$Th_4(PO_4)_4P_2O_7$, a New Thorium Phosphate: Synthesis, Characterization, and Structure Determination

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The chemistry of thorium phosphate reported in the literature has been found to be erroneous. It was reconsidered in terms of careful chemical preparations and specific analytical methods. Special attention has been paid to the atom ratio value referred to $r =$ thorium/phosphorus, which was experimentally fixed in order to obtain the correct composition of the final compound. A new compound with the chemical formula $Th_4(PO_4)_4P_2O_7$, derived from the crystal structure determination, has been obtained. The unit cell parameters were obtained from powder and single-crystal X-ray diffraction data. It is orthorhombic (space group *Pcam*, $Z = 2$) with the cell dimensions $a = 12.8646(9)$ Å, $b = 10.4374(8)$ Å, $c = 7.0676(5)$ Å, and $V = 949.00(9)$ Å^3. The atomic positions were derived from Patterson and Fourier methods and the structure was refined to an R value of 0.039. The structure consists of layers parallel to (010) containing both PO_4 and P_2O_7 groups. These layers alternate with planes of Th atoms. The coordination sphere of the two independent heavy atoms is formed by eight O atoms from five PO_4 and one P_2O_7 groups. The formula of thorium phosphate $Th_4(PO_4)_4P_2O_7$ is in good agreement with the elementary composition derived from electron microprobe analysis, which gave a ratio $r = {}^2/_3$. Any other value of r (${}^1/_2 < r < {}^3/_4$) induces the formation of polyphase systems: $Th_4P_6O_{23}$ and ThO_2 for $r > {}^2/_3$; $Th_4P_6O_{23}$ and ThP_2O_7 for $r < {}^2/_3$. The characterization of thorium phosphate diphosphate by means of infrared spectroscopy confirmed the presence of diphosphate groups in the compound.

Introduction

Natural monazites are considered as one of the most resistant minerals of the Earth's crust. Thus, phosphate matrixes have been found attractive for their potential use for radwaste storage.[1] These materials have been pointed out because of their resistance to radiation effects[2] and low solubility compared to those of glasses.[3] The ability of the monazites to be loaded with cerium[4] and actinides[5] was investigated, and the leaching of thorium and uranium from natural actinide-bearing monazite was recently carefully examined.[6−8]

For a better understanding of the chemical behavior of uranium and thorium in monazite and also to assess uranium and thorium phosphates themselves as storage materials, we have reinvestigated the chemistry of these elements in phosphoric medium. The corresponding compounds, as potential candidates for industrial applications, need a detailed knowledge of their syntheses and chemical compositions, which can only be ascertained if precise crystallographic features are known. The literature about these materials is rather poor and controversial.[9−14] In the first part of our study, we have revised the uranium phosphate system.[15] From a careful analysis of the powder diffraction patterns, it has been shown that the two compounds reported with the formula $U_3(PO_4)_4$[11] and $U_2O_3P_2O_7$[14] must be replaced by a new mixed-valence uranium uranyl phosphate $U(UO_2)(PO_4)_2$. Details about syntheses and related mechanisms involved in the preparation of this compound have been given elsewhere.[15−17]

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(1) Boatner, L. A., Sales, B. C. *Radioactive waste forms for the future*; Lutze W., Ewing, R. C., Eds.; Elsevier Science Publishers B. V.: Amsterdam, 1988; Vol. 8, p 495.
(2) McCarthy G. J.; White, W. B.; Pfoertsch, D. E. *Mater. Res. Bull.* **1978**, *13*, 1239.
(3) Sales, B. C.; White, C. W.; Boatner, L. A. *Nuclear Chem. Waste Management* **1983**, *4*, 281.
(4) Pepin, J. G.; Vance, E. R.; McCarthy G. J. *Mater. Res. Bull.* **1981**, *16*, 627.
(5) Kelly, K. L.; Beall, G. W.; Young, J. P.; Boatner, L. A. In *The Scientific Basis for Nuclear Waste Management*; Moore, J. G., Ed.; Plenum: New York, 1981; Vol. 3, p 189.
(6) Eyal, Y.; Olander, D. R. *Geochim. Cosmochim.* **1990**, *54*, 1867.
(7) Olander, D. R.; Eyal, Y. *Geochim. Cosmochim.* **1990**, *54*, 1879.
(8) Olander, D. R.; Eyal, Y. *Geochim. Cosmochim.* **1990**, *54*, 1889.
(9) Dunn, H. W. *X-rays diffraction data for some uranium compounds, Rep. ORNL-2092*, Oak Ridge National Laboratory, Oak Ridge, TN, 1956.
(10) Shankar, J.; Khubchandani, P. G. *Anal. Chem.* **1957**, *29*, 1375.
(11) Burdese, A.; Borlera, M. L. *Ann. Chim. Roma* **1963**, *53*, 344.
(12) Laud, K. R.; Hummel, F. A. *J. Am. Ceram. Soc.* **1971**, *54*, 296.
(13) Tananaev, I. V.; Rozanov, I. A.; Beresnev, E. N. *Inorg. Mater. (USSR)* **1976**, *12*, 748.
(14) Bamberger, C. E.; Haire, R. G.; Begun, G. M.; Hellwege, H. E. *J. Less Common Met.* **1984**, *102*, 179.
(15) Bénard, P.; Louër, D.; Dacheux, N.; Brandel, V.; Genet, M. *Chem. Mater.* **1994**, *6*, 1049.
(16) Dacheux, N.; Brandel, V.; Genet, M. *New J. Chem.* **1995**, *19*, 15.

