



Synthesis, Raman and Rietveld analysis of thorium diphosphate

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ABSTRACT

We report the synthesis of thorium diphosphate ThP_2O_7 and its study by Raman spectroscopy and Rietveld analysis. This compound has been found to be closely related to the zirconium diphosphate type, with space group $Pa-3$ and $a = 8.7601(3)\text{Å}$. No superstructure was observed. The metastability of ThP_2O_7 appears to stem from the six-fold oxygen environment of Th^{IV} , a unique case in the structural chemistry of this cation.

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1. Introduction

Cubic $M^{\text{IV}}\text{P}_2\text{O}_7$ diphosphates have been known since the works of Levi and Peyronel in the 1930s [1] to form a wide family of structurally-related compounds. This relationship is all the more remarkable and unusual in the chemistry of phosphates that the M^{IV} cations hosted by this framework show considerable differences in size (ionic radii in six-fold coordination) [2]: $M^{\text{IV}} = \text{Si}$ (0.40 Å) [1,3,4], Ge (0.53 Å) [5–7], Ti (0.605 Å) [8,9], Mo (0.65 Å) [10], W (0.66 Å) [11], Sn (0.69 Å) [12], Hf (0.71 Å) [1], Zr (0.72 Å) [1,13], Pb (0.775 Å) [14], Ce (0.87 Å) [15], U (0.89 Å) [16] and Th (0.94 Å) [17]. The so-called ZrP_2O_7 prototype structure (space group $Pa-3$, $Z = 4$) is built of corner-connected ZrO_6 octahedra and P_2O_7 units, with zirconium and bridging oxygen of the diphosphate occupying, respectively, the Cl and Na sites of a rock salt array.

Some of these compounds, as for Si [4], Ti [9], Zr [18] and Ce [19], show a $3 \times 3 \times 3$ cubic superstructure which origin, according to some of these authors, can be found in the ordering of bent $\text{P}-\text{O}-\text{P}$ linkages. However, very slight distortions of the prototype cell were also recently observed for Zr [20] (orthorhombic) and Ce [21] (triclinic). At last, the so-called orthorhombic varieties of ThP_2O_7 and UP_2O_7 are merely a misformulation for $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ [22].

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The thorium phosphates, until recently scarcely investigated, have become of considerable interest because of their attractive properties as crystalline matrices for the immobilization of minor actinides coming from the spent fuel reprocessing [23–29]. Otherwise, many $M^{\text{IV}}\text{P}_2\text{O}_7$ phosphates and derivatives [30–32] have shown remarkable low or negative thermal expansion, especially for big M^{IV} cations. As the end member of this family, ThP_2O_7 may be of high interest regarding this property.

To this date, ThP_2O_7 was only known through the crystallographic works of Burdese et al. [17] in the 1960s, but, as will be seen thereafter, the structural model proposed by these authors is incorrect and cannot support further investigation on the compound. Therefore, in the present work, we will revisit the preparation, Raman spectrum and crystal structure of this rare compound.

2. Experimental

2.1. Synthesis

At variance with the other $M^{\text{IV}}\text{P}_2\text{O}_7$ (such as Pu , Np or U -based compounds), that can be easily prepared by solid-state reaction, it seems that the wet chemistry is the only route that can lead to pure ThP_2O_7 . Similarly, several attempts based on the direct precipitation and evaporation of a mixture of thorium nitrate and concentrated phosphate acid solutions in the mole ratio 1/2 always led to a mixture of ThP_2O_7 and $\text{Th}_2(\text{PO}_4)(\text{P}_3\text{O}_{10})$ after

Table 1

EPMA results for α -ThP₂O₇ obtained after heating at 800 °C (average of 10 measurements)

