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Triclinic—Cubic Phase Transition and Negative Expansion in the Actinide IV (Th, U, Np, Pu) Diphosphates

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ABSTRACT: The AnP2O7 diphosphates (An = Th, U, Np, Pu) have been synthetized by various routes depending on the stability of the AnIV cation and its suitability for the unusual octahedral environment. Synchrotron and X-ray diffraction, thermal analysis, Raman spectroscopy, and 31P nuclear magnetic resonance reveal them as a new family of diphosphates which probably includes the recently studied CeP2O7. Although they adopt at high temperature the same cubic archetypal cell as the other known MP2O7 diphosphates, they differ by a very faint triclinic distortion at room temperature that results from an ordering of the P2O7 units, as shown using high-resolution synchrotron diffraction for UP2O7. The uncommon triclinic—cubic phase transition is first order, and its temperature is very sensitive to the ionic radius of AnIV. The conflicting effects which control the thermal variations of the P−O−P angle are responsible for a strong expansion of the cell followed by a contraction at higher temperature. This inversion of expansion occurs at a temperature significantly higher than the phase transition, at variance with the parent compounds with smaller MIV cations in which the two phenomena coincide. As shown by various approaches, the P−O6−P linkage remains bent in the cubic form.

INTRODUCTION

In 1935, Levi and Peyronel revealed the existence of a wide family of MIVP2O7 diphosphates, whose structure can be thought of as a rock-salt-like array of P2O7 units and MIV cations in octahedral coordination.1,2 Since then an abundant literature has established the ability of this structure to host nearly any tetravalent cation, including some which almost never occur in a six-oxygen coordination like the two end members: Si4+ and Th4+.3,4 Despite the huge difference in size (r(SiIV) = 0.40 Å; r(ThIV) = 0.94 Å, coord. VI6). In the early works the structure at room temperature was believed to be cubic (space group Pm-3, Z = 4, a ≈ 8 Å), but since the late 1960s, progress in diffraction techniques and other analytical methods have revealed superstructures for M = Si,3,5,7,8,9 Th,10,11 Ge,12,13 Sn,12 Ce,13 resulting from an ordering of the bent P2O7 units. In this family, ZrP2O7 offers perhaps one of the most remarkable examples of a long-debated crystal structure. After Hagman et al. (1969)14 and Chaunac (1971),15 confirmed Levi’s model, Khosrovani et al. proposed in 1996 a 3 × 3 × 3 superstructure, still cubic, exhibiting unusual P−O−P angles of 180°.16 Ten years later, Birkedal et al. and Stinton et al.17 demonstrated that the superstructured cell was orthorhombic with all the P−O−P linkages bent at 141–149°. However, despite the validity of Levi’s model at room temperature often being questioned, most authors agree about the existence of this simple cubic form at high temperature,13,19,20 which will be referred to in the following as the “archetype”.

Although less known than the other members of the family, the AnP2O7 (An = Th, U, Np, Pu) diphosphates have been studied during the past two decades in the frame of the exploration of the AnO2−P2O5 systems21–23 to evaluate the interest of phosphate-based matrices in the back-end of the nuclear fuel cycle.24–28 First considered as potential host matrices for the long-term minor actinides’ immobilization, these diphosphates showed two critical structural weaknesses, i.e., the presence of a bridging oxygen (O3 in the O3P−O6−PO3 unit) prone to protonation and the limited thermal stability of the big actinide cations in octahedral coordination.29 Besides,
development of spent nuclear fuel reprocessing led to the reinvestigation of the chemistry of actinide phosphates as products of the reaction with tributyl phosphate. However, available data remain limited because of the radioactivity hazards which restrict considerably both their availability and their use.

The actinide diphosphates also show several points of fundamental interest. From a structural point of view, the presence of high-radius cations like UIV and particularly ThIV in a 6-fold oxygen environment stable up to about 1000 °C is an exceptional feature from which unusual physical properties can be expected, like thermal expansion. In contrast to the other diphosphates, the title compounds are still considered to adopt a simple cubic model.25–32 However, routine X-ray powder diffraction performed during our preliminary work showed anomalous peak profiles which suggested a complex and still unknown modification of the archetype. Synchrotron diffraction has been used to address this point.

