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Plutonium and americium monazite materials: Solid state synthesis and X-ray diffraction study

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Abstract

High-temperature solid state syntheses of monazite powders containing plutonium (III), plutonium (IV) and americium (III) were performed. Resulting powders were characterized by X-ray diffraction. $Pu^{3+}PO_4$ was readily obtained as a single phase by heating a $Pu^{4+}O_2$–$NH_4H_2PO_4$ mixture under argon atmosphere. Traces of tetravalent plutonium phosphate $Pu^{4+}P_2O_7$ were detected when synthesized under air atmosphere. The incorporation of (Pu^{4+}, Ca^{2+}) in the monazite structure was investigated under air and argon atmosphere. We showed that Pu^{4+} is fully reduced in Pu^{3+} under argon atmosphere whereas, under air, the compound with the formula $Pu^{3+}_{0.4}Pu^{4+}_{0.3}Ca^{2+}_{0.3}PO_4$ was obtained. Pure $Am^{3+}PO_4$ was also synthesized under argon atmosphere. X-ray patterns revealed a complete amorphisation of the monazite structure at a relatively low cumulative alpha dose for $^{241}AmPO_4$.

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1. Introduction

In the framework of the 1991 French law regarding nuclear waste management, several studies have been carried out in order to elaborate crystalline matrices for specific immobilization of high-level and long-lived radioactive elements (i.e., minor actinides Np, Am and Cm). Monazite, a light lanthanide orthophosphate with general formula $LnPO_4$ (where Ln means lanthanide), has been proposed as a host matrix mainly due to its high-resistance to self-irradiation and its low solubility [1,2]. Monazite crystallizes in the monoclinic space group $P2_1/n$ [3]. In this structure, trivalent actinides Ac^{3+} are incorporated by substitution with the trivalent cation Ln^{3+}:

$$Ln^{3+}PO_4 \rightarrow Ac^{3+}PO_4 \qquad (1)$$

In the available literature, monazite powders containing trivalent actinides were mostly synthesized using wet chemical routes. Bjorklund reported

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the first work about synthetic actinide monazite [4]. $Pu^{3+}PO_4$ was prepared by precipitation and high-temperature decomposition of hexagonal Pu^{3+}-PO_4–$0.5H_2O$. Keller and Walter [5] used the same route to prepare $Am^{3+}PO_4$ and $Cm^{3+}PO_4$. Hobart et al. [6] synthesized monazite containing Am, Cm, Cf, Bk and Es by precipitation from a solution of $(NH_4)_2HPO_4$ followed by calcination at 1100 °C. More recently, Burakov et al. [7] studied (La, $^{238}Pu^{3+}$)PO_4 also synthesized by precipitation. To our knowledge, the high-temperature solid state route described in this paper is mentioned for the first time. Moreover, the effect of the atmosphere was never taken into account during the elaboration process, especially for (Pu)-monazite materials.

The incorporation of tetravalent cation Ac^{4+} in the monazite structure is also possible. This requires a simultaneous incorporation of an equivalent amount of bivalent cation B^{2+} as a charge compensator:

$$Ln^{3+}PO_4 \rightarrow Ac^{4+}_{0.5}B^{2+}_{0.5}PO_4 \quad (2)$$

This compound, also called brabantite, is isostructural of monazite.

According to Podor's work [8,9], the upper limit of tetravalent element incorporation in the monazite structure is associated to the elements ionic radius in the ninefold coordination (R^{IX}). $Ln^{3+}_{1-2x}B^{2+}_xAc^{4+}_x$-$PO_4$ exists in the monazite structure if $1.216\ \text{Å} \geqslant R_{\text{average}} \geqslant 1.107\ \text{Å}$ and $1.238 \geqslant R_{\text{ratio}} \geqslant 1$ with

$$R_{\text{average}} = (1-2x)R^{IX}_{Ln^{3+}} + xR^{IX}_{B^{2+}} + xR^{IX}_{Ac^{4+}}, \quad (3)$$

$$R_{\text{ratio}} = \frac{(1-2x)R^{IX}_{Ln^{3+}} + xR^{IX}_{B^{2+}}}{(1-2x)R^{IX}_{Ln^{3+}} + xR^{IX}_{Ac^{4+}}}. \quad (4)$$

