germanium phosphates published with empirical chemical formulae: Si₂P₂O₉ ([33], JCPDS 15-0508) and Ge₂P₂O₉ [33] could belong to the group of M₂O(PO₄)₂. Both crystallize in hexagonal system but their symmetry group and structure were not determined.

Table 2
Crystallographic data of cation oxide phosphates^a

Compound	System	S. G.	a (Å)	b (Å)	c (Å)	Refs.
Th ₂ O(PO ₄) ₂	Orthorhombic	<i>Cmca</i>	7.177	9.225	12.858	[13]
	Orthorhombic	<i>Cmca</i>	7.176	9.248	12.835	[14]
U ₂ O(PO ₄) ₂	Orthorhombic	<i>Cmca</i>	7.088	9.037	12.702	[25]
			7.088	9.036	12.701	[26]
Np ₂ O(PO ₄) ₂	Orthorhombic	<i>Cmca</i>	7.038	9.015	12.603	[15]
			7.033	9.024	12.587	[30]
Ti ₂ O(PO ₄) ₂	Orthorhombic	n.d.	6.363	8.40	11.63	^b
Zr ₂ O(PO ₄) ₂	Orthorhombic	<i>Cmca</i>	6.624	8.637	11.872	[27]
Hf ₂ O(PO ₄) ₂	Orthorhombic	<i>Cmca</i>	6.603	8.648	11.777	[20]
Si ₂ O(PO ₄) ₂	Hexagonal	n.d.	7.862		24.13	[33]
Ge ₂ O(PO ₄) ₂	Hexagonal	n.d.	7.998		24.86	[33]

^aSeven-fold coordination for orthorhombic M₂O(PO₄)₂.

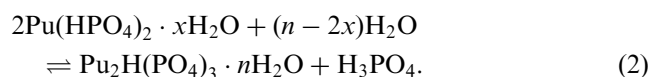
^bValues calculated from linear regression.

n.d., not determined.

2.4. Phosphates–hydrogenphosphates

$M_2(PO_4)_2HPO_4 \cdot nH_2O$ ($q=-3$ and -2 , $p=2$ and 1 , $m=2$)

The group of actinide phosphate–hydrogenphosphates $M_2(PO_4)_2HPO_4 \cdot nH_2O$ sometimes presented as $M_2H(PO_4)_3 \cdot nH_2O$ contains only few members. The last kind of formula was mentioned for cerium $Ce_2H(PO_4)_3 \cdot nH_2O$, thorium $Th_2H(PO_4)_3 \cdot nH_2O$, and plutonium(IV) $Pu_2H(PO_4)_3 \cdot nH_2O$ [34]. Their crystallized forms, found to be isomorphous, were obtained from gels (obtained by mixing M^{4+} solutions with phosphoric acid in nitric acid) heated in a sealed tube. However, no XRD data were published. King [34] also observed the formation of the plutonium compound as a conversion reaction of $Pu(HPO_4)_2 \cdot xH_2O$ as follows:



The author did not specify whether the process corresponds to a real equilibrium. Nevertheless, the initial product was stable only with an excess of phosphoric acid.

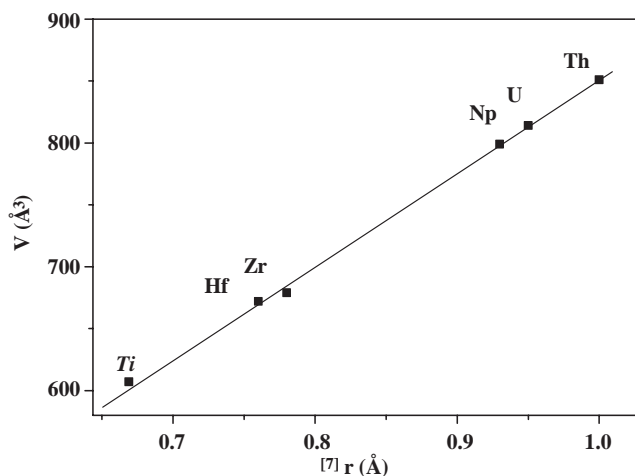


Fig. 3. Variation of the unit-cell volume as function of the ionic radii for various oxide phosphates $M_2O(PO_4)_2$ (orthorhombic). For the titanium compound the value was calculated from linear regression.

Table 3

Crystallographic data of phosphate-hydrogenphosphates and $Th_4(PO_4)_4P_2O_7$ ^a

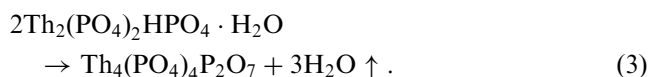
Compound	System	S. G.	a (Å)	b (Å)	c (Å)	β (deg)	Refs.
$Th_2(PO_4)_2HPO_4 \cdot H_2O$ ^b	Monoclinic	P_{21}	6.6901	7.0218	11.1863	107.16	[37]
$U_2(PO_4)_2HPO_4 \cdot H_2O$	Monoclinic	P_{21}	6.607	6.957	11.055	107.27	[38]
$Ce_2(PO_4)_2HPO_4 \cdot H_2O$	Monoclinic	P_{21}	7.336	6.260	11.012	107.39	[38]
$Th_4(PO_4)_4P_2O_7$	Monoclinic	P_{21}	6.657	7.050	11.132	107.81	[37]
$Th_4(PO_4)_4P_2O_7$	Orthorhombic	$Pcam$	12.846	10.437	7.064		[44]

^aSeven-fold coordination for monoclinic $M_2(PO_4)_2HPO_4 \cdot H_2O$ and for monoclinic $Th_4(PO_4)_4P_2O_7$ and eight-fold coordination for orthorhombic $Th_4(PO_4)_4P_2O_7$.

^bSee also M.A. Salvadó, P. Pertierra, A.I. Bortun, C. Trobajo, J.R. García, N. Clavier, N. Dacheux, Chem. Mater., submitted.