In previous work, the room-temperature forms, supposedly cubic, were generally referred to as “α” to be distinguished from a would-be orthorhombic high-temperature variety termed “β.”33–35 The transition between both phases was reported to be reversible between 800 and 1000 °C for ThP2O7 and near 750 °C for UP2O7.35 However, despite being similar in composition to a diphosphate, the β form recently appeared to correspond to an isomeric Ar12(P2O7)(P2O10) instead.36 Moreover, the symmetry of the room-temperature form of the true AnP2O7 diphosphates appears questionable. Thus, this misleading terminology will be replaced in the present work by naming the different forms after their crystal system, for example, c-UP2O7 for the cubic one.

Indeed, nothing was known about a possible polymorphism in spite of two early dilatometric experiments made several decades ago on ThP2O7,8 and UP2O7,37 ceramics, which demonstrated an inversion of the thermal expansion. Now, such a phenomenon, one of the most popular topics related to the other MP2O7,19,20,38 is commonly associated to a probable phase transition to the archetype form. However, White et al., studying recently CeP2O7, suggested that this transition occurred below the inversion temperature.19 In the present work, a wide range of analytical methods was used in order to contribute to this debate by measuring precisely the thermal expansion of the AnP2O7 and characterizing the evolution of their crystal structure.

■ EXPERIMENTAL SECTION

Owing to the toxicity and/or low radioactivity of the title compounds, all experiments except NMR and synchrotron diffraction on samples containing thorium or depleted uranium were carried out with special facilities in gloveboxes for radionuclides at ITU and ICSM.

Synthesis. Powder samples of the compounds were obtained following different synthesis routes adapted to both the stability of the AnIV cation in the octahedral environment and its tendency to oxidize or reduce. All actinide reagents were previously laboratory prepared.

As stated previously, pure ThP2O7 seems difficult to obtain by the solid state route, which yields Th(HPO4)2(P2O7), or by precipitation and evaporation (aqueous thorium nitrate and concentrated acid phosphate solution in 1:2 proportions), which leads to a mixture of Th2P2O7 and Th(HPO4)(P2O10).29 The two unwanted products, which have no known homologues with other AnIV cations, offer an eight-oxygen coordination for Th4+ in ThP2O7, undoubtedly more suitable than the 6-fold one in ThP2O7, which is indeed a unique case in the chemistry of thorium. Thus, Th(HPO4)2·2H2O was first synthesized from a stoichiometric mixture of Th(NO3)4·5H2O and NH4H2PO4 (Alfa Aesar, 99%), placed in a PTFE closed container, and heated on a sand bath at 150 °C for 1 week.22 The precipitate was recovered by centrifugation, washed several times with deionized water and ethanol, dried in an oven, and finally heated at 800 °C for 10 h.

PuIV, contrary to ThIV, UIV, and NpIV, readily reduces into PuIII, especially when bonded to phosphate to form the monazite-like PuP2O7, so the synthesis of PuP2O7 by solid state reaction from PuO2 and NH4H2PO4 at various temperatures led to significant amounts of PuP2O7 impurities. The synthesis was performed by wet chemistry in a similar way to that proposed by De et al. for ThP2O7.40 A 239Pu(NO3)4·32Pu(NO3)5 solution (115.3 mg.ml−1) from reactor-grade plutonium was added slowly to a 4-fold excess of 0.74 M H3PO4 in a Teflon beaker and held under a watch glass at ~80 °C for 4 h on a magnetic stirrer. Further treatments were analogous to those for ThP2O7. The powder obtained appeared inhomogeneous with respect to color: greenish on top and gray at the bottom. These fractions were collected separately as far as possible but eventually appeared similar by XRD. Minor impurities were observed in both, which might be plutonium homologues of those observed for the thorium compound.29

NpP2O7 was synthesized by solid state reactions using stoichiometric amounts of high-purity 237NpO2 and (NH4)2HPO4, placed in a PTFE closed container, and heated on a Teflon beaker and held under a watch glass at ~80 °C for 4 h on a magnetic stirrer. Further treatments were analogous to those for ThP2O7. The powder obtained appeared inhomogeneous with respect to color: greenish on top and gray at the bottom. These fractions were collected separately as far as possible but eventually appeared similar by XRD. Minor impurities were observed in both, which might be plutonium homologues of those observed for the thorium compound.29

Owing to their sensitivity to moisture, all samples were stored under dry N2 in gloveboxes.