	Th (wt%)	P (wt%)	PO ₄ /Th
Calculated	57.1	15.3	2
Experimental	56.1 ± 0.9	15.8 ± 0.4	2.11 ± 0.09

heating above 700 °C. So, the preparation of thorium diphosphate was performed starting from the precipitated thorium hydrogenphosphate Th(HPO₄)₂ hydrate [33,34]. A stoichiometric mixture of Th(NO₃)₄, 5 H₂O and (NH₄)(H₂PO₄) was placed in a PTFE close container, then heated on a sand bath at 150 °C for one week. The precipitate obtained was separated from the supernatant by centrifugation, washed several times with deionized water and ethanol, then finally dried in an oven. The powder obtained appeared to be poorly crystallized and was turned into the well-crystallized ThP₂O₇ after heating at 800 °C for 10 h. The chemical composition of the samples was checked through electron probe microanalysis (EPMA) using a Cameca SX50 apparatus with an acceleration voltage of 15 kV and a current of 10 nA. ThO₂ (M_α ray of thorium) and SmPO₄ (K_α ray of phosphorus) were used as calibration standards while the average of 10 measurements was considered. All the samples appeared homogeneous and single phase while the elementary weight percents was found to be consistent with that expected for ThP₂O₇ (Table 1).

ThP₂O₇ was finally found to be thermally stable up to around 1100 °C, which appears to be in good agreement with the data reported in the literature for other M^{IV}P₂O₇ diphosphates. At this temperature, it transforms into the thorium polytrioxophosphate Th₂(PO₄)(P₃O₁₀), formerly known as β-ThP₂O₇ [22]. When heating above 1250 °C, this latter turns into the more stable thorium phosphate-diphosphate (β-Th₄(PO₄)₄P₂O₇). β-TPD can also be obtained by heating directly ThP₂O₇ at this temperature, the formation of Th₂(PO₄)(P₃O₁₀) being avoided probably due to kinetic considerations.

2.2. Raman

The samples were characterized through μ-Raman spectroscopy using a Jobin–Yvon Aramis microspectrometer equipped with a He–Ne laser working at 632.8 nm with a power of 17 mW. The laser beam was focused on the sample with an Olympus BX41 microscope.

The spectrum of ThP₂O₇ recorded at room temperature (Fig. 1) matches well with that reported in the literature for various M^{IV}P₂O₇ cubic diphosphates (including M^{IV} = Ti, Zr, Ce and U) [22,35–39] or M^{III}N^{III}P₂O₇ [40] and M^IN^{III}P₂O₇ [41,42] double diphosphates. On this basis, the two intense bands located around 1072 and 1119 cm⁻¹ could be assigned to the symmetric ν_S (P–O) and anti-symmetric ν_{AS} (P–O) stretching modes of the P–O bond, respectively. The ν_{AS} (P–O–P) and ν_S (P–O–P) modes, corresponding to the stretching vibrations of the P–O–P bridge were then observed at 971 and 735 cm⁻¹, respectively. This assignment, usually reported for diphosphates, could appear rather doubtful regarding phosphate compounds Raman data: for these solids, the band observed at 1072 cm⁻¹ is mainly assumed to belong to the anti-symmetric mode while the ν_S (P–O) band overlaps with the ν_{AS} (P–O–P) vibration [43–45]. According to several authors, this difference could be induced by the distorted nature of the PO₄ tetrahedra in the condensed P₂O₇ entity, hence to the shorter P–O distance in PO₃ compared to PO₄ [46,47]. Moreover, the observation of both symmetric and anti-symmetric stretching vibrations accounts for a bent P–O–P linkage in the ThP₂O₇