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The second part of our investigation deals with thorium phosphate. The chemical formula $Th_3(PO_4)_4$ was first reported by Shankar and Khubchandani.[10] The powder compound was prepared under nitrogen atmosphere, at 1000 °C, from a gel of thorium phosphate. Later, thorium phosphate was also reported by Burdese and Borlera.[11] In the study of the $ThO_2-P_2O_5$ system, and for the mole ratio $ThO_2/P_2O_5 = {}^3/_2$, Laud and Hummel[12] reported again the chemical formula $Th_3(PO_4)_4$, for a phase obtained up to 1500 °C by reaction between ThO_2 and $NH_4H_2PO_4$. Similarly to this work, Tananaev et al.[13] have extensively studied various kinds of thorium phosphate (hydrated and anhydrous phases), starting from aqueous mixtures of thorium nitrate and sodium phosphate or phosphoric acid. In these syntheses the precipitates were separated, calcined, and analyzed. The authors concluded the formation of several polyphased systems. However, the chemical formula $ThO_2 \cdot 0.8\ P_2O_5$ was assigned to one of these phases. More recently, Bamberger et al.[14] have reproduced the results of their predecessors about thorium phosphate, although some different reactants were used: ThO_2 or ThF_4 and BPO_4 as phosphating agent. Moreover, a thorium oxide phosphate $(ThO)_3(PO_4)_2$ has also been synthesized at high temperature and characterized.[12]

In most of these investigations, the existence of thorium phosphate, formulated as $Th_3(PO_4)_4$, was always referred to the previous studies.[10−12] It was claimed that X-ray powder diffraction patterns were in good agreement with the previous ones, and the reported chemical analysis seemed in accordance with the proposed chemical formula (see, for example, Table 1 in ref 14). Thus, at the beginning of our study on this material, the existence of thorium phosphate was also believed. In the course of our investigation, two polymorphic phases of "thorium phosphate" were found,[18,19] and one of them was labeled with ^{223}Ra and leached.[20] Nevertheless, all along this research plan development, some experimental problems were found, e.g.:

(i) It was very difficult to establish a precise value for the atom ratio r = thorium/phosphorus, whatever the way of synthesis selected (dry or wet chemistry).

(ii) Some diffraction lines of the X-ray diffraction patterns of the so-called thorium phosphate exhibited overlaps with lines of thorium dioxide.

These features made the situation unclear. That is why new types of experiments on thorium phosphate were undertaken, based on a special attention to the stoichiometry of starting chemical compositions, to the solid-state reactions occurring during the thermal treatments and to a precise characterization of the crystallographic properties of the phases. In spite of efforts to prepare the thorium phosphate (r = 3/4), it was demonstrated that an unreported pure phase has been prepared, instead of $Th_3(PO_4)_4$. Its chemical formula, derived from the crystal structure determination, is $Th_4(PO_4)_4P_2O_7$. The present study deals with the chemical conditions needed for the preparation of this new compound, the experimental evidence of its chemical composition, the collection of precise X-ray powder diffraction data for pattern indexing, and the crystal structure determination from single-crystal diffraction data.

Experimental Procedures

Preparation of Thorium Phosphate. For a typical tetravalent ion such as Th^{4+}, which does not undergo any redox reactions, its combination with no condensed phosphate ions PO_4^{3-}, for an atom ratio r = thorium/phosphorus = ${}^3/_4$, should form the phosphate $Th_3(PO_4)_4$. Thus, with respect to these conditions, a thorium phosphate phase should be prepared, from both dry and wet chemistry. The first way consists of a reaction between ThO_2 and $NH_4H_2PO_4$, while for the second, a concentrated thorium chloride (or nitrate) solution is mixed with 15 M H_3PO_4. This mixture is then heated to get a dry residue, which is calcined at high temperature. These procedures are comparable to that used in previous studies; a few differences were however detected in the X-ray diffraction patterns, registered with an usual diffractometer, by comparison with the reported data. When syntheses via wet routes were reproduced many times, we observed intensity variations for a few reflections, especially diffraction lines with d spacings 3.24 and 2.81 Å. It has also been found, by electron microprobe analysis (EMA), that the prepared "compound" was composed, in fact, of two phases. The major phase can be considered as a new material, since values for r ratios were frequently around ${}^2/_3$, while the minor phase was attributed to ThO_2. At this stage, it is worthwhile to note that the two strongest lines of ThO_2 diffraction pattern correspond to the d spacings given above.

It appeared difficult to set up the ratio r at the desired value ${}^3/_4$ when very concentrated solutions of thorium salt and phosphoric acid are used. The main error arose from the difficulty in measuring the volume of highly viscous solutions. Reproducible results were obtained only when careful attention was paid to the starting chemical conditions. Thus, a pure compound was prepared and checked by EMA; it corresponds to the atom ratio value ${}^2/_3$. Whatever the chemical reactants used, from dry or aqueous solutions routes, always the same thorium phosphate was obtained, clearly identified through its X-ray powder diffraction pattern.

High-temperature treatments of samples in alumina crucibles, in air or argon atmosphere, were realized in the range from 50 to 1200 °C. The thermal treatment applied to the mixture of reactants in concentrated solutions, $ThCl_4$ or $Th(NO_3)_4$ and H_3PO_4, corresponded to the following stages:

(i) Elimination of volatile compounds (H_2O and HCl or HNO_3) at 140 °C, until a dry residue is obtained.

(ii) Drying of the residue up to 400−500 °C during 2 h to get rid of last traces of water and hydrochloric acid or nitrogen oxides.

(iii) Calcination between 850 and 1200 °C to obtain the crystallization of the material.

The amount of the product obtained by this procedure was typically between 2 and 20 g. It was verified that the acidity of the reacting medium has no influence on the final obtained product. The chemical nature of the crucible does not play any rôle on the quality of the compound. There is no special change for the dry procedure when thorium is provided as $Th(C_2O_4)_2$, $Th(NO_3)_4 \cdot 4H_2O$, ThO_2, etc., while phosphate is provided by the use of $NH_4H_2PO_4$ or BPO_4. In the latter case, the raw material is washed with hot water to dissolve the byproduct B_2O_3 formed during the synthesis.

The density was measured by two different techniques, using a helium pycnometer Accupyc 1330 from Micromeritics and a pycnometer calibrated with diethylphtalate (ρ = 1.118 g cm^{-3}). The values found were 5.12 and 5.22(1) g·cm^{-3}, respectively.

Surprisingly, the X-ray powder diffraction patterns collected with a conventional diffractometer were almost identical for r atom ratio values varying from ${}^2/_3$ to ${}^3/_4$. Nevertheless, out of these limits, Tananaev et al.[13] reported the existence of a compound written $ThO_2 \cdot 0.8P_2O_5$ for which the X-ray diffraction pattern presents some similarities with that of the new phase

(17) Dacheux, N.; Brandel, V.; Genet, M. *New J. Chem.* **1995**, *19*, 1029.
(18) Baglan, N. Thesis, Université Paris-Sud, IPNO-T-92.04, 1992.
(19) Mérigou, C.; Genet, M.; Ouillon, N.; Chopin, T. *New J. Chem.* **1995**, *19*, 275.