Synchrotron Powder Diffraction. A 4 mg amount of UP2O7, poweder was sealed in a glass capillary (ø = 0.5 mm) and analyzed on the high-resolution diffractometer of the ID31 line of the European Synchrotron Radiation Facility, Grenoble, France. For safety reasons, the high-resolution diffractometer of the ID31 line of the European Synchrotron Radiation Facility, Grenoble, France, where it was synthesized by heating uranyl monophosphate with a stoichiometric amount of P2O10 at about 650 °C in a closed silica tube, as described in detail by Cordfunke et al.41

Owing to their sensitivity to moisture, all samples were stored under dry N2 in gloveboxes.

Table 1. Main Acquisition and Refinement Parameters and Crystallographic Data for t- and c-UP2O7

<table>
<thead>
<tr>
<th>form</th>
<th>t-UP2O7</th>
<th>c-UP2O7</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
<td>25 °C</td>
<td>600 °C</td>
</tr>
<tr>
<td>diffractometer</td>
<td>ESRF ID31</td>
<td>Siemens D8</td>
</tr>
<tr>
<td>wavelength, monochromator</td>
<td>0.35409 Å, Si (111)</td>
<td>1.5405 Å, Ge (111)</td>
</tr>
<tr>
<td>2θ scan range, step</td>
<td>2.3°–30°, 0.001°</td>
<td>15°–118°, 0.007°</td>
</tr>
<tr>
<td>obsd reflns</td>
<td>10627</td>
<td>164</td>
</tr>
<tr>
<td>l-dependent, profile parameters</td>
<td>125, 13</td>
<td>11, 6</td>
</tr>
</tbody>
</table>

conventional reliability factors

| Rint | 0.078 | Rint |
| Rexp | 0.11 | Rexp |
| Rint | 0.037 | Rint |
| Rint | 0.065 | Rint |
| Rint | 0.093 | Rint |

χ2 = 2.8

χ2 = 4.6

cryst syst, space group

tetragonal, P1 (no. 1) | cubic, Pa3 (no. 205)
cell params*, volume

| a = 6.6180(2) Å | a = 8.6387(3) Å |
| b = 6.6326(3) Å | V = 644.69(7) Å3 |
| c = 8.6349(2) Å | V = 644.69(7) Å3 |
很久之前出现了β-UP2O7的可能，但最终似乎相似于XRD。少量杂质出现于低温范围,尤其是当磷酸键形成单斜晶系时。

To take into account possible systematic errors, esd’s of the refinement program were multiplied by 10.
High-Temperature X-ray Powder Diffraction. Diffraction experiments above room temperature (HTXRD) were carried out under He flow on a conventional diffractometer equipped with a heating platinum holder. Temperature was calibrated according to the transition point of UP₂O₇, measured by DSC. Samples were studied at various temperatures from room temperature to 800 °C (500 °C for PuP₂O₇ because of the reduction of PuIV under He that led to formation of PuIIIPO₄) with counting times and scan ranges depending on whether the pattern was to be used for measuring the cell parameters and peak width or refine the crystal structure (only in the cubic model). See Table 1 for experimental conditions in the latter case. A complete series of long XRD measurements was carried out on ThP₂O₇ in order to follow the thermal evolution of the P–P and Th–P distances.

Differential Scanning Calorimetry. DSC measurements of UP₂O₇ were performed under He flow at a heating/cooling rate of 15 °C min⁻¹ on a Netzsch STA 409 A Cell analyzer.

³¹P Nuclear Magnetic Resonance. ³¹P NMR experiments on UP₂O₇ were conducted using a Bruker 400 MHz spectrometer operating at a Larmor frequency of 161.97 MHz. The sample was packed in a 4 mm zirconia rotor and spun at a magic-angle spinning (MAS) rate of 9 kHz. ³¹P chemical shifts were referenced to the signal from H₃PO₄ (80% aqueous solution) at 0 ppm. Temperature calibration was made prior to experiments using the temperature dependence of the ²⁰⁷P resonance of PbNO₃. Correction factors resulted in a temperature increase of less than 5 °C. All temperatures given in the following have been corrected taking into account the previous observations.

