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Actinides immobilization in new matrices based on solid solutions: $Th_{4-x}M^{IV}_x(PO_4)_4P_2O_7$, ($M^{IV}=^{238}U,^{239}Pu$)

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Abstract

A complete reexamination of thorium and tetravalent uranium phosphate chemistry has been achieved. The main results led to the thorium phosphate-diphosphate (TPD): $Th_4(PO_4)_4P_2O_7$ which can be prepared via wet and dry chemistry routes. Its crystal structure was determined. Attempts to replace thorium by U^{4+} or Pu^{4+} have been successfully reached. Thus solid solutions of the type: $Th_{4-x}M^{IV}_x(PO_4)_4P_2O_7$ were synthesized. For $M^{IV}=U^{4+}$, x values are in the range zero to three, whereas for $M=Pu^{4+}$, x values are between zero and one. The total replacement of thorium by Pu^{4+} to get the hypothetical compound '$Pu_4(PO_4)_4P_2O_7$' was unsuccessfully attempted. © 1998 Elsevier Science S.A.

Keywords: Thorium; Uranium; Plutonium; Solid-solution; Phosphate

1. Introduction

Various kinds of materials have been already proposed for the final disposal of the plutonium excess from dismantled nuclear weapons. Independently of different types of glasses, some ceramics like monazites [1], synroc [2], zircon [3] have been studied in this perspective. Besides monazites, some other phosphates seem to be promising; among them we decided to investigate a new system based on the thorium phosphate chemistry.

This chemistry was developed either in aqueous media (acid or neutral), or through dry processes. In given conditions, all these ways lead to an unique compound: $Th_4(PO_4)_4P_2O_7$ which is the thorium phosphate-disphosphate (TPD) [4]. The crystal structure of TPD was determined [4] and numerous leaching tests on TPD were performed to qualify this compound as a good one in terms of its very low solubility [5]. By decay ^{239}Pu ($T_{1/2}$= 24 500 years), which is the major component of plutonium wastes, gives ^{235}U ($T_{1/2}=7.10^8$ years). Thus, the material we need to store plutonium must be also efficient for the immobilization of uranium. In this objective, TPD has been considered as a host matrix for tetravalent ions like Pu^{4+} and U^{4+}. To be sure that these ions are well incorporated in the TPD, solid solutions of the type $Th_{4-x}M^{IV}_x(PO_4)_4P_2O_7$ (with $M=Pu^{4+}$ or U^{4+}) were synthesized. The occurrences of real solid solutions were checked through the variations of the cell parameters followed through XRD data.

2. Experimental methods

2.1. Chemicals

Uranium (IV) chloride solution was prepared by dissolving uranium metal chips in concentrated hydrochloric acid. Thorium chloride as well thorium nitrate pentahydrate from Rhône–Poulenc were used to get thorium solutions. Plutonium nitrate solution was prepared by dissolving plutonium dioxide in concentrated nitric acid. Other chemicals used for syntheses, i.e. phosphoric and nitric acids, were from Fluka or Merck.

2.2. Syntheses

– Pure thorium phosphate-diphosphate (TPD)

Previous works concerning thorium phosphate chemistry have shown that, for the mole ratio $r=(Th/PO_4)$ in the range $0.5<r<1$, only the thorium phosphate-diphosphate ($r=(2/3)$ is well defined at high temperature (1250°C). For other r values, polyphase systems composed of thorium phosphate-diphosphate and thorium diphosphate (for $1/2<r<2/3$) or thorium oxide (for $2/3<r<1$) have been obtained. For this reason, all systems ThO_2 - MO_2 - P_2O_5

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(M=U, Pu) were studied using the mole ratio $r=Th+M/PO_4=2/3$.

– Solid solutions of thorium-uranium (IV) phosphate-diphosphate (TUPD)

In the soft chemistry method [6,7], 1.6 M U (IV) hydrochloric solution and 1 M thorium chloride solutions were mixed with 15 M phosphoric acid considering a lot of mole ratios Th/U from 39 down to 0.33. The obtained gelatinous precipitate was dried at 140°C, ground and heated in argon, first at 400–500°C for 2 h to eliminate volatiles, then at 1050–1250°C for 10 h at least.