Table 1. Single-Crystal X-ray Diffraction Data and Structure Refinement Parameters

Data Collection	
diffractometer type	Syntex-Nicolet P3F
radiation type	Mo ($\lambda = 0.710\ 69$ Å)
scan type	$\theta/2\theta$
scan width	$(2\theta_1 - 1)° \leq 2\theta \leq (2\theta_2 + 1)°$; θ_1 and θ_2 are diffraction angles with $\lambda(K\alpha_1)$ and $\lambda(K\alpha_2)$
θ range (deg)	$1 < \theta < 30$
h, k, l ranges	$0 \leq h \leq 18, 0 \leq k \leq 14, 0 \leq l \leq 9$
no. of standard reflections	3 (interval: 60 reflections)
temp (K)	293
no. of measd reflns	1498
linear absorption coefficient (mm^{-1})	μ (Mo Kα) = 33.18
crystal size (mm)	$0.25 \times 0.07 \times 0.05$
absorption correction type	analytical method[27]
min and max transmission values	0.127/0.218
Crystal Data	
chemical formula	$Th_4P_6O_{23}$
mol wt (g mol^{-1})	1482
crystal system	orthorhombic
cell parameters (Å)	$a = 12.869(4)$, $b = 10.447(5)$, $c = 7.079(2)$
vol (Å^3)	951.7(5)
density: ρ_{calc} (g cm^{-3})	5.171
formula units per cell	$Z = 2$
space group	*Pcam*
$F(000)$	1636
Refinement	
method of refining	least-squares method[28]
no. of refined parameters	93
weighting scheme	$w = 1/\sigma(F)$
R/R_w with 1064 reflections $I > 3\sigma(I)$	0.039/0.044
R/R_w with 1498 reflections	0.059/0.046
Δ/σ_{max}	10^{-3}
secondary extinction value	$g = 0.15 \times 10^{-6}$
extinction	type I by Becker and Coppens[29]
source of atomic scattering factors	*International Tables for X-ray Crystallography*[30]

prepared in this work, although the atom ratio was 0.625 instead of 0.667 ($^2/_3$ value). This comment explains why most previous authors have missed the stoichiometry of the thorium phosphate.

To check the validity of the results obtained from powder thorium phosphate, attempts to grow single crystals were undertaken and were successful. This was proceeded by the flux method in sealed Pt tube, since the compound has no congruent melting. Thorium phosphate (0.3 g) prepared from an atom ratio $r = {}^3/_4$ was mixed with B_2O_3 (0.5 g), ammonium borate (0.3 g), and phosphotungstic acid (0.3 g). The mixture was sealed in a platinum tube and heated according to the following schedule: 500 °C (l h), 800 °C (1 h), 1000 °C (1 h), 1500 °C (2 h) with a heating rate equal to 1 °C min^{-1}. For cooling, the rate was of 0.5 °C min^{-1} down to a plateau at 1200 °C (0.5 h), then a cooling rate of 0.8 °C min^{-1} with a plateau at 900 °C (0.5 h), and finally a regime of 1 °C min^{-1} down to 100 °C. The content of the tube was then put into 50 cm^3 of hot water. Insoluble parts were separated and dried with alcohol. Microscope examination showed needlelike crystals, the largest size of which was about 10 μm; most of them were twinned. The powder X-ray diffraction patterns of ground crystals was the same as that obtained from a $^2/_3$ atom ratio value. This means that even when the medium is richer in thorium (r equal to $^3/_4$), the produced crystals have the same chemical composition thorium/phosphorus = $^2/_3$, which could be due to the phosphate excess provided by the flux.

X-ray Diffraction. Precise powder diffraction data were collected with a Siemens D500 high-resolution powder diffractometer using monochromatic Cu Kα_1 X-rays ($\lambda = 1.540\ 598$ Å) obtained with an incident-beam curved-crystal germanium monochromator and asymmetric focusing (short focal distance 124 mm, long focal distance 216 mm). The alignment of the instrument was checked by means of the 00l reflections of fluorophlogopite mica (NIST SRM 675)[21] and the error on the zero point was estimated less than 0.005°(2θ). The instrument resolution function has been described elsewhere.[22] The diffraction pattern was scanned with a step length of 0.02°(2θ). Precise determination of peak positions was carried out by means of the Socabim fitting program PROFILE, available in the PC software package DIFFRAC-AT supplied by Siemens. From these data the SOCABIM search/match program was used for interrogating the ICDD PDF database,[23] by constraining the search to thorium phosphates compositions. Among the thorium compounds found, four of them were kept for further analysis. They are $Th_3(PO_4)_4$ [Files No. 12-399, 16-234, 27-1470], $(ThO)_3(PO_4)_2$ [File No. 24-1324], β-ThP_2O_7 [File No. 17-576] and $ThO_2{\cdot}0.8P_2O_5$ [File No. 31-1388]. In particular, it was found that only the last (unindexed) pattern roughly matches, in terms of both peak position and intensity, the pattern of the new thorium compound. Additional comments are given in the pattern indexing section.

Single crystals have been studied by X-ray diffraction according to oscillation, Weissenberg (λ(Cu Kα)) and precession (λ(Mo Kα)) methods. Photographs indicating orthorhombic symmetry and no superstructure reflections were observed. Diffracted intensities from a selected single crystal were collected on a four-circle diffractometer. The experimental conditions are listed in Table 1.

Infrared Spectroscopy. The infrared spectra were recorded with a Hitachi I-2001 spectrophotometer (4000−400 cm^{-1}) using samples of 2−3 wt % in KBr.

Electron Microprobe. Quantitative determination of the elements in solid phases was carried out on polished grain-mounts by using a Cameca SX 50 electron microprobe with a working voltage acceleration of 15 kV and a 10 nA current beam. The diameter of the analytical spot was about 1 μm. Standards were used for the calibration of thorium (ThO_2) and phosphorous (apatite).

(20) Mérigou, C.; Le Dû, J-F.; Genet, M.; Ouillon, N.; Chopin, T. *New J. Chem.* **1995**, *19*, 1037.
(21) Louër, D. *Mater. Sci. Forum* **1991**, *79*, 17.
(22) Louër, D.; Langford, J. I. *J. Appl. Crystallogr.* **1988**, *21*, 17.
(23) International Centre for Diffraction Data, PDF database, Newton Square, PA.