High-Temperature Micro-Raman Spectroscopy. HT-µ-Raman spectra of ThP₂O₇ and UP₂O₇ were collected with a Horiba-Jobin Yvon Aramis apparatus equipped with an edge filter and using a Nd:YAG laser (λ = 532 nm, 45 mW). Samples were placed in a platinum crucible and brought to the chosen temperature at a rate of 5 °C min⁻¹ on a Netzsch STA 409 A Cell analyzer. Temperature was calibrated according to the transition point of UP₂O₇, measured by DSC. Samples were placed in a 4 mm zirconia rotor and spun at a magic-angle spinning (MAS) rate of 9 kHz. HT-µ-Raman spectra were then recorded after a few minutes of thermal stabilization. The laser beam was focused on the sample using an Olympus BX41 microscope, resulting in a spot area of about 1 mm². Several locations were investigated at the surface of each sample, usually considering a dwell time of 30 s and an average of 4 scans. Band areas were finally determined from a Gaussian–Lorenzian fitting using the Peakfit 4.12 software.

RESULTS AND DISCUSSION

Crystal Structures of t- and c-UP₂O₇. The search for the crystal unit cell in the low-temperature form was initiated by careful examination of the synchrotron diffraction pattern taken at −173 °C, which exhibits the strongest deviation from the cubic model. No other peaks except those corresponding to the archetype form confirm the nearly cubic geometry that was not detected in previous studies on UP₂O₇⁵,3⁰ based only on conventional XRD. The final positions of the cations are very close to those of the cubic model (ΔxO₋O₁, Δy, Δz ≤ 0.017(5) Å for uranium and ΔxO₋O₁, Δy, Δz ≤ 0.138(6) Å for phosphorus), so the faint triclinic distortion of the cell...
results in a splitting into peaks of similar intensities, as shown by decomposition of the cubic 311 peak into 12 nearly equal reflections (Figure 1). The shifts of the oxygen atoms are far stronger, but the unrestrained U–O distances and O–P–O angles are satisfactory (Table 2).

Table 2. Selected Cation–Anion Distances and Angles for t-UP$_2$O$_7$ (-173, 25 °C) and c-UP$_2$O$_7$ (600 °C)$^a$

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>U–O (Å)</th>
<th>P–O$_b$–P (deg)$^b$</th>
<th>U–P (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-173</td>
<td>2.20(2)–2.27(3)</td>
<td>135(2)–140(2)</td>
<td>3.57(1)–3.76(1)</td>
</tr>
<tr>
<td>25</td>
<td>2.21(3)–2.28(3)</td>
<td>136(2)–142(3)</td>
<td>3.55(1)–3.73(1)</td>
</tr>
<tr>
<td>600</td>
<td>2.276(6)</td>
<td>139(2)</td>
<td>3.656(2)</td>
</tr>
</tbody>
</table>

$^a$O$_b$ is a bridging oxygen and O a nonbridging one. $^b$Esd’s are underestimated because of the restraints on the P–O distances.

The four independent P$_2$O$_7$ units show a staggered conformation with a strong bending of the P–O$_b$–P linkages. The bond angles are in good agreement with those determined from the Raman spectra using Lazarev’s empirical correlation rule based on the $\nu_2$ (P–O$_b$–P) and $\nu_{AS}$ (P–O$_b$–P) stretching wavenumbers (about 140° at 20 °C). They are also comparable to the 137° angle of Cabeza’s room-temperature cubic model featuring split positions for O$_b$. The bending of the P–O–P linkages results in a strong distortion of the PO$_4$ tetrahedra. Typically, as shown in Figure 3 for the P$_2$O$_7$ unit near (1/2,1/2,1/2), the O$_b$–P–O angles involving a nonbridging O on the same side as the opposite phosphorus are higher than the other ones. This asymmetric distortion justifies a posteriori the choice of acentric space group P1 instead of P–1. This ordered model is also validated by the moderate thermal factor of the bridging oxygens ($B_{eq} = 5.0(4)$ Å$^2$ at 20 °C, common to the four O$_b$’s), comparable to that of the nonbridging ones (3.9(1) Å$^2$).