Amorphous thorium phosphate–hydrogenphosphate $Th_2(PO_4)_2HPO_4 \cdot (3-7)H_2O$ was obtained by precipitation from thorium nitrate or thorium chloride solution using diammonium hydrogenphosphate [35]. It appears as an ion exchanger where the proton can be partly exchanged (for $pH > 2$) by a monovalent or divalent cation [36]. The complete replacement of proton leads to derivatives of $MTh_2(PO_4)_3$ -type compounds ($M = Na, Cs$) [35]. The crystallized form $Th_2(PO_4)_2HPO_4 \cdot H_2O$ was recently synthesized in hydrothermal conditions [13]. Its crystal symmetry is monoclinic [37] which unit-cell parameters are given in Table 3.

The P–O–H group in this compound was evidenced by means of IR spectroscopy and ^{31}P and 1H NMR experiments [13,37]. By heating between 900 and 1100 °C, thorium phosphate–hydrogenphosphate (amorphous or crystallized) was converted into $Th_4(PO_4)_4P_2O_7$ as follows:



A crystallized uranium(IV) phosphate–hydrogenphosphate was synthesized according to the same method [38]. The XRD diagram and IR spectrum of both compounds are very close. It was found from preliminary studies that $U_2(PO_4)_2HPO_4 \cdot H_2O$ crystallizes, like its thorium analogue, in the monoclinic system (Table 3).

Contrarily to $Th_2(PO_4)_2HPO_4 \cdot H_2O$, $U_2(PO_4)_2HPO_4 \cdot H_2O$ could not be transformed into uranium(IV) phosphate–diphosphate, similar to TPD [38]. Neptunium(IV) and plutonium(IV) phosphate–hydrogenphosphate hydrate were prepared in polyphase systems using the same process as well as solid solutions $Th_{2-x/2}M_{x/2}(PO_4)_2HPO_4 \cdot H_2O$ (with $M = U, Np$, and/or Pu) [15].

A crystallized precipitate of cerium(IV) phosphate with mole ratio $PO_4:Ce \approx 1.5$ was prepared by König and Meyn [39] from solutions of cerium sulfate and phosphoric acid. Basing on the known, in aqueous solution, $(Ce-O-Ce)^{6+}$ ion and on the condensation of the HPO_4 group at 900 °C, the authors postulated the

initial composition as $(\text{Ce}-\text{O}-\text{Ce})(\text{HPO}_4)_3 \cdot \text{H}_2\text{O}$ and the final as $(\text{Ce}-\text{O}-\text{Ce})_2(\text{P}_2\text{O}_7)_3$ (empirical formula $\text{Ce}_4\text{P}_6\text{O}_{23}$). Nevertheless, the initial formula could also be written as $\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ without excluding the fact of condensation of the hydrogenphosphate ion. However, the temperature of condensation is doubtful. Moreover, cerium(IV) diphosphate is completely reduced into CePO_4 above 900°C [40], while the reduction of cerium(IV) hydrogenphosphate occurs at 800°C [41].

Alberti et al. [41] synthesized a cerium(IV) phosphate with a mole ratio $\text{PO}_4:\text{Ce}$ equal to 1.55 without any suggestion of the chemical formula. The XRD diagram of this product is similar to that of König and Meyn [39].

A well-crystallized $\text{Ce}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ isotypic to $\text{Th}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ was recently obtained in the same conditions [38]. Its unit-cell parameters are reported in Table 3.

Two zirconium phosphates, obtained in hydrothermal synthesis, were reported by Ono and Yajima [42,43]: $\text{H}_3\text{OZr}_2(\text{PO}_4)_3 \cdot 0.1\text{H}_2\text{O}$ and $\text{HZr}_2(\text{PO}_4)_3$. For the first one, two crystalline forms were found to be: cubic (metastable) and rhombohedral, while only a cubic form was reported for the second one. Their formulae may be also written as $\text{Zr}_2(\text{PO}_4)_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Zr}_2(\text{PO}_4)_2\text{HPO}_4$. The lattice constants of both cubic phases were found 10.190 and 10.165 Å, respectively. Neither XRD pattern of these phases nor results of quantitative analysis were published. Their chemical composition was only deduced from TGA results. As the presented results are ambiguous, the existence of both compounds is rather doubtful. The titanium(IV) phosphate $\text{TiO}(\text{H}_2\text{PO}_4)_2 \cdot \text{TiOHPO}_4 \cdot 3\text{H}_2\text{O}$ or lead(IV) phosphate published in oxide form $2\text{PbO}_2 \cdot 1.5\text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ [2] may also be interpreted as hydrated phosphate–hydrogenphosphates: $\text{Ti}_2(\text{PO}_4)_2\text{HPO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Pb}_2(\text{PO}_4)_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$, but the right formulae should be accepted only after detailed investigations.

The formation of $\text{M}_2(\text{PO}_4)_2\text{HPO}_4$ -type phosphates seems to be a characteristic of M^{4+} cations with large ionic radii (Th, U, Np, Pu, Ce). Nevertheless, derivatives of the phosphate–hydrogenphosphates where the proton is replaced by a monovalent or divalent cation, i.e., $(\text{M}^n)_x\text{M}_2(\text{PO}_4)_3$ were obtained for both small and large ionic radii (see next sections). These widespread compounds ($k < 0$ family) were most often synthesized by dry chemistry methods.