Ionic radii of Np^{4+} and Pu^{4+} in the ninefold coordination are still unknown but can be extrapolated (Table 1) from the values of Pa^{4+} and U^{4+} given by Shannon [10], with the hypothesis that the evolution of the actinide ionic radius is linear versus the atomic number, as in the eightfold coordination (Fig. 1). Based upon ionic radii and according to Eqs. (3) and (4), the maximum incorporation ($x_{\max}$) of tetravalent actinides in the monazite structure can be estimated (Table 1). Based upon sterical considerations only, it appears that Th^{4+}, U^{4+}, Np^{4+} and Pu^{4+} could be nearly fully incorporated in their tetravalent form in the monazite structure. $Th^{4+}_{0.5}Ca^{2+}_{0.5}PO^4$, $U^{4+}_{0.5}Ca^{2+}_{0.5}PO_4$ and $Np^{4+}_{0.5}Ca^{2+}_{0.5}PO_4$, have already been synthesized [8,9,11,12], but no work on the synthesis of $Pu^{4+}_{0.5}Ca^{2+}_{0.5}PO_4$ has been reported.

Table 1
Ionic radii of some tetravalent actinides in the ninefold coordination and their maximum incorporation in the La-monazite ($La^{3+}_{1-2x}Ac^{4+}_xCa^{2+}_xPO_4$)

	Th^{4+}	U^{4+}	Np^{4+} (extrapolated)	Pu^{4+} (extrapolated)
$R^{IX}_{Ac^{4+}}$	1.09	1.05	1.03	1.01
$x_{\max}$	0.5	0.5	0.49	0.45

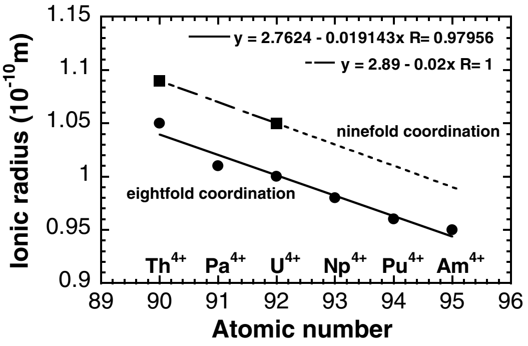

Fig. 1. Ionic radii of tetravalent actinides in eightfold and ninefold coordinations.

The aim of the current work was to experiment the solid state synthesis protocol developed for lanthanide elements described elsewhere [13,14] for the elaboration of Am^{3+}, Pu^{3+} and Pu^{4+} monazite orthophosphates powders. The resulting materials were characterized by X-ray diffraction. In addition, in the case of (Pu)-monazite, the role of the atmosphere was investigated.

2. Materials and methods

All experiments were performed in a glove box at the LEFCA, a nuclear facility from CEA Cadarache, France. Monazite powders were prepared by high-temperature solid state route according to the following expected reactions:

$$\text{Exp. A: } Pu^{4+}O_2 + NH_4H_2PO_4 \rightarrow Pu^{3+}PO_4 + NH_3\uparrow + {}^{3}/{}_{2}H_2O\uparrow + {}^{1}/{}_{4}O_2\uparrow \quad (5)$$

$$\text{Exp. B: } {}^{1}/{}_{2}Pu^{4+}O_2 + {}^{1}/{}_{2}CaO + NH_4H_2PO_4 \rightarrow Pu^{4+}_{0.5}Ca^{2+}_{0.5}PO_4 + NH_3\uparrow + {}^{3}/{}_{2}H_2O\uparrow \quad (6)$$

$$\text{Exp. C: } Am^{4+}O_2 + NH_4H_2PO_4 \rightarrow Am^{3+}PO_4 + NH_3\uparrow + {}^{3}/{}_{2}H_2O\uparrow + {}^{1}/{}_{4}O_2\uparrow \quad (7)$$