As will be shown below, UP$_2$O$_7$ transforms to the cubic archetype form (c-UP$_2$O$_7$) at high temperature. This structure was refined from a conventional X-ray pattern on the basis of Levi’s cubic model (space group Pa-3, U (0,0,0), P (x,y,z)) and nonbridging O (x,y,z), but particular attention was paid to the location of bridging O$_b$ (near (1/2,1/2,1/2)), which monitors the bending of the unique P–O$_b$–P linkage. A Fourier synthesis of the observed structure factors at 600 °C was made introducing all atoms but O$_b$ to obtain an electron density map of the (111) mid-distance plane perpendicular to the P–P (3-fold) axis (Figure 4). This reveals a dense and homogeneous annular zone centered on (1/2,1/2,1/2), which accounts for the delocalization of O$_b$ about 0.56 Å away from the inversion center. This distribution of O$_b$ in the archetype confirms that a ring-like model, even discontinuous, with off-centered positions is more satisfactory than an ellipsoidal model with a maximum probability of the presence at the center, in agreement with the absence of $\pi$ bonding. P–O$_b$–P was estimated at about 139° on the basis of the P–P distance, assuming P–O$_b$ = 1.60 Å. Although the nonbridging oxygen atoms are also affected by the disorder as shown by the anomalous short P–O distances, they are too close to the heavy uranium atoms to be observed in the same way as O$_b$.

Other AnP$_2$O$_7$. According to XRD, the other AnP$_2$O$_7$ compounds (An = Th, Np, Pu) also exhibit broadened peaks without any evidence of a superstructure, but the distortion appears more intense when the An$^{IV}$ cation is small (i.e., extremely faint for ThP$_2$O$_7$, but clearly visible for PuP$_2$O$_7$). On this basis, the AnP$_2$O$_7$ can be supposed to adopt also the triclinic symmetry at room temperature. In this way, the actinide cations differ from smaller ones like Si$^{IV}$, Ti$^{IV}$, and Zr$^{IV}$, whose diphosphates have a 3 × 3 × 3 cubic or orthorhombic superstructure. On the other hand, White et al. using synchrotron diffraction recently noted a faint distortion of the CeP$_2$O$_7$ cell and proposed a triclinic cell with parameters remarkably analogous to those of UP$_2$O$_7$, considering both the metric distortion (0.20% vs 0.20% for the latter) and the maximum deviation from the right angle (0.17° vs 0.17°), also with two nearly equal cell edges. Thus, owing to the similar ionic radius of the tetravalent cation (rCe$^{IV}$ = 1.01 Å; 1.00 ≤ rAn$^{IV}$ ≤ 1.08 Å in 6-fold coordination), CeP$_2$O$_7$ is probably isotypic with the title compounds.

Figure 4. c-UP$_2$O$_7$: annular distribution of O$_b$ in the (111) plane around the (1/2,1/2,1/2) inversion center shown by the 3D electron density map at 600 °C.
the DSC curve (Figure 5). Although intense, this transition shows a negligible hysteresis. HTXRD, less accurate than synchrotron diffraction, does not allow deconvolution of the strongly overlapped peaks of the triclinic form and following the thermal evolution of the six cell parameters. However, measurement of the integral width (IFWHM) of four strong composite peaks revealed a continuous decrease on heating, followed by a sudden break near the transition point (Figure 6).

At higher temperatures, all IFWHMs remain nearly constant and equal to that of a corundum standard, thus proving the cubic symmetry of the archetype and the probable absence of an intermediate form. As shown on the same figure, the $t\rightarrow c$ transition of UP$_2$O$_7$ is also associated with a marked increase of the cell edge, like for CeP$_2$O$_7$\textsuperscript{13} in agreement with the first-order nature of the transition observed by DSC.

Further evidence of the $t\rightarrow c$ transition is given by $^{31}$P NMR. At low temperature, $t$-UP$_2$O$_7$ shows a complex spectrum, where the peaks of the eight independent phosphorus sites present in the triclinic cell strongly overlap (Figure 7). Consequently, a best-fit simulation of the $^{31}$P spectra over the whole temperature range could not reasonably be performed. The presence of heavy uranium atoms in the neighborhood also results in an anisotropic chemical shift and numerous rotation bands. The chemical shift appears very sensitive to temperature (0.49 ppm °C$^{-1}$ from linear fit), probably due to the strong thermal expansion of the cell, as described in the following section. However, the most remarkable thermal transformation of the NMR spectrum is the collapse of each grouping into a single peak upon reaching the cubic form at 155 °C, in agreement with the presence of phosphorus in a single site of the archetype form.