For all samples (TPD and TUPD), a natural sintering occurs during the heat treatment. A study is now under progress using a cold pressing before heating. The final materials have a surface area of 0.5–1.0 $m^2\ g^{-1}$ with an average grain size in the range 10 to 20 μm.

– Solid solutions of thorium-plutonium (IV) phosphate-diphosphate (TPPD)

These solid solutions were synthesized by the soft method. Thorium nitrate solution was prepared by dissolution of $Th(NO_3)_4 \cdot 5\ H_2O$ in 1 M nitric acid. The determination of the thorium concentration was performed using two methods: complexometric titration with EDTA and a liquid scintillation method (PERALS®) [8]. In our conditions, the average concentration of this starting solution was found to be equal to 1.51 M.

Thorium and plutonium (IV) nitrate solutions were mixed with 5 M phosphoric acid considering the following mole ratios: Th/Pu=9, Th/Pu=3 and Th/Pu=0 in order to obtain solid solutions $Th_{4-x}Pu_x(PO_4)_4P_2O_7$ with $x=0.4$, 1.0 and 4.0 respectively. These mixtures were slowly evaporated at 160°C for 6 h in porcelain crucibles. The obtained amorphous residues were ground and heated at 300°C for 2 h in alumina nacelles (in order to eliminate water and nitric acid). At this stage of the synthesis, the solid is still amorphous. After a second step of grinding in water, powders were heated at 1000–1050°C during 18 h in air with a heating and cooling rate of 5°C min^{-1} to get a crystallized compound.

2.3. Apparatus and methods of characterization

High temperature treatment was performed with a Pyrox MDB15 and Adamel (for thorium-plutonium phosphates in glove box) furnaces. X-ray powder diffraction diagrams were obtained with a Philips PW 1050/70 diffractometer using Cu K_α radiation and a Ni filter or a Jobin-Yvon CGR apparatus using Cu K_α rays in glove box. In all cases, silicon [JCPDS File 27-1402] as internal reference was added to samples in order to calibrate the peak positions. Patterns were scanned using the following conditions: 0.01° $step^{-1}$ and 12 s $step^{-1}$ from 10 to 50° (2θ).

As the crystal structure of thorium phosphate-diphosphate is already well known [4], it is possible to observe the deformation of the unit cell when thorium is substituted by a smaller tetravalent cation M^{4+}. The refinement of the cell parameters has been obtained using the *U*-Fit program [9].

3. Results and discussion

3.1. The system ThO_2 - UO_2 - P_2O_5

The X-ray powder diffraction patterns obtained for solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ are basically the same as for the pure thorium phosphate-diphosphate. Nevertheless, this result cannot give a precise information about the homogeneity of the synthesized products. Thus, we checked by electron microprobe analysis whether the systems were single phase or polyphase. For all samples ($0<x<3.0$) the system is found to be single phase. Moreover, all powders are homogeneous.

In order to verify whether uranium (IV) takes place of thorium in the thorium phosphate-diphosphate structure, the unit cell parameters of several solid solutions were refined in the space group Pcam. Their variations in terms of *x* value are presented in Fig. 1. These results show that for $x=3.0$, the thorium phosphate-diphosphate lattice deformation is respectively equal to 1.3% along the **a** axis, 1.07% along the **b** axis and 1.1% along the **c** axis. The contraction of the cell volume is about 3.35%.

If thorium is replaced by another tetravalent cation, the variations of the unit cell parameters and volume in solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ can be formulated as a function of the radius of the cation, as follows:

$$\mathbf{a} = 4.400^{[8]}r_{cat} + 8.2500 \quad (1)$$

$$\mathbf{b} = 2.448^{[8]}r_{cat} + 7.8597 \quad (2)$$

$$\mathbf{c} = 2.112^{[8]}r_{cat} + 4.8506 \quad (3)$$

$$\mathbf{V} = 820.72^{[8]}r_{cat} + 87.044 \quad (4)$$

where $^{[8]}r_{cat}$ is the average tetravalent cation radius (in the eight fold coordination).