2.5. Phosphates of $\text{M}_4(\text{PO}_4)_4\text{A}$ type ($q = -4$ and -3 , $p = 1$ and 4 , $m = 4$)

This group of phosphates includes only species where A is a tetranegative anion like diphosphate P_2O_7 or silicate SiO_4 . Thorium phosphate–diphosphate $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ (TPD) was prepared as a pure phase between 850 and 1250°C starting from a mixture of any

thorium compound and any phosphating reagent provided that the mole ratio $\text{P}:\text{Th}$ was equal to 1.5, using either wet or dry chemistry methods [44]. Dehydration of the thorium phosphate–hydrogenphosphate followed by condensation leads to the same result [13,35]. The TPD crystal structure (Fig. 4) was determined as well from single crystal as from powder diffraction data. The unit cell is orthorhombic with the parameters presented in Table 3. In the ThO_8 polyhedron, thorium is surrounded by oxygen atoms of monodentate and bidentate PO_4 tetrahedra and bidentate P_2O_7 [44].

Because of a high thermal stability and a very good resistance to water and acid alteration, TPD appears as a good host matrix for the long-term storage of radionuclides [36,45–52]. Actually, large amounts of uranium(IV), neptunium(IV), plutonium(IV), and probably protactinium(IV) can replace thorium in the TPD lattice to form solid solutions $\text{Th}_{4-x}\text{M}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ [30,51,52]. The highest calculated and experimental x values are equal to 3 for uranium [51,52], 2.14 for neptunium [30], 1.67 for plutonium [51], and 3.75 expected for protactinium [53]. Above these values, polyphase systems were obtained, which showed the impossibility to synthesize the TPD analogues for protactinium, uranium, neptunium, and plutonium. Instead of $\text{M}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ ($\text{M} = \text{U}, \text{Np}, \text{Pu}$) solid solutions, polyphase systems were obtained (Table 3). Attempts to synthesize “ $\text{Ce}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ ” at high temperature led to the formation of CeP_2O_7 and CePO_4 [51]. Thus, the orthorhombic TPD seems to be the unique tetravalent cation phosphate–diphosphate even though large amounts of tetravalent actinides can be incorporated into the structure [15].

More recently, a low-temperature form of TPD was obtained in the temperature range 300 – 950°C [37]. This compound crystallizes in the monoclinic system

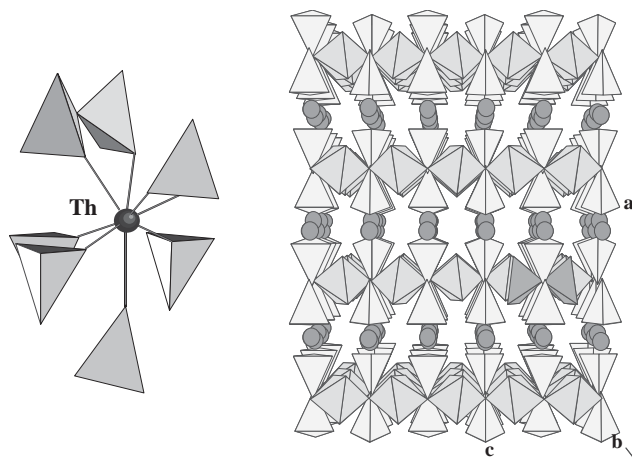


Fig. 4. Polyhedron of coordination of thorium and structure representation of $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ [44].

Table 4
Systems obtained at high temperature for the initial mole ratio P/M(IV)=1.5

Expected compound	Heating conditions	Compound(s) obtained	Refs.
Th ₄ (PO ₄) ₄ P ₂ O ₇	1100–1250 °C	Th ₄ (PO ₄) ₄ P ₂ O ₇	[44]
U ₄ (PO ₄) ₄ P ₂ O ₇	1200 °C, air	UP ₂ O ₇ + U(UO ₂)(PO ₄) ₂	[51]
U ₄ (PO ₄) ₄ P ₂ O ₇	1250 °C, argon	UP ₂ O ₇ + U ₂ O(PO ₄) ₂	[51]
Np ₄ (PO ₄) ₄ P ₂ O ₇	1000 °C, air	NpP ₂ O ₇ + Np ₂ O(PO ₄) ₂	[30]
Pu ₄ (PO ₄) ₄ P ₂ O ₇	1000 °C	PuP ₂ O ₇ + PuPO ₄	[51]
Ce ₄ (PO ₄) ₄ P ₂ O ₇	1200 °C	CeP ₂ O ₇ + CePO ₄	[51]
Zr ₄ (PO ₄) ₄ P ₂ O ₇	1300 °C	ZrP ₂ O ₇ + Zr ₂ O(PO ₄) ₂	[54]
Hf ₄ (PO ₄) ₄ P ₂ O ₇	1200–1300 °C	HfP ₂ O ₇ + Hf ₂ P ₂ O ₉ + HfO ₂	[54]
Sn ₄ (PO ₄) ₄ P ₂ O ₇	1200 °C, air	SnP ₂ O ₇ + SnO ₂	[54]

Table 5
Various phosphates of tetravalent cations for $k > 0$

Compound	Th	U	Np	Pu	Ce	Ti	Zr	Hf	Si	Ge	Sn	Pb
M(HPO ₄)(H ₂ PO ₄) ₂ ^a	+	+	–	–	–	–	–	–	–	–	–	–
M(OH)PO ₄	+	+ ^a	+	–	–	+	+	+	–	+	+	+
M ₂ O(PO ₄) ₂	+	+	+	–	–	+	+	+	+	+	–	–
M ₂ (PO ₄) ₂ HPO ₄ ^a	+	+	+	+	+	+?	+?	–	–	–	–	+?
M ₄ (PO ₄) ₄ P ₂ O ₇	+	–	–	–	–	+?	+?	–	–	–	–	–

^aHydrated compounds.

–, References not found in the literature; +?, uncertain or doubtful.

(Table 3) and leads to orthorhombic TPD through a phase transition evidenced at 950 °C.