The transition temperatures of the other AnP$_2$O$_7$ (Table 3) were determined from the inflection point of the expansion curves as shown thereafter. To summarize, this phenomenon can be described according to three criteria: the first-order character, shown by DSC and the discontinuity of the cell volume; the order–disorder character, evidenced by the

![Figure 5. Differential scanning calorimetry analysis of UP$_2$O$_7$: heating (upper) and cooling (lower) plots.](image)

![Figure 6. Thermal variation of average cell parameter $a$ (black, left scale) of UP$_2$O$_7$, and integral widths of four composite diffraction peaks in the 45° ≤ 2θ ≤ 57° range (colors, right scale). $a$, $h$, $k$, and $l$ refer to the cubic lattice.](image)

![Figure 7. $^{31}$P MAS spectra of UP$_2$O$_7$ as a function of temperature, recorded at a spinning speed of 9 kHz.](image)

**Table 3. Effect of the Ionic Radius of M$^{IV}$ on the Temperatures of Transition and Inversion of Expansion for Several MP$_2$O$_7$.**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Zr$^{IV}$</th>
<th>Pu$^{IV}$</th>
<th>Ce$^{IV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{MIV}$ (Å)</td>
<td>0.86</td>
<td>1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>$T_{trans}$ (°C)</td>
<td>290</td>
<td>180(5)</td>
<td>160(10)\textsuperscript{*}</td>
</tr>
<tr>
<td>$T_{inv}$ (°C)</td>
<td>450</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation</th>
<th>Np$^{IV}$</th>
<th>U$^{IV}$</th>
<th>Th$^{IV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{MIV}$ (Å)</td>
<td>1.01</td>
<td>1.03</td>
<td>1.08</td>
</tr>
<tr>
<td>$T_{trans}$ (°C)</td>
<td>160(10)</td>
<td>155(2)</td>
<td>85(5)</td>
</tr>
<tr>
<td>$T_{inv}$ (°C)</td>
<td>400</td>
<td>330</td>
<td>200</td>
</tr>
</tbody>
</table>

\textsuperscript{*}Our estimation from ref 13 expansion curve; these authors state 115–175 °C. Inversion temperatures are estimated from the thermal expansion graphs (Figure 9).
delocalization of O₅; the direct change from triclinic to cubic (HTXRD, ³¹P NMR), unless a possible intermediate form occurs in a very narrow range of temperature near the transition. This very uncommon increase of the order of symmetry by a factor of 24 is comparable to that between the cubic 3 × 3 × 3 and the 1 × 1 × 1 cells but higher than that between the orthorhombic Pbcn 3 × 3 × 3 and the cubic 1 × 1 × 1 cells of ZrP₂O₇ (≈7.1).

**Thermal Expansion and Contraction.** The thermal variation of the cubic/pseudo-cubic cell parameter a was determined for the AnP₂O₇ diphosphates (An = Th, U, Np, Pu) by HTXRD and Rietveld analysis (Figure 8). Except at the highest temperatures, the expansion of the cell edge of ThP₂O₇ is in fair agreement with the dilatometric curve recorded on a ceramic by Laud et al. in 1971.

Note also the superimposability of the expansion curves of NpP₂O₇ and CeP₂O₇,

\[
\text{AnP}_2\text{O}_7, \text{ZrP}_2\text{O}_7, \text{ZrV}_2\text{O}_7, \text{and their solid solutions,}
\]

which, beyond the similarity of the ionic radii, with a CTE \(\alpha = -3.5 \times 10^{-6} \text{°C}^{-1} (R = 0.999)\), an extremely rare value over such a wide range. One can compare this behavior to those of ZrP₂O₇, ZrV₂O₇, and their solid solutions, which also exhibit a strong expansion at low temperature. However, at variance with the AnP₂O₇, the transition is marked by a sharp break followed by a moderate but still positive expansion for ZrP₂O₇, (a moderate contraction for the vanadium-rich forms).