Structure Determination

Powder Pattern Indexing. Indexing of the powder diffraction pattern was performed using the program DICVOL91[24] from the first 20 lines with an absolute error of 0.02°(2θ) on peak positions. The successive dichotomy method yields to an unique orthorhombic solution with the figures of merit $M_{20} = 67$ and $F_{20} = 117(0.0038, 45)$. The correctness of this solution was checked by reviewing the complete data by means of the computer evaluation program NBS*AIDS83.[25] A least-squares refinement of the unit cell parameters led to $a = 12.8646(9)$ Å, $b = 10.4374(8)$ Å, $c = 7.0676(5)$ Å, and $V = 949.00(9)$ Å^3. The corresponding figures of merit [$M_{20} = 47$ and $F_{30} = 94(0.0071, 45)$] were calculated taking into account the systematic absences consistent with the space groups *Pcam* and *Pca*2$_1$. The X-ray powder diffraction data are given in Table 2. From the indexing results and the observed density, it was clear that no chemical composition of thorium phosphates reported in the literature could explain the unit cell found for this new phase. On the other hand, from the stoichiometric global formula derived from the single crystal analysis, $Th_4P_6O_{23}$, and $Z = 2$, the calculated density is 5.19 g cm^{-3}, which is in accordance with the observed values. As indicated above, the powder diffraction data of $ThO_2{\cdot}0.8P_2O_5$ can be partially compared to that of $Th_4P_6O_{23}$, and an approximate indexing of the pattern may be proposed from the solution found in this study. However, the figures of merit [$M_{14} = 3$ and $F_{14} = 2(0.068, 93)$] mirror the very poor quality of the data, and if the chemical composition of $ThO_2{\cdot}0.8P_2O_5$ is multiplied by a factor of 4, a global formula of $Th_4P_{6.4}O_{24}$ is obtained which is not in good agreement with the formula of the new thorium phosphate. This result demonstrates that the formula proposed by Tananaev et al.[13] is not correct. Also, apparent crystallographic relationships can be noted between the orthorhombic unit cell proposed for β-ThP_2O_7 ($a = 11.62$ Å, $b = 12.80$ Å, $c = 7.12$ Å; $\rho_{obs} = 5.093$ g cm^{-3}) and the cell found for $Th_4(PO_4)_4(P_2O_7)$. Moreover, from the accurate high-resolution diffraction data, it is clear that there is no apparent analogy between the patterns of the new thorium phosphate and those of the two phases reported previously, $Th_3(PO_4)_4$ and $(ThO)_3(PO_4)_2$. Also, it should be noted that the quality of the indexing of these patterns is very low (figures of merit F_{30} lower than 5), and it should be improved to be convincing. At last, from the unit cell of $Th_4(PO_4)_4P_2O_7$ no chemically related materials with known crystal structure has been revealed from an interrogation of the NIST-CDF database.[26]

Crystal Structure Determination. Crystallographic details, experimental data, and programs used are gathered in Table 1. The systematic observed reflections agreed with the possible space groups: *Pcam* and *Pca*2$_1$. It can be noted that the unit cell parameters *a*, *b*, and *c* obtained from the single crystal analysis agree with the results of the powder diffraction pattern analysis within 1, 2, and 5 combined esd's, respectively.

Table 2. X-ray Powder Diffraction Data for $Th_4(PO_4)_4P_2O_7$

hkl	$2\theta_{obs}$ (deg)	$2\theta_{calc}$ (deg)	d_{obs} (Å)	I/I_0
1 1 0	10.889	10.907	8.12	2
2 0 0	13.737	13.756	6.44	5
2 1 0	16.157	16.173	5.48	47
1 1 1	16.626	16.629	5.33	<1
0 2 0	16.962	16.976	5.22	68
1 2 0	18.317	18.331	4.840	2
2 0 1	18.621	18.637	4.761	<1
2 1 1	20.487	20.501	4.332	100
1 2 1	22.245	22.256	3.993	1
3 1 0	22.387	22.396	3.968	8
0 0 2	25.173	25.181	3.535	43
3 1 1	25.731	25.735	3.459	4
1 3 0	26.511	26.519	3.359	12
3 2 0	26.889	26.888	3.313	<1
1 1 2	27.507	27.513	3.240	12
4 0 0	27.709	27.715	3.217	6
4 1 0	29.028	29.029	3.074	3
2 3 0	29.155	29.158	3.060	13
2 1 2	30.068	30.072	2.970	15
4 0 1	30.516	30.513	2.927	78
0 2 2		30.526		
2 3 1	31.840	31.840	2.808	47
4 2 0	32.678	32.680	2.738	4
2 2 2	33.619	33.621	2.664	2
0 4 0	34.339	34.340	2.609	8
4 2 1	35.122	35.121	2.553	31
3 3 1	35.545	35.544	2.524	2
5 1 0	35.912	35.919	2.4986	<1
0 3 2	36.217	36.203	2.4783	<1
1 3 2	36.891	36.893	2.4346	3
2 4 0	37.157	37.153	2.4177	<1
3 2 2		37.169		
1 4 1	37.367	37.366	2.4046	1
4 0 2	37.793	37.792	2.3785	4
4 3 0	38.072	38.073	2.3617	1
5 1 1	38.174	38.179	2.3556	<1
4 1 2	38.806	38.799	2.3187	2
2 3 2	38.902	38.900	2.3133	9
5 2 0	39.001	38.999	2.3076	2
2 4 1	39.353	39.352	2.2877	<1
1 1 3	39.809	39.815	2.2626	<1
3 4 0	40.436	40.432	2.2289	1
5 2 1	41.102	41.114	2.1943	1
4 2 2	41.704	41.697	2.1640	23
2 1 3		41.703		
6 0 0	42.129	42.110	2.1432	<1
3 4 1	42.488	42.488	2.1259	2
1 2 3	42.636	42.656	2.1189	<1
6 1 0	43.050	43.033	2.0994	25
0 4 2		43.057		
1 4 2	43.667	43.655	2.0712	1
1 5 0	43.912	43.905	2.0602	3
6 0 1	44.107	44.102	2.0515	2
2 2 3	44.456	44.445	2.0362	<1
4 4 0	44.706	44.686	2.0254	1
3 1 3		44.704		
6 1 1	45.004	44.992	2.0127	2
2 5 0	45.667	45.654	1.9850	4
5 3 1		45.658		
1 5 1	45.820	45.834	1.9788	1
4 3 2	46.200	46.195	1.9634	1
4 4 1	46.595	46.590	1.9476	14
3 2 3	47.311	47.307	1.9198	1
2 5 1	47.541	47.528	1.9111	17
4 0 3	47.826	47.821	1.9003	14
3 4 2	48.239	48.230	1.8850	1
2 3 3	48.747	48.741	1.8666	16
5 4 0	49.734	49.726	1.8318	1
6 3 0	49.934	49.923	1.8249	8
3 5 1	50.258	50.255	1.8139	1
6 1 2	50.518	50.511	1.8052	13