Attempts to synthesize other TPD analogues like “Zr₄(PO₄)₄P₂O₇”, “Hf₄(PO₄)₄P₂O₇”, and “Sn₄(PO₄)₄P₂O₇” were unsuccessful too [54] (Table 4). Solid solutions of orthorhombic TPD with cerium(IV) or zirconium were not obtained too [51]. In both cases, polyphase systems were formed: TPD + CePO₄ and TPD + Zr₂O(PO₄)₂ + ZrO₂; cerium(IV) was reduced to cerium(III) even in oxidizing atmosphere and zirconium radius was probably too small to replace thorium in the TPD structure.

However, zirconium and titanium phosphates of global formula Ti₄P₆O₂₃ and Zr₄P₆O₂₃ that looks like Th₄P₆O₂₃ (empirical formula of TPD) were reported by Ono [42,43,55]. Their chemical composition was estimated only from thermogravimetric curves. Ti₄P₆O₂₃ was obtained in polyphase system from a mixture of NH₄H₂PO₄ and TiO₂ heated at various temperatures under the pressure of 0.15–0.20 GPa. Its crystal lattice was defined as hexagonal [55]. Cubic Zr₄P₆O₂₃ was obtained by dehydration of HZr₂(PO₄)₃ [42,43]. Beside these compounds, other phases are formed in the system obtained. Thus, their purity is brought into question.

If the P₂O₇ group is replaced by silicate SiO₄ in TPD, thorium phosphate-silicate Th₄(PO₄)₄SiO₄ is formed. This compound, which XRD diagram is similar to that

of TPD, was synthesized at 1100 °C starting from a mixture of thorium nitrate solution, phosphoric acid, and TEOS tetra-ethyl-ortho-silicate (C₂H₅O)₄Si [9].

As a summary, the phosphates of tetravalent cations with $k > 0$ referred in the literature are gathered in Table 5.

3. Phosphates of negative framework: $k < 0$, $[M_m(A^q)_p]^k$

The $k < 0$ family gathers several compounds of tetravalent cation and PO₄^{3–} anion where the p value varies from 2 to 6. The main groups of derivatives of the $[M(PO_4)_p]^{(4-3p)}$ and $[M_2(PO_4)_3]^-$ frameworks for which the negative charge is compensated by a monovalent or divalent cation are reported in Table 6. These crystallized compounds were generally synthesized from mixtures of dioxides MO₂ and carbonates M_{*n*}CO₃ ($n = 1, 2$) or MO oxides and ammonium phosphates by heating at high temperature. They may be also obtained from aqueous solutions.

3.1. Phosphates of $(M^n)_xM(PO_4)_p$ type ($q = -3$ and $m = 1$)

In this group, the charge of the cation M is equal to 1 or 2, while $nx = 3p - 4$. Compounds of general formulae

Table 6
Various phosphates of tetravalent cations for $k < 0$

Cation M^{4+}	$M_2M(PO_4)_2$	$MM(PO_4)_2$	$M_7M(PO_4)_6$	$MM_2(PO_4)_3$	$M_{0.5}M_2(PO_4)_3$
Th	Li, Na, K	Ca, Sr, Ba, Cd, Pb	Sr, Ba, Pb	^a Ag, Cu, Tl	Ca, Sr, Ba, Cd, Pb
U	Na (K ?)	Ca, Sr, Ba	–	^a	–
Np	–	Ca	–	Li, Na, K	–
Pu	–	–	–	^a	–
Ti	–	–	Pb	Li, Na, K, Cu	Ca
Zr	^a	Ca, Sr, Ba, Co, Mn, Ni, Zn	Pb	^a Ag, Cu	Ca, Sr, Ba, Cd, Co, Pb, Cu, Mg, Mn, Zn
Hf	–	–	Pb	^a Ag, Cu	Ca, Sr, Ba, Cd, Pb Co, Cu, Mn, Zn
Ge	–	Ca	–	Li, Na, K	Ca
Sn	–	–	Pb	Na, Cu	–

^aLi, Na, K, Rb, Cs.

M, monovalent or divalent cation; –, references not found in the literature.

Table 7
Crystallographic data of $(M^n)_xM(PO_4)_p$ actinide phosphates

Compound	System	S. G.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	Refs.
Na ₂ Th(PO ₄) ₂	Monoclinic	<i>P2₁/c</i>	7.055	21.66	9.095		111.56		[66]
Na ₂ Np(PO ₄) ₂	n.d.	n.d.							[67]
CaTh(PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.708	6.914	6.409		103.78		[56]
	Monoclinic	<i>P2₁/n</i>	6.714	6.921	6.424		103.68		[60]
CdTh(PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.670	6.881	6.390		104.29		[60]
SrTh(PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.800	7.022	6.522		103.53		[56]
	Monoclinic	<i>P2₁/n</i>	6.792	7.017	6.501		103.51		[60]
PbTh(PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.849	7.070	6.581		103.72		[56]
	Monoclinic	<i>P2₁/n</i>	6.848	7.081	6.565		103.80		[60]
BaTh(PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.944	6.171	6.670		102.88		[60]
Sr ₇ Th(PO ₄) ₆	Cubic	<i>I$\bar{4}$3d</i>	10.186						^a
Ba ₇ Th(PO ₄) ₆	Cubic	<i>I$\bar{4}$3d</i>	10.582						^b
Pb ₇ Th(PO ₄) ₆	Cubic	<i>I$\bar{4}$3d</i>	10.371						[65]
CaU(PO ₄) ₂	Monoclinic	n.d.	6.70	6.91	6.41		104.0		[58]
	Monoclinic	<i>P2₁/n</i>	6.654	6.841	6.359		103.98		[61]
	Orthorhombic	<i>Pnma</i>	13.926	6.958	6.136				^c
(UO ₂)U(PO ₄) ₂ ^d	Triclinic	<i>P1</i>	8.821	9.217	5.477	102.62	97.75	102.46	[62]
CaNp(PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.673	6.800	6.375		104.11		^e
CaNp _{0.7} Pu _{0.3} (PO ₄) ₂	Monoclinic	<i>P2₁/n</i>	6.649	6.840	6.351		104.14		^f

^aJCPDS File No. 33-1354.