In all the cases, the low or negative expansion observed above the transition point is typical of a thermal rocking of the corner-connected MO₆ and PO₄ polyhedra, even though these units sustain some distortion in this phenomenon and cannot be treated as rigid. No explanation was found in the literature for the strong positive expansion that precedes the inversion in all these compounds.

As clearly observed for UP₂O₇, the jump in the domain of positive expansion corresponds to the change of symmetry, which obviously occurs below the inversion. Thus, these two phenomena should be considered as definitely distinct in the AnP₂O₇, like in CeP₂O₇. On the other hand, the break in the expansion curve of the ZrP₂O₇--ZrV₂O₇ solid solutions matches with the transition to the archetypal form. Indeed, differences in behavior are conceivable because the low-temperature distortions of these two families of diphosphates are also different.

We tried to explain the remarkable variations of the CTE considering the evolution of the crystal structure over a wide range of temperature. In ThP₂O₇, which has the lowest transition point, the triclinic distortion can be considered as faint enough to be ignored in the Rietveld refinement, which was performed therefore in the cubic model, whatever the temperature. Because the oxygen atoms are light, distant from their ideal positions in the triclinic form and subject to strong thermal displacements in the cubic form, the cation–oxygen distances were not considered as reliable enough to follow the evolution of the crystal structure. Conversely, the unambiguous positions of Th and P in the two domains allow consideration of the Th–P and P–P distances as suitable for this purpose.

The thermal rocking of the corner-connected ThO₆ and PO₄ polyhedra is the probable cause of the moderate but continuous decrease of the Th–P distance in both t and c forms (Figure 9), although the intensity of this contraction is limited by the expected faint thermal expansion of the Th–O bond. This contraction is also observed between −173 and 25 °C by synchrotron diffraction in the triclinic domain of UP₂O₇ (Table 2). On the other hand, the expansion of the covalent P–O bonds can be considered as negligible, so the intense and nonmonotonous variations of the P–P distance only result from the two modes of deformation of the P–O₅–P linkage: the stretching at low temperature and tetrahedra rocking at high temperature, which rule the expansion of the whole cell by their intensity.

We can propose an explanation for the expansion in the low-temperature domain on the basis of Birkedal’s DFT model,
which the energy of an isolated staggered P$_2$O$_7$ unit was calculated as a function of the P–O–P angle. Figure 10 shows

![Figure 10. Energy ΔE of the isolated P$_2$O$_7$ unit as a function of the P–O$_b$–P angle, reproduced from Birkedal et al., and theoretical curve of the P–O$_b$–P angle vs T (right scale) explaining the thermal stretching of the P$_2$O$_7$ unit. Compare to the experimental curve for ThP$_2$O$_7$, inset, shifted horizontal scale.](image)

the anharmonic potential well, whose minimum corresponds to the equilibrium angle at 0 K. The energy increases very rapidly when the angle decreases, whereas the slope is much lower at high angles. From this model we can infer that the average value of the P–O$_b$–P angle increases with energy ΔE. Thus, assuming ΔE = kT, the P–O$_b$–P linkage should expand on heating in the same way as the thermal expansion of a chemical bond A–B arises from the asymmetry of the potential well of $E_{A–B}$ vs $d_{A–B}$. Note that the P–O$_b$–P angle actually observed in ThP$_2$O$_7$ has a very similar behavior up to the transition point (Figure 10, inset).

Although some improvements could be performed by taking into account the interactions with the tetravalent cation and the torsion of the P$_2$O$_7$–unit, the DFT model offers an interesting correlation with the experimental measurements, suggesting that a precise analysis of the expansion mechanisms in the diphosphates could be obtained using this method.

The HT-μ-Raman study of the t–c phase transition was first conducted on UP$_2$O$_7$ samples. However, the interaction with the laser beam always led to a partial oxidation of U$^{IV}$ into U$^{III}$, even under inert Ar atmosphere. In these conditions the appearance of the very intense $\nu_1$ vibration mode associated to the uranyl molecular ion$^{53}$ precluded any reliable analysis of the spectrum. The study was then undertaken on ThP$_2$O$_7$ samples between room temperature and 280 °C.