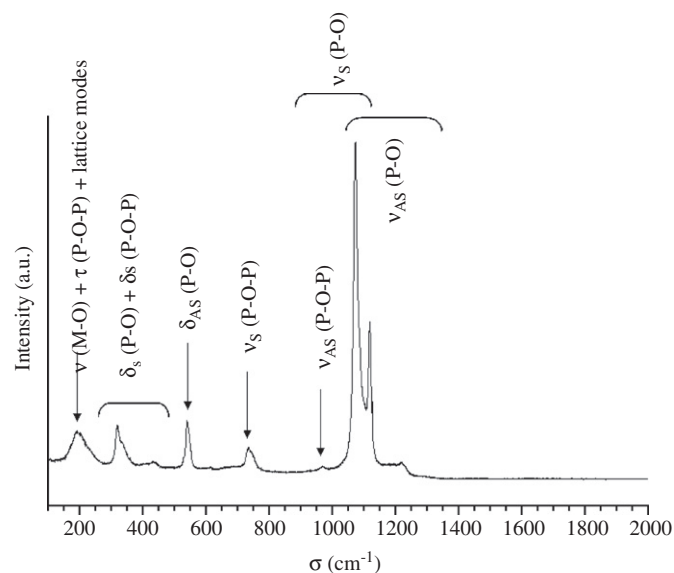


Fig. 1. μ-Raman spectrum of ThP₂O₇ recorded at room temperature.

structure. Indeed, in the case of a linear P–O–P bridge, only the symmetric vibration should be Raman active [48].

The sharp band located around 540 cm⁻¹ was associated to the anti-symmetric deformation of the P–O bond δ_{AS} (P–O) while vibration bands observed in the 300–530 cm⁻¹ range were assigned to the symmetric deformation modes of both P–O bonds and P–O–P bridge. Finally, the broad band recorded slightly below 200 cm⁻¹ probably results from the overlap of the stretching ν (M–O) vibration with the torsional τ (P–O–P) and the lattice modes.

It is worth to note that no vibration band was detected in the 900–930 cm⁻¹ zone, which is usually characteristic of hydrogenphosphate entities (P–O–(H) groups) [49]. The conversion of Th(HPO₄)₂ into ThP₂O₇ was thus considered to be complete after heating above 800 °C.

2.3. Microdiffraction

Prior to the structural analysis of ThP₂O₇, we tried to observe a possible supercell. Finely ground powder was dispersed in hexane by ultrasound and mounted on a carbon-coated microgrid. The microdiffraction measurements were performed on a JEOL TEM 100 CX III ultra-high resolution microscope with tungsten filament, at an acceleration voltage of 100 kV. Gold nanospheres were used as standard for the measurement of the reciprocal distances. All electron diffraction patterns taken on different grains only show the reciprocal cell of the prototype form, without any evidence of superstructure.

2.4. Rietveld analysis

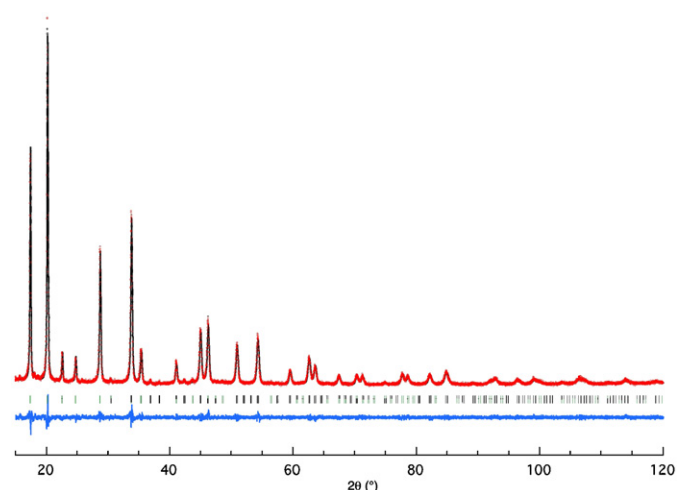
The powder diffraction pattern of ThP₂O₇ was recorded following conditions reported in Table 2. The compound appeared free of impurities. Consistently with the electron microdiffraction results, even a careful observation of the background did not allow to evidence the existence of peaks of a multiple cell parameter; neither did a Le Bail (profile-matching) analysis.