^bJCPDS File No. 33-0180.

^cJCPDS File No. 86-0687.

^dUranyl ion is considered here as an *M*(II) cation.

^eJCPDS File No. 49-947.

^fJCPDS File No. 49-948.

n.d., not determined.

$M_2M(PO_4)_2$ and $MM(PO_4)_2$ can be considered as derivatives of hydrogenphosphates $M(HPO_4)_2$ where two monovalent or one divalent cation replace both protons. Calcium–thorium phosphate $CaTh(PO_4)_2$ is a mineral called brabantite [56]. Schwarz as well as other workers [57–59] synthesized a series of thorium phosphates $MTh(PO_4)_2$ (Tables 6 and 7), which exhibit a monoclinic cell of the huttonite ($ThSiO_4$) type (JCPDS

File Nos. 04-0613 and 34-0188). According to the author, the crystal structure can be compared to the synthetic monazite $LaPO_4$ (JCPDS File No. 46-1326). Rose [56] determined the unit-cell parameters for $CaTh(PO_4)_2$, $SrTh(PO_4)_2$, and $PbTh(PO_4)_2$. Recently, $BaTh(PO_4)_2$ was also reported [9,60]. The unit-cell parameters of $BaTh(PO_4)_2$ and $CdTh(PO_4)_2$ were determined by Montel et al. [60].

Uranium compounds of the formula $MU(PO_4)_2$ ($M=Ca, Sr, Ba$) were also described [2]. A special attention was focused on calcium uranium(IV) phosphate [58,59,61] supposed to be, like $CaTh(PO_4)_2$ [56], one of the constituents of natural monazites. Its unit cell (Table 7) is monoclinic [57]. Nevertheless, an orthorhombic form was also synthesized (JCPDS File No. 86-0687). The monoclinic $CaNp(PO_4)_2$ was also reported (JCPDS File No. 49-947). No plutonium(IV) analogue of this type of compounds was found in the literature, except the solid solution $CaNp_{0.7}Pu_{0.3}(PO_4)_2$ (JCPDS File No. 49-948).

The uranium–uranyl phosphate $U(UO_2)(PO_4)_2$ [10,62,63] may be considered as a $MU(PO_4)_2$ -type compound, the uranyl group working as a divalent cation. This compound was synthesized through various chemistry routes [10,63]. The crystal system is triclinic ($Z=2$) with unit-cell parameters presented in Table 7. The structure (Fig. 5) was solved from X-ray powder diffraction pattern [62]. In the crystal lattice, uranium (IV) and uranium(VI) form UO_7 polyhedra, both linked in edge-sharing pairs. The uranyl entity is linear with two terminal oxygen atoms [O–U–O]. Uranium–uranyl phosphate is a rare case of mixed valence uranium compound. Schaekers [24] and Bamberger et al. [23,64] reported for the same empirical formula a compound “ $U_2O_3P_2O_7$ ”, although they did not observe the ν_s frequencies of the P–O–P bridge in the IR and Raman spectra.

Actinide phosphates of $M_7Th(PO_4)_6$ formula ($M=Ba, Pb, Sr$) are known only for thorium and for divalent cations of large ionic radii. They crystallize in the cubic system (JCPDS File Nos. 33-0180, 33-0775, and 33-1354).

It is interesting to compare the crystal structure of metal(II)-thorium phosphates against the ionic radii of

the M cations [9]. Those whose radii (in the eight-fold coordination) spread from 1.10 to 1.42 Å ($Cd^{2+}, Ca^{2+}, Sr^{2+}, Pb^{2+}, Ba^{2+}$) form the monoclinic lattice of $MTh(PO_4)_2$, while strontium, lead, and barium cations (with radii 1.26, 1.29, and 1.42 Å, respectively) also form a cubic lattice of $M_7Th(PO_4)_6$ type. The crystal data for the presented compounds are listed in Table 7.

Non-actinide phosphates of $M_7M(PO_4)_6$ formula where $M=Pb$ and $M=Ti, Zr, Hf,$ and Sn were also synthesized [65]. Their cubic lattice is of eulytite $Bi_4(SiO_4)_3$ type. Phosphates of $(M^n)_xM(PO_4)_p$ with a monovalent compensation charge cation are uncommon. Only few examples can be reported: $Na_2Th(PO_4)_2$ [66], $Na_2Np(PO_4)_2$ [67], $Na_5Th(PO_4)_3$ [2], $Na_5Ti(PO_4)_3$ [68], $Na_2Zr(PO_4)_2 \cdot 3H_2O$ [69], $Na_5Zr(PO_4)_3$ [70], $Na_8Zr(PO_4)_4$ [2], and $Na_{14}Zr(PO_4)_6$ [71]. Pentasodium–titanium and pentasodium–zirconium phosphates belong to the Nasicon-type structure (acronym for Na super ionic conductor) of $NaZr_2(PO_4)_3$.

3.2. Phosphates of $(M^n)_xM_2(PO_4)_3$ type ($q=-3, p=3, m=2$)

A large group of actinide phosphates of general formula $(M^n)_xM_2(PO_4)_3$ ($n=1, 2$) was reported in the literature. They can be considered as derivatives of phosphate–hydrogenphosphates $M_2(PO_4)_2HPO_4$ where the proton is replaced by a monovalent or divalent cation. Especially, $MTh_2(PO_4)_3$ compounds with $M=Li-Cs, Cu, Ag, Tl$ [72–78] and $M=0.5 Ba, Ca, Cd, Pb, Sr$ [79] were intensively investigated. Topić et al. [75,76] determined the crystal structure of $NaTh_2(PO_4)_3$ and $KTh_2(PO_4)_3$ (Fig. 6). The system is monoclinic with the space group Cc or $C2/c$. The lattice is centrosymmetric with ThO_9 polyhedra, where the monovalent ion with coordination number 8 is placed in the central hole.