So as to protect oneself from γ irradiation, americium dioxide was handled in a dedicated glovebox (i.e., leaded glass and gloves) and all compounds were prepared on the scale of a few milligrams. Prior to synthesis, polycrystalline PuO_2 and AmO_2 were manually ground/mixed and calcined in a platinum crucible under oxidizing atmosphere (i.e., air) at 1173 K for 4 h so as to bring the O/M ratio to 2 and to get rid of impurities. For each experiment, the initial compounds were mixed in the appropriate ratios and calcined in platinum crucibles under the suitable atmosphere at 1673 K for 2 h, and the entire process repeated. The furnace was heated and cooled at the rate of 4 K/h. All syntheses were performed under air and argon atmosphere, except Exp. C which was only carried out under argon atmosphere since it is now well-known that americium only exists in the monazite structure in the trivalent state [15].

Powders were characterized by X-ray diffraction at room temperature using a high-resolution Siemens D5000 X-ray diffractometer with a curved quartz monochromator and copper radiation from a conventional tube source. Radioactive powders were analysed using a specific sample preparation and a sealed sample-holder described elsewhere [16]. The powder is embedded in epoxy, involving the presence of a high-level diffusion background in the X-ray patterns.

Cell parameters were determined from the X-ray patterns refinement using the Windows software PowderCell. The cell volume of the monazite structure was calculated from the monoclinic cell parameters (a, b, c and β) according to the following equation:

$$V = a \times b \times c \times \sin\beta. \quad (8)$$

The theoretical density was calculated with the hypothesis that there is no structural defect in the monazite structure according to the following reaction:

$$d = \frac{MZ}{NV}. \quad (9)$$

In this equation, M is the molecular weight, Z is the number of the structural unit per cell ($Z = 4$ in the monazite structure), N is the Avogadro number and V is the cell volume.

3. Results and discussion

3.1. Synthesis of $Pu^{3+}PO_4$

X-ray diffraction patterns revealed a monazite structure as the main phase (Fig. 2) for both reactions (i.e., air and argon atmosphere). The measured cell parameters of the monazite phase are in good agreement with those proposed by Roof [17] (Table 2).

Under argon atmosphere, the resulting material was monophasic as opposed to the one elaborated under air atmosphere for which a secondary phase was identified as a tetravalent plutonium phosphate $Pu^{4+}P_2O_7$ revealing that under the considered thermodynamic conditions, Pu^{4+} is not fully reduced in Pu^{3+}. This is in agreement with our previous results showing that $Ce^{4+}P_2O_7$ first appears during calcination and then slowly decomposes in $Ce^{3+}PO_4$ [13,14]. This also tends to prove that the decomposition of $Pu^{4+}P_2O_7$ is the limiting step in the formation of $Pu^{3+}PO_4$, which is in agreement with Bjorklund and Bamberger who showed that the apparent stability of $Pu^{4+}P_2O_7$ in air is due to its very slow rate of decomposition in $Pu^{3+}PO_4$ [4,18]. Therefore, it is better to carry out the reaction under argon atmosphere in order to obtain more rapidly pure $Pu^{3+}PO_4$ powder by high-temperature solid state route from a $Pu^{4+}O_2$–$NH_4H_2PO_4$ starting mixture.