In these conditions, when *x* atoms of thorium are replaced by uranium (IV) in the formula $Th_{4-x}U_x(PO_4)_4P_2O_7$ and taking $x=3$ as the maximum substitution of thorium by uranium in the thorium phosphate-diphosphate lattice (which has been verified experimentally), e.g. $ThU_3(PO_4)_4P_2O_7$, the *x* value for other tetravalent cations may be calculated (for example in case of the **a** parameter) as follows:

$$12.705 = 4.4^{[8]}r_{cat} + 8.25$$

$$12.705 = \frac{4.4[(4 - x_{max}) \times {}^{[8]}r_{Th} + x_{max} \times r]}{4} + 8.25 \quad (6)$$

where *r* is the average value of the cation radius. Finally:

$$x_{max} = \frac{0.15}{1.05 - r} \quad (7)$$

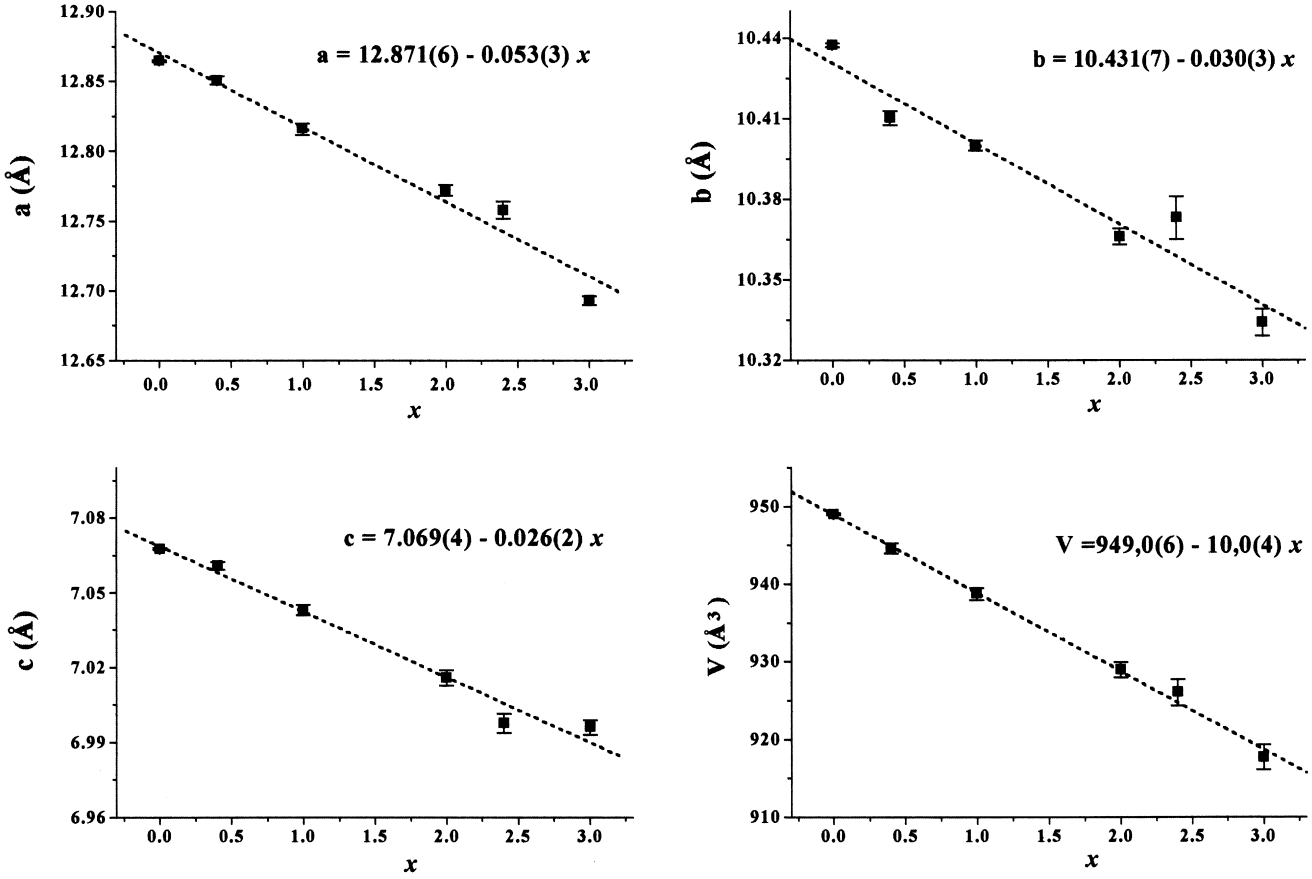

Fig. 1. Variation of unit cell parameters and cell volume of thorium-uranium (IV) phosphate-diphosphate as a function of x value.