The diffracted intensities extracted with the Fullprof program [50] were used to compute Patterson maps, from which the thorium atom was found to occupy the 4a site. Fourier-difference syntheses were used to find the position of the other atoms. Finally, the structure was refined without constraints using

Table 2
Data collection, refinement conditions and crystallographic data

Data collection	
Formula	ThP ₂ O ₇
Temperature	293 K
Apparatus	Siemens D5000
Radiation, λ, monochromator	CuKα, 1.54178 Å, graphite (001) (rear)
Scan limits, step	14.00 < 2θ < 120.00°, 0.01°
Observed reflections	186
Refinement conditions	
I-dependent/profile parameters	10/8
Conventional reliability factors ^a	R _p = 0.068 R _{wp} = 0.088 R _{bragg} = 0.032 R _e = 0.076 R _{exp} = 0.019 χ ² = 1.25
Crystallographic data	
System, space group	Cubic, Pa-3 (n° 205)
Cell parameter, volume	a = 8.7601(3) Å V = 672.25(3) Å ³
Formula weight, Z, calc. density	405.98 g mol ⁻¹ , 4, 10.03

$$^a R_p = \frac{\sum |y_o - y_c|}{\sum y_o}; R_{wp} \text{ (id., weighted)}; R_{bragg} = \frac{\sum |f_o - I_c|}{\sum f_o}; R_{exp} = \frac{((n-p)/\sum w y_o^2)^{1/2}}{\sum (f_o)^{1/2}}; R_e = \frac{(\sum (f_o)^{1/2} - (f_c)^{1/2}) / \sum (f_o)^{1/2}}{\sum (f_o)^{1/2}}; \chi^2 = (R_{wp}/R_{exp})^2.$$

**Fig. 2.** Rietveld plot for ThP₂O₇: I_{obs} (circles), I_{cal} (solid), Bragg positions (bars) and $I_{obs} - I_{cal}$ (solid, lower).**Table 3**
Fractional atomic coordinates and thermal parameters (Å²)

Atom	Site	x	y	z	B_{iso}^a
Th	4a	0	0	0	3.03 (2)
P	8c	0.4016 (3)	x	x	3.6 (1)
O (1)	4b	1/2	1/2	1/2	12.4 (5)
O (2)	24d	0.2506 (5)	0.5551 (9)	-0.0519 (9)	7.8 (3)

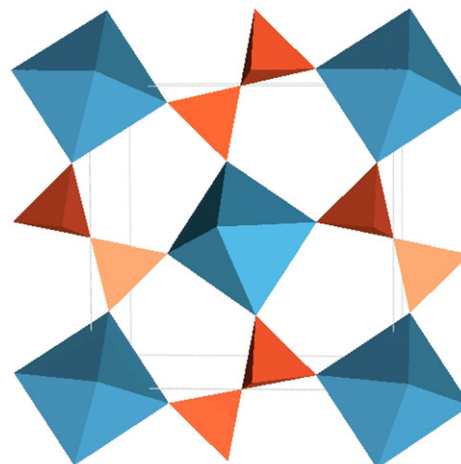
^a B_{eq} for Th.

Fullprof. Conditions and final parameters are reported in Table 2. Fig. 2 shows the final Rietveld plot. Atomic positions are given in Table 3 and cation–anion distances in Table 4.

The so-obtained structure (Fig. 3) is analogous to those of the other $M^{IV}P_2O_7$ compounds. It features thorium in an octahedral environment with all $d_{Th-O} = 2.28 \text{ \AA}$ (bond valence sum is 4.5 valence units [51]), more realistic than that found by Burdese et al. [17]: all distances $d_{Th-O} = 2.17 \text{ \AA}$ (bvs = 6.0 vu).

Table 4
Cation–anion distances (Å)

Th–O:	2.283 (5) Å (6x)
P–O (1):	1.493 (3) Å (1x)
P–O (2):	1.445 (6) Å (3x)

**Fig. 3.** Crystal structure of ThP₂O₇, made of ThO₆ octahedra and P₂O₇ ditetrahedra (only one polyhedra layer is shown).