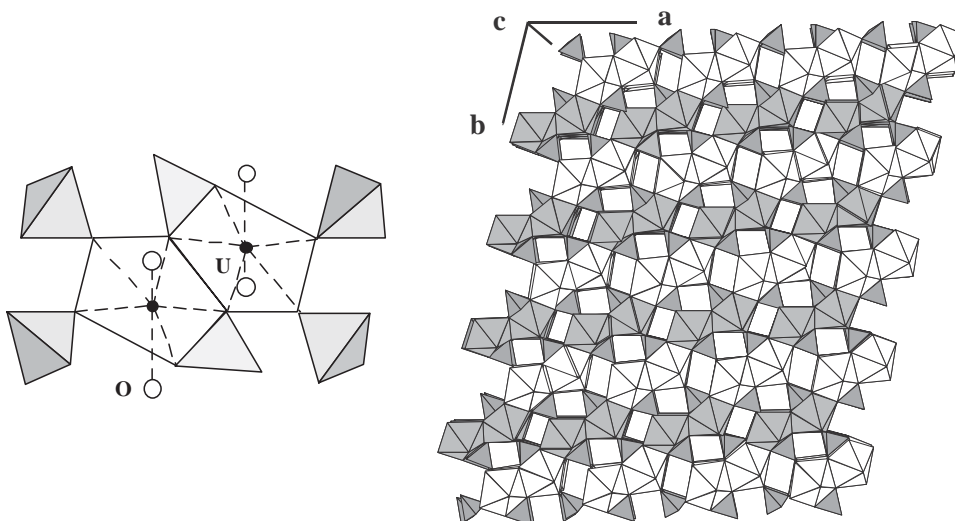


Fig. 5. Polyhedron of coordination of uranium(IV) and structure representation of $U(UO_2)(PO_4)_2$ [62].

All these compounds are isostructural. Uranium phosphates $MU_2(PO_4)_3$ ($M=Li-Cs$) were also reported [72,73,80,81]. The crystal structure was determined for lithium, sodium, and potassium derivatives. Neptunium [66,82] and plutonium [80–83] form a series of analogous phosphates $MNp_2(PO_4)_3$ ($M=Li-K$) and $MPu_2(PO_4)_3$ ($M=Li-Cs$). However, the existence of the monoclinic $NaPu_2(PO_4)_3$ phosphate published by Skiba et al. [83] was contested by Bamberger [4]. Burnaeva et al. [84] synthesized the hexagonal variety of $NaPu_2(PO_4)_3$. The unit-cell parameters of metal–actinide phosphates are presented in Table 8. Fig. 7 depicts the linear relation between the unit-cell volumes of $NaAn_2(PO_4)_3$, which is concomitant with the raise of the actinide ionic radii. For these compounds, the linear function $V = f(r_{cat})$ can also be observed like for M(IV) hydrogenphosphates or M(IV) diphosphates.

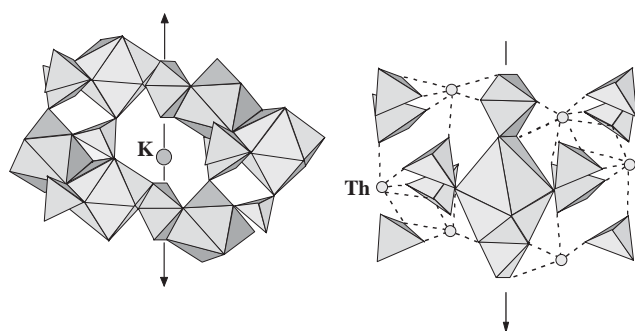


Fig. 6. Simplified structure of the $KTh_2(PO_4)_3$ [77].

For thorium derivatives $(M^n)_xTh_2(PO_4)_3$, where M is a monovalent or divalent cation, the variation of the unit-cell volume versus the ionic radii is presented in Fig. 8. For other actinide elements there are not enough available data in the literature.

Non-actinide tetravalent cation phosphates $(M^n)_xM_2(PO_4)_3$ ($x = 1$ or 0.5) (with $M=Ge, Sn, Ti, Zr, Hf$) crystallize in the hexagonal system [74,85–94]. The crystal structure was determined for $NaZr_2(PO_4)_3$ (NZP) [85] and $NaTi_2(PO_4)_3$ [88]. The $[M_2(PO_4)_3]$ framework is based on MO_6 surrounded by six PO_4

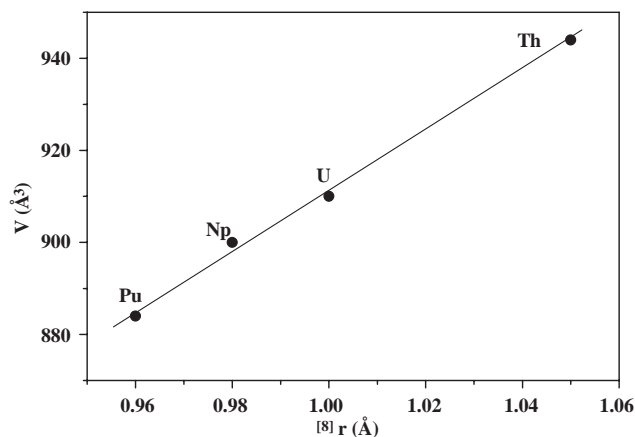


Fig. 7. Relation between unit-cell volume and ionic radii for $NaAn_2(PO_4)_3$ (the function is plotted for the eight-fold coordination number for actinides because the radii for the nine-fold coordination of neptunium and plutonium are unknown).