(24) Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, *21*, 987.
(25) Mighell, A. D.; Hubbard, C. R.; Stalick, J. K. NBS*AIDS80: A Fortran Program for Crystallographic Data Evaluation; Nat. Bur. Stand. Tech. Note 1141 (NBS*AIDS83 is an expanded version of NBS*AIDS80), 1981.
(26) International Centre for Diffraction Data, NIST CDF database, Newton Square, PA.
(27) De Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.
(28) Busing, W. R. *Acta Crystallogr.* **1971**, *A27*, 683.
(29) Becker, P. J.; Coppens, P. *Acta Crystallogr.* **1975**, *A31*, 417.
(30) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

atoms	*x*	*y*	*z*	U_{eq} (Å²)
Th(1)	0.18183(5)	0.97720(6)	$^1/_4$	0.0089(3)
Th(2)	0.91329(5)	0.48779(6)	$^1/_4$	0.0105(3)
P(1)	$^1/_4$	0.2752(4)	0	0.039(3)
P(2)	0.9160(3)	0.1242(4)	$^1/_4$	0.010(2)
P(3)	0.1354(3)	0.6248(4)	$^1/_4$	0.009 (2)
O(11)	$^1/_4$	0.137(1)	0	0.05(1)
O(12)	0.3422(8)	0.348(1)	0.057(2)	0.035(6)
O(13)[a]	0.208(3)	0.247(5)	$^1/_4$	0.07(3)
O(21)	0.937(1)	0.266(1)	$^1/_4$	0.018(7)
O(22)	0.8468(6)	0.0823(8)	0.080(1)	0.015(4)
O(23)	0.021(1)	0.049(1)	$^1/_4$	0.022(7)
O(31)	0.139(1)	0.769(1)	$^1/_4$	0.019(6)
O(32)	0.245(1)	0.570(1)	$^1/_4$	0.032(8)
O(33)	0.0712(6)	0.5755(8)	0.081(2)	0.013(4)

[a] Occupancy rate 0.5.

Table 4. Parameters of Anisotropic Thermal Motion U_{ij} (Å² × 10²)

atoms	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Th(1)	0.85(3)	1.05(3)	0.76(3)	0.07(2)	0	0
Th(2)	1.00(3)	1.33(3)	0.80(3)	−0.32(2)	0	0
P(1)	1.3(3)	0(2)	10.5(6)	0	−2.3(3)	0
P(2)	0.9(2)	1.4(2)	0.7(3)	0(2)	0	0
P(3)	0.9(2)	1.0(2)	0.7(2)	−0.1(2)	0	0
O(11)	4.0(9)	2.0(7)	10(2)	0	−2(2)	0
O(12)	3.4(6)	3.1(5)	4.2(8)	−0.4(5)	−0.2(6)	−1.5(6)
O(13)	6(3)	12(4)	2(2)	−6(3)	0	0
O(21)	2.1(7)	0.9(5)	2.5(9)	0.3(5)	0	0
O(22)	1.1(4)	2.4(4)	0.9(5)	0.0(4)	0.0(4)	−0.2(4)
O(23)	1.5(7)	2.7(7)	2.5(8)	0.2(6)	0	0
O(31)	3.3(8)	1.0(5)	1.3(7)	−0.4(6)	0	0
O(32)	1.7(7)	2.6(7)	5(1)	−0.4(7)	0	0
O(33)	0.8(4)	1.5(4)	1.7(6)	−0.4(3)	0.1(4)	−0.4(4)

The structure determination was undertaken using the centrosymmetric space group *Pcam*, in agreement with the repartition of normalized structure factors. Thorium atoms were located by deconvolution of Patterson functions. Next, an electron density analysis allowed to locate the 12 phosphorus atoms and 44 atoms among the 46 oxygen atoms present in the unit cell. Then, an electron density residue with a magnitude equal to that of half an oxygen atom was found on difference Fourier maps; it is located roughly at the same distance between phosphorus atoms P(1) along the [001] direction, i.e., in a symmetry plane. This residue was attributed to one oxygen atom, labeled O(13) and assigned to a $^1/_2$-site occupancy rate, in order to be in accordance with the chemical formulation and the electron density value.

The refinement converged after a few cycles. Final atomic positions, parameters of anisotropic thermal motion and selected bond distances and angles are listed in Tables 3−5, respectively. The two independent phosphorus P(2) and P(3) atoms are located inside slightly distorted oxygen tetrahedra, while the atom P(1) is approximately located at the center of a triangle built up from O(11), O(12), and O(12^i) atoms. The addition of the bridging atom, O(13), between the two triangles defines the eclipsed configuration of a diphosphate group. Nevertheless, the P_2O_7 group exhibits two anomalies:

(i) The phosphorus atoms are exactly located within the terminal oxygenated faces, at unusually short distances of the three corners (P−O ≈ 1.46 Å, whereas P−O_t ≈ 1.513 Å according to Baur[31]) and correlatively very far from the bonding oxygen atom (P−O(13) = 1.87 Å, whereas P−O_b ≈ 1.584 Å according to Baur[31]) with $\overline{\text{P−O(13)−P}} = 142(3)°$.

(ii) The atomic displacement parameters of the constituent atoms are very high: O(13) moves strongly along the *b* direction, whereas P(1), O(11), and O(12) move along the *c* axis (Table 3).