3. Discussion

3.1. Thorium coordination and thermal stability

This study allows to confirm that ThP₂O₇ actually belongs to the ZrP₂O₇ structural family, despite the size of the tetravalent cation, commonly considered as unfit for octahedral environment. Indeed, according to the ICS Data Base [52], there is no other known compound featuring this cation in a six-fold oxygen environment (it usually prefers an eight-fold (65%) or higher (9–12: 32%) coordination). A parallel can be drawn with the recently reported structure of Th₂O(PO₄)₂ [53], obtained by water loss from the ThOHPO₄ precursor: the condensation of two OH vertices of the ThO₆(OH)₂ polyhedron into a single O generates an uncommon Th₇ polyhedron. Likewise, despite we still ignore the crystal structure of the Th(HPO₄)₂·xH₂O precursor, we can suppose that it hosts Th in a bigger (hydrated) polyhedron than the title compound. So, the analysis of the thermal transformation of these two thorium phosphates explains why they can only be achieved through a topotactic condensation. By this way, the structure of the precursor can be preserved, whereas in both cases, the solid-state route fails to elaborate the expected compound.

The unusual coordination of thorium in these compounds can be also the main reason of their rather low temperature of irreversible decomposition (1100 °C for ThP₂O₇, 1050 °C for Th₂O(PO₄)₂). Both finally yield β-thorium phosphate-diphosphate (β-TPD), along with ThO₂ concerning the latter (Th^{IV} in eight-fold coordination). On the contrary, β-TPD forms by either dry or wet chemistry routes [49]. Following the latter route, the thermal condensation of the precursor also gives a poorly stable intermediate form (α-TPD) involving seven-fold thorium IV cations, but at variance with ThP₂O₇ and Th₂O(PO₄)₂, the structure eventually collapses (950 °C) without any decomposition to achieve eight-fold coordination, thus improving its thermal stability (up to 1350 °C) [49,54]. The thermal evolutions of these different forms of thorium phosphates are summarized on Fig. 4.

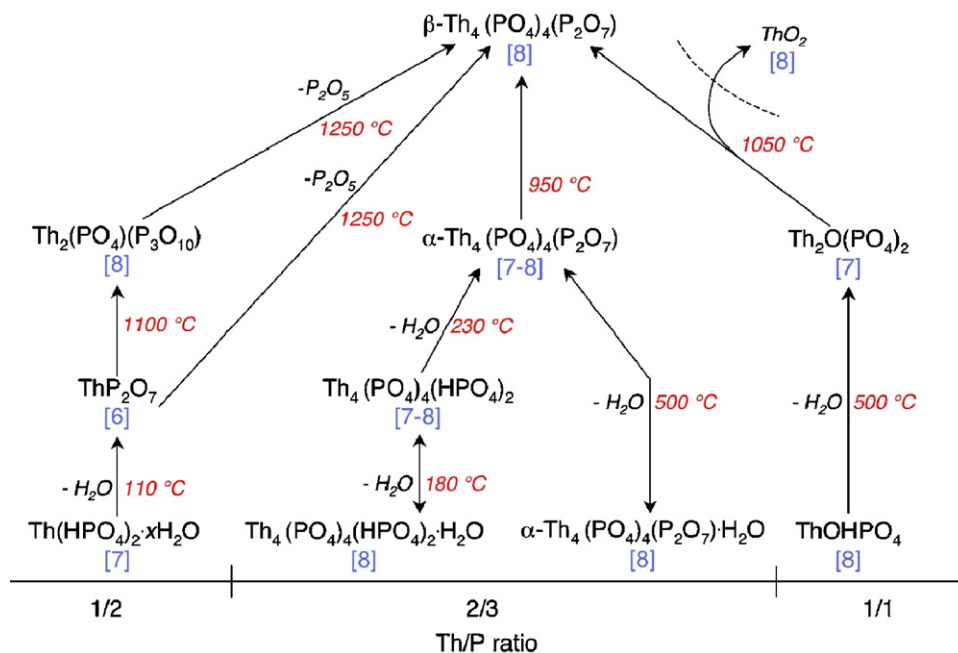


Fig. 4. Thermal evolution of the thorium phosphates, with coordination numbers for Th^{IV} bracketed.