Table 8
Crystallographic data of $(M^n)_xM_2(PO_4)_3$ actinide phosphates

Compound	System	S. G.	a (Å)	b (Å)	c (Å)	β (deg)	Refs.
$LiTh_2(PO_4)_3$	Monoclinic	$C2/c$	17.43	6.82	8.14	101.33	[74]
$NaTh_2(PO_4)_3$	Monoclinic	$C2/c$	17.37	6.81	8.13	101.00	[74]
$KTh_2(PO_4)_3$	Monoclinic	$C2/c$	17.57	6.86	8.14	101.08	[74]
$RbTh_2(PO_4)_3$	Monoclinic	$C2/c$	17.55	6.84	8.14	102.00	[74]
$CsTh_2(PO_4)_3$	Monoclinic	$C2/c$	17.73	6.88	8.17	102.00	[74]
$AgTh_2(PO_4)_3$	Monoclinic	$C2/c; Cc$	17.385	6.815	8.148	101.10	[76]
$TlTh_2(PO_4)_3$	Monoclinic	$C2/c; Cc$	17.686	6.885	8.315	102.01	[78]
$CuTh_2(PO_4)_3$	Monoclinic	$C2/c; Cc$	21.99	6.740	7.013	108.46	[78]
$Ca_{0.5}Th_2(PO_4)_3$	Monoclinic	n.d.	17.273	6.813	8.139	100.83	[79]
$Sr_{0.5}Th_2(PO_4)_3$	Monoclinic	n.d.	17.403	6.829	8.148	101.16	[79]
$Ba_{0.5}Th_2(PO_4)_3$	Monoclinic	n.d.	17.563	6.861	8.144	101.56	[79]
$Cd_{0.5}Th_2(PO_4)_3$	Monoclinic	n.d.	17.415	6.791	8.160	100.38	[79]
$Pb_{0.5}Th_2(PO_4)_3$	Monoclinic	n.d.	17.457	6.842	8.143	101.22	[79]
$LiU_2(PO_4)_3$	Monoclinic	Cc	17.39	6.73	8.04	101.49	[74]
$NaU_2(PO_4)_3$	Monoclinic	$C2/c$	17.23	6.70	8.03	101.10	[74]
$KU_2(PO_4)_3$	Monoclinic	$C2/c$	17.479	6.758	8.019	102.01	[79]
		n.d.	17.470	6.754	8.025	102.02	[80]
$NaNp_2(PO_4)_3$	Monoclinic	Cc	17.17	6.701	7.972	101.06	[67]
$NaPu_2(PO_4)_3$	Monoclinic	Cc	17.14	6.65	7.99	101.12	[84]
	Hexagonal	$R3c$	9.09	23.69			[84]
$KPu_2(PO_4)_3$	Monoclinic	n.d.	17.2 ^a	n.d.	n.d.	n.d.	[80]

^aCalculated from linear regression.

n.d., not determined.

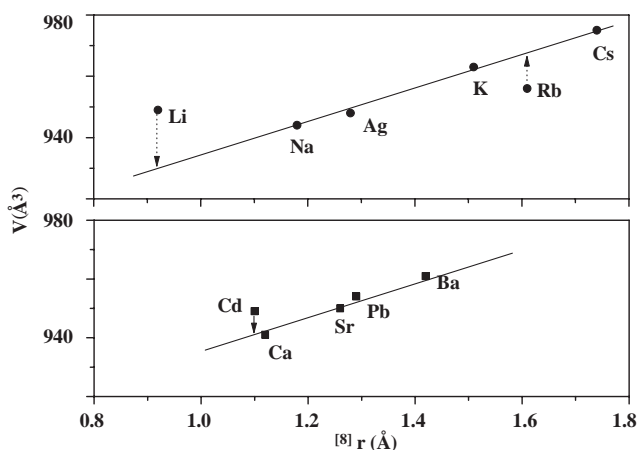


Fig. 8. Relation between unit-cell volume and ionic radii for monoclinic thorium phosphates $M\text{Th}_2(\text{PO}_4)_3$ and $M_{0.5}\text{Th}_2(\text{PO}_4)_3$.

tetrahedra and on PO_4 tetrahedra surrounded by four MO_6 octahedra. This results in channels where M^{n+} ions are located and where the conductivity occurs. Their analogues are isostructural.

Zirconium and hafnium phosphates (M^n) $_x\text{M}_2(\text{PO}_4)_3$ ($x = 0.5$) with divalent cations M were obtained for large ionic radii (Ca, Sr, Ba, Cd, Pb) and small ones (Co, Cu, Mn, Zn) (Table 6). The dimensions of all these cations fit very well in the $\text{NaZr}_2(\text{PO}_4)_3$ structure. This phenomenon is not observed for thorium or uranium phosphates (of analogous chemical composition), for which only derivatives with $M = \text{Ca, Sr, Ba, Cd, Pb}$ were reported (Table 6). Probably, small cations cannot be kept in the hole of the monoclinic structure.

4. Miscellaneous phosphates

Five thorium phosphates with $m = p = 1$ and $q = -3$, for which the charge of the framework is compensated simultaneously by an anion A and by a cation M , are also reported in the literature. Two of them, $\text{NaTh}(\text{OH})_2\text{PO}_4 \cdot 4.5\text{H}_2\text{O}$ and $\text{KTh}(\text{OH})_2\text{PO}_4 \cdot 3.5\text{H}_2\text{O}$, were obtained by precipitation from aqueous solution containing thorium nitrate and sodium or potassium phosphates [95,96]. Both compounds were converted into $\text{NaThO}(\text{PO}_4)$ and $\text{KThO}(\text{PO}_4)$ at about 600°C .