The same relation can be obtained considering the variations of **b** and **c** parameters and cell volume *V*. The maximum x value calculated from the Eq. (7) for plutonium is 1.67.

3.2. The system ThO_2-PuO_2-P_2O_5

Three kinds of solid solutions of initial composition $Th_{3.6}Pu_{0.4}(PO_4)_4P_2O_7$ and $Th_3Pu(PO_4)_4P_2O_7$ were heated in a glove box at 300°C for 2 h and then at 1050°C for 18 h. From X-ray powder diffraction, the system is single phase: the presence of plutonium (IV) (or thorium) diphosphate, oxide or monazite ($PuPO_4$) has not been evidenced. Moreover, for both pink-coloured powders, we observed a shift of the peaks positions in the XRD diagram (compared to the TPD diagram). The higher is the x value in $Th_{4-x}Pu_x(PO_4)_4P_2O_7$, the larger is the shift observed, as expected for the substitution of thorium by another cation in the lattice.

The variations of the unit cell parameters and volume of thorium-plutonium (IV) phosphate-diphosphate, obtained by linear regression from experimental data, can be described by the four equations gathered in Fig. 2.

The **a, b, c** and *V* values decrease with the increase of the x value because thorium is replaced by a smaller cation. Using the *U*-Fit program [9] the maximum x values for TPPD solid solutions have been calculated. They are equal to 1.81 from **a**, 1.38 from **b**, 1.86 from **c** and to 1.63 from the cell volume *V*. The last value is very close to that calculated from Eq. (7): $x=1.67$. Thus, the formula of the richer solid solution in plutonium could be considered as $Th_{2.4}Pu_{1.6}(PO_4)_4P_2O_7$ (40 mole per cent of thorium substituted by plutonium). The existence of such a compound needs to be verified.

Aiming at the synthesis of the plutonium (IV) phosphate-diphosphate $Pu_4(PO_4)_4P_2O_7$, plutonium (IV) nitrate and phosphoric acid solutions were mixed with the ratio $(Pu/PO_4)=(2/3)$. The residue obtained after evaporation (according to the same procedure as for solid solutions) is still amorphous. After heating at 1050°C for 18 h, the final product is a polyphase system. It is composed of the plutonium (IV) diphosphate (JCPDS File no. 43-1097) and plutonium (III) phosphate (monazite structure, JCPDS File no. 43-1096).

The storage of plutonium in such materials needs to take into account criticality problems. So, the study of other solid solutions containing neutrons absorbers as hafnium, gadolinium or samarium should be continued.