The spectrum recorded at room temperature fits well with that reported earlier$^{29}$ and exhibits the vibration bands assigned to P–O bonds and P–O$_b$–P bridges. Particular attention was paid to the P–O$_b$–P $\nu_4$ and $\nu_6$ stretching bands since they could give precise information on this linkage. The symmetric elongation appears as a split band with components between 733 and 747 cm$^{-1}$, in agreement with the triclinic model, whereas the faint $\nu_6$ vibration mode is observed around 970 cm$^{-1}$ (Figure 11). According to Lazarev’s relation,$^{51}$ these values account for P–O$_b$–P angles ranging between 137° and 145°, in good agreement with the average value (138°) inferred from the Rietveld refinement. As expected, the $\nu_4$ (P–O$_b$–P) vibration band reveals a progressive symmetrization on heating, yielding a single peak at 732 cm$^{-1}$ between 80 and 90 °C to be correlated to the t–c transition observed in the same range by XRD (Figure 9). Although it is commonly admitted that the $\nu_4$ vibration band should be extinct if the P$_2$O$_7$–unit becomes centrosymmetric,$^{54}$ this mode can still be observed clearly at least up to 130 °C, that is, far above the transition point to Pa–3. However, the band becomes very diffuse at higher temperatures. A possible explanation of this behavior can be proposed on the basis of the structural observations: even in the archetypal form, the P–O$_b$–P linkage remains strongly bent, so the inversion center is relevant to a global disorder in the mean crystal cell, not to the real geometry of the diphosphate unit. Therefore, this mode remains active in the cubic form. The crossing of the inversion barrier, predicted to occur above 160 °C by DFT, conceivably results in intense variations of the angle. A wide dispersion of the phonon modes can be expected as well as a shortening of the coherence length, which both contribute to the broadening of the signal observed.

In the archetypal form, the annular distribution of O$_b$ around the inversion center allows a rocking of the corner-connected tetrahedra. Actually, this effect starts at the transition point, as shown by the inflection of the P–P expansion curve (Figure 9). At higher temperatures, the rocking becomes more intense and prevails over the stretching of the P–O$_b$–P angle, resulting in a negative definite expansion of both the P–P linkage and the cell edge. Thermal rocking, a common feature in corner-connected arrays of polyhedra, is known as one of the most efficient ways to achieve zero or negative thermal expansion.$^{19}$ As shown in Figure 9, the conflicting effects, each of them predominant in a domain of temperature, do not govern only the expansion of the P$_2$O$_7$ unit but also that of the cell. For this reason, the expansion plots of the five compounds (Figure 8) show roughly similar slopes at high temperature. However, in agreement with the previous mechanism, An$^{IV}$ cations smaller than Th$^{IV}$ form stronger An–O bonds, more resistant to thermal disorder, so the temperatures of t–c transition and inversion of expansion logically increase when the ionic radius of An$^{IV}$ decreases (Table 3).

Although negative thermal expansion is a very rare property among crystalline solids, several recent studies have pointed out the outstanding tendency of the phosphates of tetravalent actinides to contract over wide ranges of temperature. For example, whereas zirconium oxophosphate Zr$_2$O(PO$_4$)$_2$ has been known since 1985 for its ultralow expansion ($+1.5 \times 10^{-6}$
Iglesias, J. E.; Alonso, J. A.; Zhang, Y. for providing facility for working with actinides. Globally, the unequaled high-radius, high-valence An expansion is the high valence of the actinide which makes the actinide-substituted isotypes show a negative definite expansion. \( \beta - \text{Th}_O (\text{PO}_4)_2 (\text{P}_2 \text{O}_7) \) between 20 and 600 °C. The structure, made of MO₆ (M = Zr, U, Th) and PO₄ tetrahedra connected by edges and corners, is a priori unfavorable to a global rocking of the polyhedra, but the high ionic radii of the AnIV cations allow independent transverse oscillations of the oxygen anions, responsible for the negative expansion. Likewise, \( \beta - \text{Th}_O (\text{PO}_4)_2 (\text{P}_2 \text{O}_7) \) exhibits a near-zero expansion (+1.9 × 10⁻⁶ °C⁻¹, 20–800 °C). Another strong point of the AnIV phosphates regarding thermal expansion is the high valence of the actinide which makes the An–O bond strong and therefore only faintly sensitive to temperature. Globally, the unequaled high-radius, high-valence combination makes this family an attractive field of research for low and negative expansion mechanisms.

**REFERENCES**

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