Kojić-Prodić et al. [97] synthesized and characterized a compound of $\text{Na}_6[\text{Th}(\text{PO}_4)\text{P}_2\text{O}_7]_2$ formula crystallizing in triclinic symmetry. Its interesting structure (Fig. 9) is based on ThO_9 dimer polyhedra, where thorium atoms are coordinated by oxygen atoms from four P_2O_7 and three PO_4 groups. The dimer units are linked by two PO_4 tetrahedra. Sodium atoms have an octahedral environment.

Finally, thorium and uranium phosphates of formula $(\text{ThO})_3(\text{PO}_4)_2$ and $(\text{UO})_3(\text{PO}_4)_2$ [22] after accurate

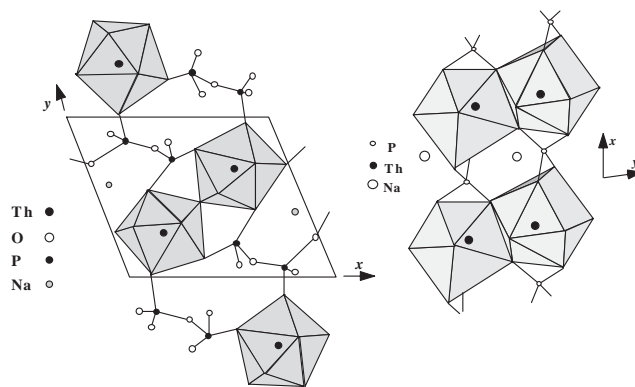


Fig. 9. Projection of the structure of $\text{Na}_6[\text{Th}(\text{PO}_4)\text{P}_2\text{O}_7]_2$ [97]: $a = 8.734 \text{ \AA}$, $b = 8.931 \text{ \AA}$, $c = 6.468 \text{ \AA}$, $\alpha = 93.33^\circ$, $\beta = 108.29^\circ$, and $\gamma = 110.10^\circ$.

Table 9

Tetravalent cation phosphates compounds and derivatives

Compound formula	Derivative compounds
$\text{M}(\text{H}_2\text{PO}_4)_4^{\text{a}}$	$\text{M}(\text{PO}_3)_4^{\text{a}}$, $\text{M}_8\text{Zr}(\text{PO}_4)_4$
$\text{M}(\text{HPO}_4)_2^{\text{a}}$	$\text{MP}_2\text{O}_7^{\text{a}}$, $\text{MM}(\text{PO}_4)_2$, $\text{M}_2\text{M}(\text{PO}_4)_2$,
$\text{M}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2$	$\text{M}_3\text{M}(\text{PO}_4)_3$
$\text{M}_2(\text{PO}_4)_2(\text{HPO}_4)$	$\text{M}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$, $\text{MM}_2(\text{PO}_4)_3$, $\text{M}_{0.5}\text{M}_2(\text{PO}_4)_3$
$\text{M}(\text{H}_2\text{PO}_4)_4 \cdot 2\text{H}_3\text{PO}_4^{\text{a}}$	$\text{M}_7\text{Th}(\text{PO}_4)_6$, $\text{M}_{14}\text{Zr}(\text{PO}_4)_6$
$\text{M}(\text{OH})\text{PO}_4$	$\text{M}_2\text{O}(\text{PO}_4)_2$, MXPO_4

^aSee Ref. [5]; M , monovalent or divalent cation; X , halogenide ion.

examination of the XRD patterns recorded seem to correspond to polyphase systems.

5. Conclusions

Phosphates of tetravalent elements were intensively investigated in the last 50 years. In this paper a review of tetravalent actinide phosphates referred in the literature is presented. Their crystal structures and some chemical properties are compared to that of non-actinide elements.

A classification of tetravalent cation M^{4+} phosphates based on the framework $[(\text{M})_m(\text{A}^q)_p]^k$ with $k = 4m + pq$ is proposed [5]. In this framework, A is an anion (simple or condensed) derived from phosphoric acid H_3PO_4 .

As general observation, it can be concluded that most of the tetravalent cation phosphates are derivatives of dihydrogenphosphates, hydrogenphosphates, or hydroxide phosphates, whatever the chemical way of synthesis. They result from condensation reaction or replacement of the proton by a monovalent or divalent cation (Table 9).

The interest to tetravalent cation phosphates is due to the special properties and/or potential application for several of them. For example, phosphate–hydrogenphosphate

derivatives $M\text{Th}_2(\text{PO}_4)_3$ ($M = \text{Na}, \text{K}, \text{Ag}$) show ferroelectric properties [75–77,98], $\text{NaTh}_2(\text{PO}_4)_3$ and $\text{AgTh}_2(\text{PO}_4)_3$ also behave as solid ionic conductors [98]. The $\text{CuTh}_2(\text{PO}_4)_3$ - or copper-activated lithium and silver dithorium phosphates have pronounced fluorescence effect [72]. Thorium phosphate–diphosphate [45–47,50] was already proposed as ceramic matrix for the long-term storage of plutonium(IV) and neptunium(IV). It appears as a good host matrix for the immobilization of long-lived radionuclides needed in new ways of waste management, especially for tetravalent actinides [15,36,44–50]. Other radionuclides [36], e.g., fission products such as cesium, strontium, or lanthanide isotopes could be added to this matrix leading to the $\text{CsTh}_2(\text{PO}_4)_3$, $\text{SrTh}(\text{PO}_4)_2$, and $M\text{PO}_4$ forms [99,100]. $\text{NaZr}_2(\text{PO}_4)_3$ [96,101–103] or $\text{NaTi}_2(\text{PO}_4)_3$ [104] where sodium was partly replaced by cesium or strontium are also proposed for some radionuclide immobilization in the ceramic form.

NZP, the first NASICON material and its analogues (sodium replaced by Li, K, etc.) are solid ionic conductors [89]. NZP ceramics and its derivatives [86,87,89,105] as well ceramics of the thorium phosphate–diphosphate exhibit low thermal expansion materials [106].

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