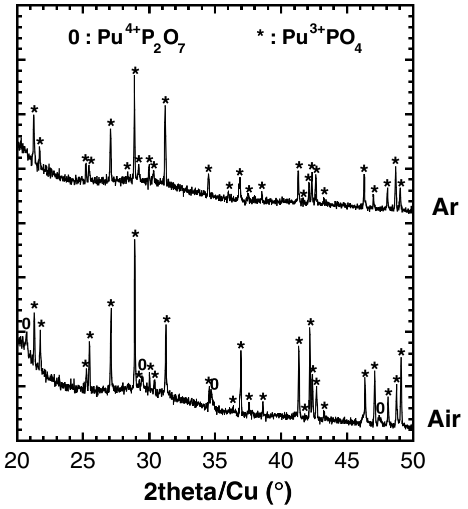

Fig. 2. X-ray diffraction patterns of $Pu^{3+}PO_4$ powders synthesized under argon and air atmosphere.

Table 2
Cell parameters of the synthesized monazite compared to values from the literature

		a (nm)	b (nm)	c (nm)	β (nm)	$V \times 10^3$ (nm^3)	d
Exp. A ($Pu^{3+}PO_4$)	Air	0.674	0.695	0.642	103.70	292.17	7.592
	Argon	0.676	0.698	0.644	103.66	295.27	7.513
Exp. B ($Pu^{3+}_{1-2x}Pu^{4+}_xCa^{2+}_xPO_4$)	Air	0.667	0.687	0.636	103.99	282.79	Function of x
	Argon	0.674	0.695	0.643	103.75	292.57	Function of x
Exp. C ($Am^{3+}PO_4$)	Argon	0.674	0.696	0.643	103.75	295.11	7.509
$Pu^{3+}PO_4$ – [17]	Argon	0.673	0.700	0.642	103.80	293.72	7.666
$Am^{3+}PO_4$ – [5]	Argon	0.673	0.693	0.641	103.50	290.70	7.66

3.2. Incorporation of Pu^{4+} in the monazite structure (Exp. B)

The incorporation of tetravalent plutonium in the monazite structure was tested with the calcium as a charge compensator. According to our previous works dealing with tetravalent cerium incorporation in the monazite structure by the same route [19], Eq. (6) should be modified in order to take into account that the incorporation could be incomplete.

$$\begin{aligned}
&\frac{1}{2}PuO_2 + \frac{1}{2}CaO + NH_4H_2PO_4 \\
&\quad \rightarrow \frac{1}{2(1-x)}Pu^{3+}_{1-2x}Pu^{4+}_xCa^{2+}_xPO_4 \\
&\quad + \frac{1-2x}{4(1-x)}Ca_2P_2O_7 + NH_3\uparrow \\
&\quad + \frac{3}{2}H_2O\uparrow + \frac{1-2x}{8(1-x)}O_2\uparrow \qquad (10)
\end{aligned}$$

In this equation, $x = 0$ if the plutonium is completely reduced ($Pu^{3+}PO_4$) and $x = 0.5$ if the plutonium is incorporated in the monazite structure only in its tetravalent form ($Pu^{4+}_{0.5}Ca^{2+}_{0.5}PO_4$).