These features and the occupancy rate of 0.5 of the bonding atom O(13) point out the existence of two P_2O_7 groups per cell; these two groups are independent and would be distributed with disorder on four equivalent sites which are determined by the crystalline symmetry. Attempts to refine the structure model with lower symmetry space groups ($Pca2_1$, $P2_1/m$, $P2$, Pa, and Pc with a set of reflections collected into two octants) were unsuccessful: the diphosphate groups always show abnormal interatomic distances and geometry, and their constituent atoms exhibit very high thermal agitation; otherwise, the reliability factors were higher than that corresponding to the centrosymmetric group *Pcam*. Consequently, in spite of a thorough analysis of the structure of $Th_4(PO_4)_4P_2O_7$, we can neither describe the real symmetry of the unit cell nor depict the actual geometry of P_2O_7 groups because their position disorder leads only to average atomic positions. Under these conditions, the orthorhombic space group *Pcam* allows the more simple structural description in accordance with the X-ray diffraction data. The final structure refinement parameters are listed in Table 1.

Table 5. Interatomic Distances (Å) and Bond Angles (deg)[a]

Tetrahedra PO_4				
P(1)	O(11)	O(12)	O(12^i)	O(13)
O(11)	1.44(2)	2.54(2)	2.54(2)	2.18(4)
O(12)	121.3(5)	1.47(1)	2.51(3)	2.44(4)
O(12^i)	121.3(5)	117.4(9)	1.47(1)	2.51(3)
O(13)	81(2)	93(2)	96(2)	1.87(2)
P(2)	O(21)	O(22)	O(22^{ii})	O(23^{iii})
O(21)	1.51(2)	2.55(2)	2.55(2)	2.52(2)
O(22)	112.2(5)	1.56(1)	2.41(2)	2.57(2)
O(22^{ii})	112.2(5)	101.0(7)	1.56(1)	2.57(1)
O(23^{iii})	109.9(8)	110.6(5)	110.6(5)	1.56(2)
P(3)	O(31)	O(32)	O(33)	O(33^{ii})
O(31)	1.51(2)	2.49(2)	2.51(2)	2.51(2)
O(32)	110.4(9)	1.53(2)	2.54(2)	2.54(2)
O(33)	110.4(5)	111.9(5)	1.54(1)	2.39(3)
O(33^{ii})	110.4(5)	111.9(5)	101.6(8)	1.54(1)

Polyhedra ThO_8

Th(1)−O(23^i) = 2.20(2)	Th(2)−O(32^x) = 2.24(2)
Th(1)−O(31) = 2.24(12)	Th(2)−O(21) = 2.33(2)
Th(1)−O(22^v) = 2.44(1)	Th(2)−O(12^x) = 2.37(1)
Th(1)−O(22^{vi}) = 2.44(1)	Th(2)−O(12^{xi}) = 2.37(1)
Th(1)−O(22^{vii}) = 2.519(9)	Th(2)−O(33^v) = 2.45(1)
Th(1)−O(22^{viii}) = 2.519(9)	Th(2)−O(33^{vi}) = 2.45(1)
Th(1)−O(11^{iv}) = 2.59(1)	Th(2)−O(33^{iii}) = 2.529(9)
Th(1)−O(11^{ix}) = 2.59(1)	Th(2)−O(33^{xii}) = 2.529(9)

[a] Symmetry code: (i) $^1/_2 - x, y, -z$; (ii) $x, y, ^1/_2 - z$; (iii) $1 + x, y, z$; (iv) $x, 1 + y, z$; (v) $1 - x - ^1/_2, 1 - y, -z$; (vi) $1 - x, 1 - y, ^1/_2 + z$; (vii) $x - ^1/_2, 1 - y, ^1/_2 - z$; (viii) $x - ^1/_2, 1 - y, z$; (ix) $x,1 + y, ^1/_2 - z$; (x) $^3/_2 - x, y, ^1/_2 + z$; (xi) $^1/_2 + x, 1 - y, z$; (xii) $1 + x, y, ^1/_2 - z$.

Structure Description. As shown in projection along [100] in Figure 1, the 3-dimensional structure of

(31) Baur, W. H. *Acta Crystallogr.* **1974**, *B30*, 1195.

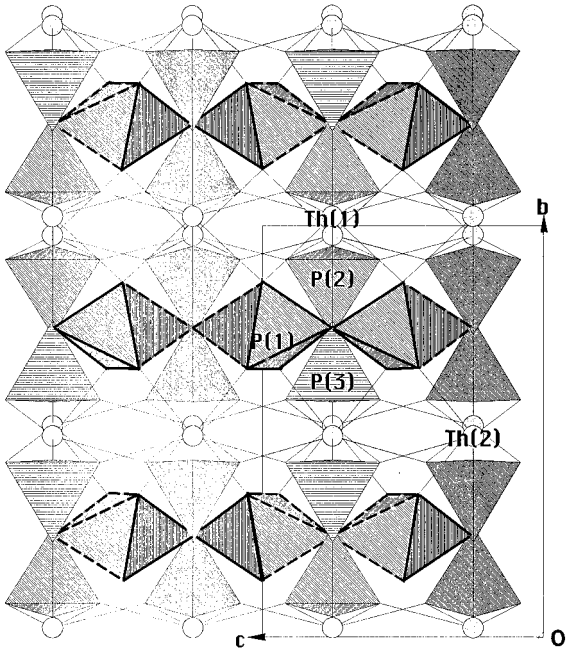


Figure 1. Projection parallel to the [100] direction (P_2O_7 groups are represented with solid lines or dashed lines to show up the position disorder).

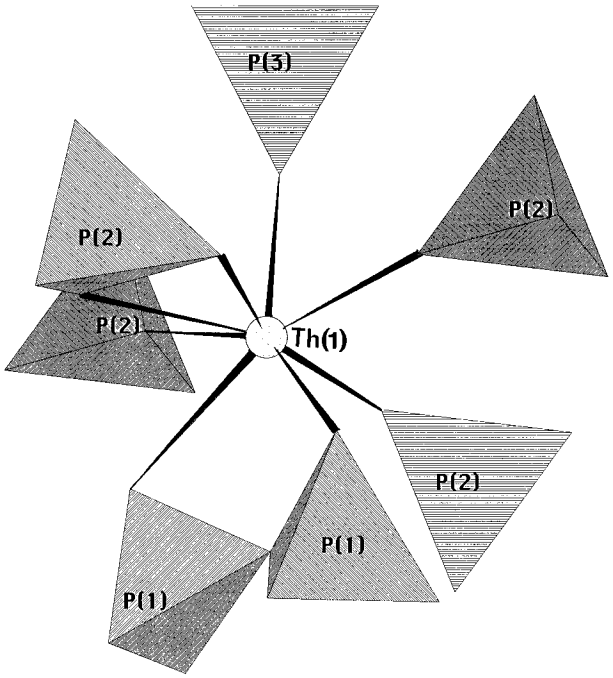


Figure 2. Perspective view of the environment of Th(1) atom.