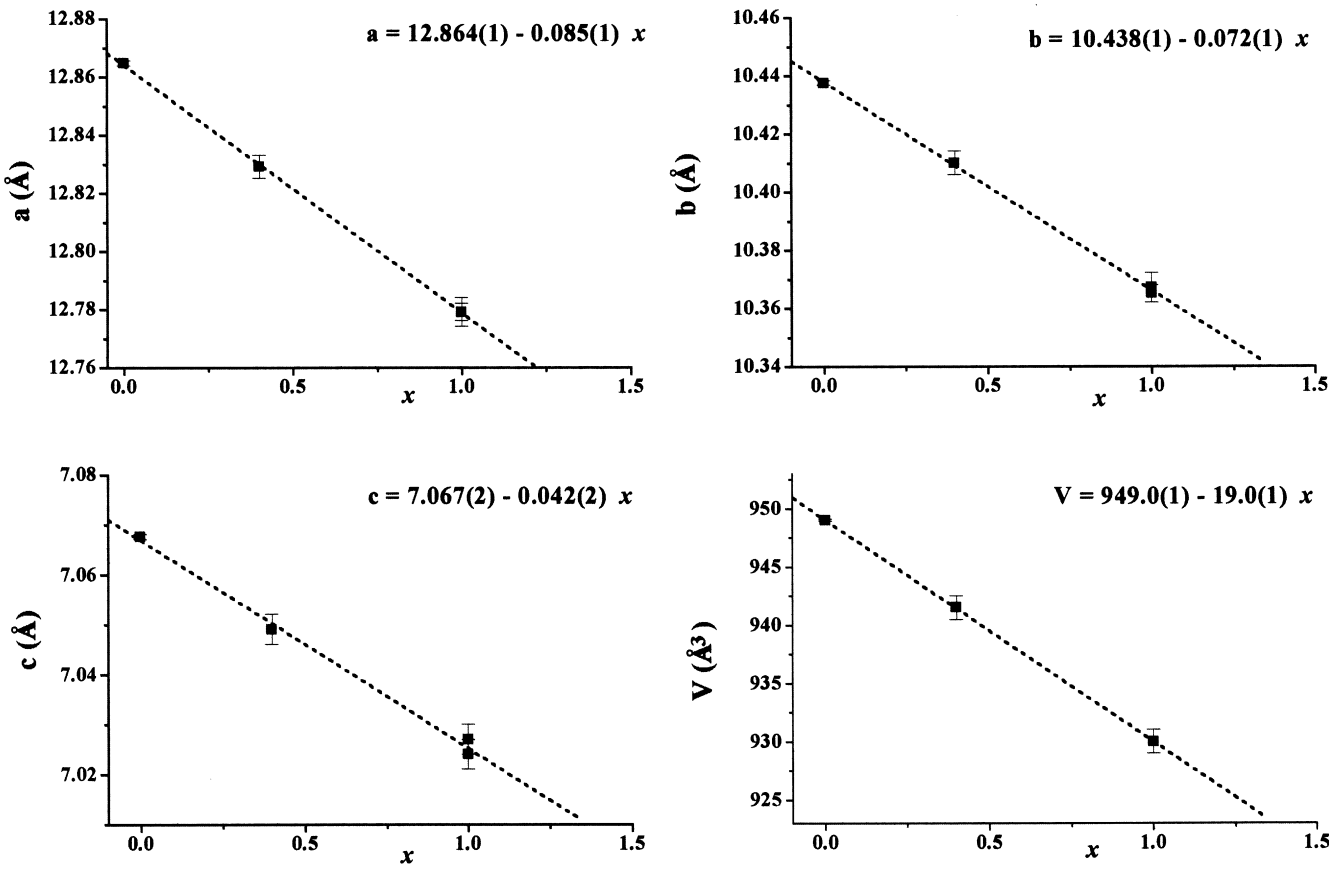

Fig. 2. Variation of unit cell parameters and cell volume of thorium-plutonium (IV) phosphate-diphosphate as a function of x value.

4. Conclusions

Thorium-uranium solid solutions $Th_{4-x}U_x(PO_4)_4P_2O_7$ have been synthesized up to $x=3.0$. Starting from these results, thorium phosphate-diphosphate (TPD) unit cell parameters have been refined and their evolution as well the evolution of the cell volume in terms of x value have been established. The maximum x value of thorium replaced by other tetravalent elements can be calculated taking into account their ionic radii.

Thorium-plutonium phosphate-diphosphate solid solutions have been synthesized for several values in the range $0<x<1$. In this case, the TPD lattice undergoes greater deformation than in the ThO_2-UO_2-P_2O_5 system. The calculated maximum x value is equal to 1.67 which suggests that a solid solution of composition $Th_{2.4}Pu_{1.6}(PO_4)_4P_2O_7$ could be obtained. Thus, solid solutions such as $Th_{2.4}Pu_{1.6}(PO_4)_4P_2O_7$ and $Th_{1.6}Pu_{2.4}(PO_4)_4P_2O_7$ are now under progress.

Analogues to the TPD compound $M_4(PO_4)_4P_2O_7$ (M= U, Pu) have not been synthesized: the final products are always polyphase.

The results obtained show that thorium phosphate-diphosphate may be used as a host matrix for large amounts of uranium and plutonium. Leaching tests of TPD and TUPD have been already published [7], those of TPPD are in progress. Irradiation effects on pure matrix and solid solutions are also under study.

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