Similarly, the so-called thorium IV divanadate is the atypical end member of the $M^{IV}V_2O_7$ family: whereas these vanadates are isotopic with ZrP_2O_7 for $M = Zr$ [55] and Hf [56], the thorium compound is made of both independent and chain-connected VO_4 tetrahedra and should rather be formulated $ThVO_3VO_4$ [57]. Such an array allows Th^{IV} to build eight- and nine-fold polyhedra, a more suitable environment than the octahedron of the classical divanadate form.

3.2. A possible ordering?

As soon as in the early 70s, Laud and Hummel observed that ThP_2O_7 first expands on heating, then contracts from about 200 °C on [58]. Since then, similar inversions of thermal expansion have been observed in other MX_2O_7 compounds and explained by a phase transition driven by the disordering of the X_2O_7 units ($X-O-X$ linkages, bent at low temperature, tend to 180° on heating).

The $3 \times 3 \times 3$ superstructure observed in ZrP_2O_7 [18] is very faint: all reflections with h, k or $l \neq 3n$ have intensities less than 1% (JCPDS file 01-086-0781), because the zirconium atoms ($Z = 40$) remain close to the prototype position (all $\delta x/y/z < 0.006$, supercell coordinates). In such a structural configuration, the overwhelming diffusion factor of the thorium atom ($Z = 90$) wouldn't allow to observe any ordering of the diphosphate groups.

On the other hand, the ordered model suggested for ZrP_2O_7 [20] and CeP_2O_7 [21] account for a very faint orthorhombic or triclinic distortions, with deviations from the prototype cubic cell less than 0.01 Å for parameters a, b, c and 0.2° for α, β, γ in the latter case. Except by resorting to neutron and/or synchrotron radiation, as these authors did, those variations would be even more difficult to observe.

Our failure to evidence a superstructure or a cell distortion does not mean the absence of an order in ThP_2O_7 , but for the previous reasons, the resolution of this structure using X-ray diffraction can only be performed on the basis of the prototype cell.

This simplified model, by ignoring the bending of the PO_4 tetrahedra, leads logically to Th–O and P–O distances somewhat shorter than the classical ones (usually 1.60 and 1.53 Å for

bridging and non-bridging d_{P-O}) and abnormally high thermal factors for the oxygens, especially for O(1).

Considering the Lazarev's relationship [59]:

$$\Delta = (v_{AS}(POP) - v_S(POP)) / (v_{AS}(POP) + v_S(POP)) = f(\alpha)$$

which was verified for numerous disilicates, digermanates and diphosphates [60], and the plots reported by Rulmont et al. [61], the value of the POP angle (α) could be deduced from the wavenumbers of these vibrations. Once integrated into these plots, the Δv and Δ values obtained from the Raman spectrum of ThP_2O_7 ($v_S(POP) = 735 \text{ cm}^{-1}$; $v_{AS}(POP) = 971 \text{ cm}^{-1}$), account for a mean P–O(1)–P angle around 142°. Considering the usual bridging P–O length (1.60 Å) and the observed P...P distance (2.99 Å), we obtain an angle of 138°, in good agreement with the spectroscopic model. As a comparison, the six independent P–O–P angles in ZrP_2O_7 range from 134 to 180° [18].

A second cause of delocalization of the atoms and abnormally short interatomic distances lies in the dynamics of the network: corner-connected polyhedra are known to sustain thermal rocking, causing low or negative expansion phenomena in other $M^{IV}X_2O_7$ compounds [30]. Further studies will be intended to clear up this question.

4. Conclusion

At variance with the other $M^{IV}P_2O_7$, ThP_2O_7 can be obtained only by wet route and topotactical condensation. This results in a very uncommon six-fold coordination of Th^{IV}, responsible for the metastability of the compound, a major flaw regarding its intended use as a host matrix for actinides radwastes. As a rule of thumb, it appears that compounds in which Th^{IV} has less than eight oxygen neighbors are of limited thermal stability. Nevertheless, as the end-member of the $M^{IV}P_2O_7$ family, the title compound could be highly interesting regarding its thermal expansion, to which a further study will be dedicated. The issue of a possible superstructure could be indirectly solved consecutively.

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