$Th_4(PO_4)_4P_2O_7$ can be described from layers, parallel to (010), formed by both PO_4 tetrahedra and P_2O_7 groups. These layers alternate with planes containing all the Th atoms. The link between these layers allows each Th atom to be connected to a P_2O_7 group by two corners, to one PO_4 tetrahedron by edge-sharing and to four other monodentate PO_4 tetrahedra (Figures 2 and 3). The P_2O_7 groups are running along [001]; the center of each of them, occupied by O(13), is nearly superimposed with two corners of independent PO_4 tetrahedra, which point a corner along $\vec{b}$ and $-\vec{b}$ (Figure 1).

Regarding the similar 8-fold coordination spheres of the two nonequivalent heavy atoms, it may be pointed out that the Th(1)−O distances, in the range 2.20−2.59 Å, are slightly more scattered than the Th(2)−O distances (2.24−2.529 Å). The Th−O mean lengths, respectively 2.442 and 2.402 Å, agree with the average distance of 2.42 Å reported for eight-coordinated thorium in oxygen environment.[32,33] Furthermore it can be noted that Th(1)−O(13) = 2.84 Å. The shape of the two independent PO_4 tetrahedra is well-defined, with no significant distortion and rather regular dimensions. The maximum deviations of the P−O bond lengths from the mean values, 1.55 Å for $P(2)O_4$ and 1.53 Å for $P(3)O_4$, are 0.04 and 0.02 Å, respectively, whereas the O−P−O angles vary from 101.0 to 112.2° (mean value 109.42°) for the first polyhedra and from 101.6 to 111.9° (mean value 109.43°) for the second polyhedra. These results are in very good agreement with the values obtained at the term of a systematic structural study of numerous phosphates.[31] Concerning the $P(1)O_4$ group, no clear conclusion can be made; the distances and angles are poorly indicative because the corresponding atoms appear with average coordinates as a consequence of the position disorder described above.

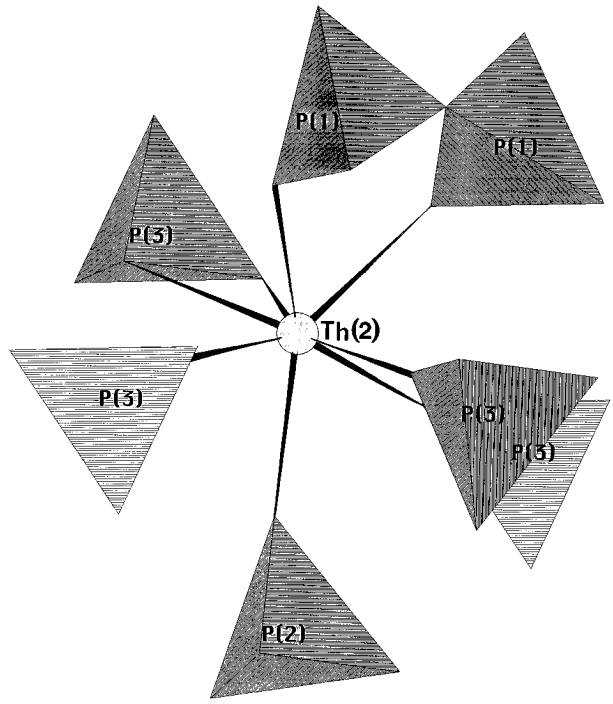


Figure 3. Perspective view of the environment of Th(2) atom.

Physicochemical Characteristics

Infrared Spectroscopy. Since the chemical formula revealed from X-ray diffraction (powder and single crystal) is $Th_4(PO_4)_4P_2O_7$, the infrared spectrum must point out the presence of two types of phosphate groups. The characteristic vibration modes of PO_4 (symmetric and asymmetric stretching) are usually observed in the range 950−1250 cm^{-1}, while deformation modes are present between 350 and 650 cm^{-1}. The number of observed bands depends on the distortion of the regular tetrahedron which is the usual symmetry of PO_4 groups. The signature of P_2O_7 groups is not generally so intense, thus the assignment of bands to the diphosphate is never obvious. Taking into account these general com-

(32) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1968, Vol. III.
(33) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

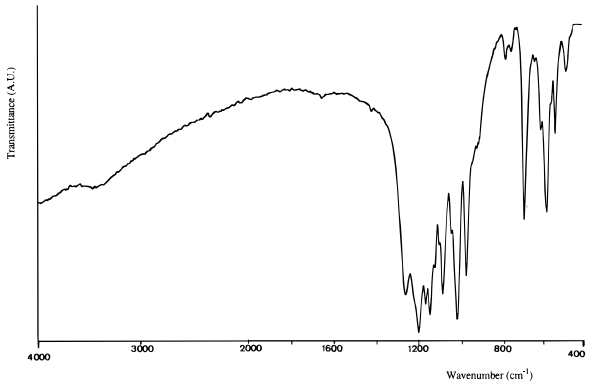


Figure 4. Infrared spectrum of thorium phosphate−diphosphate $Th_4(PO_4)_4P_2O_7$.

ments, and by comparison with ThP_2O_7 used as a reference, two bands at 950 and 750 cm^{-1} can be assigned to the P−O−P bridge (Figure 4). The occurrence of such modes in the infrared spectrum is in favor of a nonlinear diphosphate group. This fact is in agreement with the structure determination results. All other bands of the spectrum can be assigned to PO_4 and PO_3 distorted groups.[16]

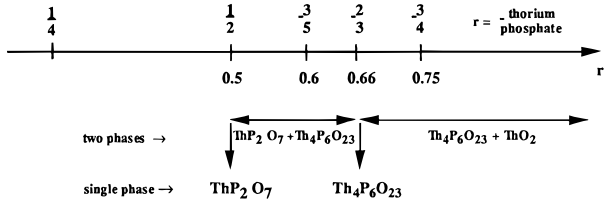
Electron Microprobe Analysis. The new thorium phosphate has a very low solubility, even in strong acids. Thus, analytical methods based on solution chemistry become unefficient. Nondestructive analysis by EMA should be well adapted to the problem, but the presence of a heavy metal (Th) and light elements (P, O) makes the experiment difficult. Grain sizes of powdered compound were about 10−20 μm, and the analyses were performed with a micron diameter beam that allows us to do several determinations on the same grain. The measurements were made over 15 different spot analyses on various grains for the same material. The obtained value is the average of these 15 measures. Additionally, from the image recorded during the examination of the sample, it was possible to detect a monophase compound from a polyphase system. In these conditions phosphate samples, derived from the atom ratio $r = {}^3/_4$, were identified as made of two different phases. The experimental results give a atom ratio ${}^2/_3$ for the major phase; the second one has been assigned to ThO_2 from the crystallographic data. These results are enough to propose the way by which these compounds are produced.

The ratio value ${}^3/_4$, compared to ${}^2/_3$, represents conditions where the reacting medium is richer in thorium. Thus, thorium excess from the ${}^2/_3$ stoichiometry must appear under the oxide form according to the global reaction

$$9ThCl_4 + 12H_3PO_4 \rightarrow 2Th_4P_6O_{23} + ThO_2 + 36HCl\uparrow$$

The proportion of ThO_2 is ${}^1/_9$ of the total thorium amount, i.e., 8.18 wt %. With these conditions it can be understood why previous studies missed this compound. The main reason is the presence of ThO_2 which cannot be easily identified on X-ray diffraction patterns due to line overlap with those of $Th_4P_6O_{23}$. Only a careful analysis of line intensities is able to show a difference between samples prepared from $r = {}^2/_3$ to $r = {}^3/_4$.

Scheme 1



When the synthesis is done with the ratio value ${}^2/_3$, the corresponding global reaction is

$$4ThCl_4 + 6H_3PO_4 \rightarrow Th_4P_6O_{23} + H_2O\uparrow + 16HCl\uparrow$$

The phase is pure, and the experimental value for r, determined by electron microprobe, is 0.671 ± 0.024.

Conclusions

As far as the atom ratio r (=thorium/phosphorus) is responsible for the compounds produced, we have shown that a new thorium phosphate, $Th_4P_6O_{23}$, must be considered. For the correct stoichiometry ${}^2/_3$, the thorium phosphate−diphosphate is formed. When an excess of thorium is brought into the reacting medium (${}^2/_3 < r < {}^3/_4$), a two-phases system is obtained: $Th_4P_6O_{23}$ remains the major phase, whereas ThO_2 is always present (for the temperature range 850−1200 °C). For lower values of the ratio r ($r < {}^2/_3$), the excess of phosphate appears as the diphosphate form ThP_2O_7, when the temperature is not greater than 1000 °C (for a chloride medium). The reaction involved is, for example, for a r ratio value equals to ${}^3/_5$:

$$6ThCl_4 + 10H_3PO_4 \rightarrow Th_4P_6O_{23} + 2ThP_2O_7 + 24HCl\uparrow + 3H_2O\uparrow$$

For values between ${}^1/_2$ and ${}^2/_3$, we should observe also both compounds with an increasing amount of ThP_2O_7 as the ratio is going toward the ${}^1/_2$ value. Thus, the "compound" reported by Tananaev et al.[13] belongs to this type of two-phases system since the ratio value for $ThO_2 \cdot 0.8P_2O_5$ is equal to 0.625.

At higher temperatures (1200 °C), it has been found that thorium diphosphate decomposes and gives the thorium phosphate−diphosphate according to the following reaction:

$$8ThP_2O_7 \rightarrow 2Th_4P_6O_{23} + P_4O_{10}\uparrow$$

In terms of the r value, the different domains for mono and two phases system existence, for the temperature range 850−1200 °C, are shown in Scheme 1.

To conclude, the crystal structure determination has demonstrated that the new compound is a thorium phosphate−diphosphate, $Th_4(PO_4)_4P_2O_7$. The structure has been precisely determined; it has been shown that the P_2O_7 group exhibits a position disorder, and consequently only an average description can be reported for this group. The presence of both phosphate and diphosphate groups in the same compound is infrequent. Nevertheless, it has been observed in some compounds, e.g., $Na_6[ThPO_4(P_2O_7)]_2$,[34] $Na_7M^{III}{}_4PO_4(P_2O_7)_4$ (M^{III} = Al,

(34) Kojic-Prodic, B.; Sljukic, M.; Ruzic-Toros, Z. *Acta Crystallogr.* **1982,** *B38,* 67.

Cr, Fe),[35] $K_2H_8(PO_4)_2P_2O_7$,[36] $Rb_3Ti_3O(PO_4)_3P_2O_7$,[37] ξ-$Ag(MoO)_2PO_4P_2O_7$,[38] $Ca_8(PO_4)_4(P_2O_7)$,[39] and Ca_2-$VPO_4P_2O_7$.[40]

Acknowledgment. We are indebted to Dr C. Nguyen-Trung from CREGU Laboratory (Nancy, France) who kindly provided the results of the electron microprobe analysis (EMA). Also, we want to thank him for helpful discussions about the phosphate chemistry of thorium.

Supporting Information Available: Tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(35) De La Rochère, M.; Kahn, A.; D'Yvoire, F.; Bretey, E. *Mater. Res. Bull.* **1985**, *20*, 27.
(36) Norbert, A.; Maurin, M.; André, D.; Larbot, A. *Bull. Soc. Fr. Minéral. Crist.* **1970**, 579.
(37) Duhlev, R. *Acta Crystallogr.* **1994**, *C50*, 1523.
(38) Hoareau, T.; Borel, M.-M.; Grandin, A.; Leclaire, A.; Raveau, B. *C. R. Acad. Sci. Paris* **1994**, *II-319*, 47.
(39) Lebugle, A.; Zahidi, E.; Bonel G. *Reactivity Solids* **1986**, *2*, 151.
(40) Lii, K. H.; Wen, N. S.; Su, C. C.; Chueh, B. R. *Inorg. Chem.* **1992**, *31*, 439.