The incorporation of Pu^{4+} in the monazite structure was tested under air and argon atmosphere. X-ray diffraction patterns of the resulting materials are both representative of a monazite structure (Fig. 3). Considering the low intensity of the diffraction peaks, no other phases are observable. Under air atmosphere, cell parameters of the resulting powder are lower than those of $Pu^{3+}PO_4$, which is in agreement with an incorporation of Pu^{4+} in the monazite structure, since Pu^{4+} is smaller than Pu^{3+}. On the other hand, cell parameters of the monazite powder obtained under argon atmosphere are close to those of $Pu^{3+}PO_4$. The main difficulty is now to estimate the Pu^{4+} amount (x in Eq. (10)) incorporated in the monazite structure. It is necessary to establish the relationship between x and the cell parameters of the monazite phase. Recently, Terra showed that in the case of the $La^{3+}_{1-2x}Th^{4+}_xCa^{2+}_xPO_4$ and $La^{3+}_{1-2x}U^{4+}_xCa^{2+}_xPO_4$ solid solutions, the evolution of the cell parameters of the monazite phase changes linearly as a function of x [11]. One can suppose that a similar evolution should be observed in the case of $Pu^{3+}_{1-2x}Pu^{4+}_xCa^{2+}_xPO_4$ solid solution. It is thus essential to determine the cell parameters of two known compositions to establish their dependence with respect to x. $Pu^{3+}PO_4$ ($x = 0$) cell parameters were determined in the first part of the present work. The knowledge of the cell parameters of $Pu^{4+}_{0.5}Ca^{2+}_{0.5}PO_4$ can be extrapolated (open circles in Fig. 4) from the two compositions of the $Ca^{2+}_{0.5}Np^{4+}_{0.5-y}Pu^{4+}_yPO_4$ solid solution reported by Tabuteau, assuming a similar linear evolution [13]. It is thus possible to estimate the Pu^{4+} incorporation ratio in the synthesized powders from their cell parameters (Fig. 4 right). Results show that under

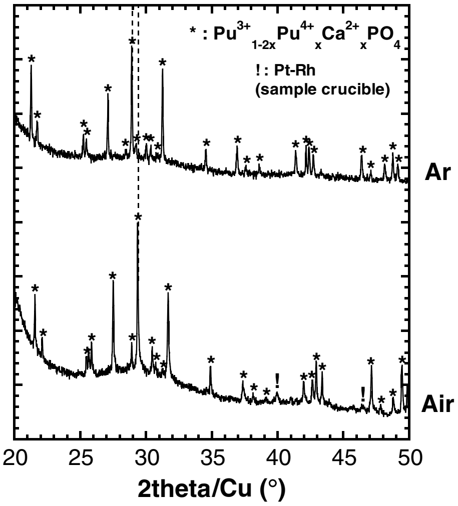

Fig. 3. X-ray diffraction patterns of $Pu^{3+}_{1-2x}Pu^{4+}_xCa^{2+}_xPO_4$ powders synthesized under argon and air atmosphere.

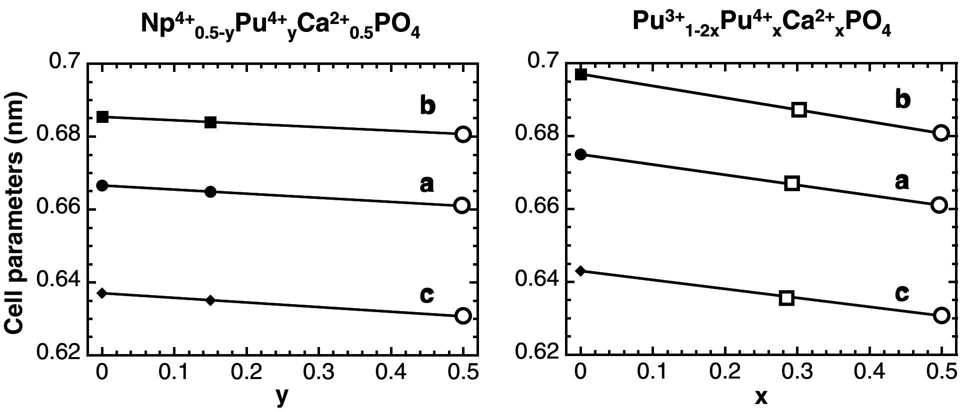

Fig. 4. Lattice parameters of $Np^{4+}_{1-y}Pu^{4+}_{y}Ca^{2+}_{0.5}PO_4$ and $Pu^{3+}_{1-2x}Pu^{4+}_{x}Ca^{2+}_{x}PO_4$ solid solutions versus y and x.

air, plutonium can be introduced in the tetravalent state in the monazite structure to a rate up to 40% ($x = 0.3$, squares in Fig. 4). On the other hand, under argon atmosphere, x is close to 0. Thus, under inert conditions, plutonium is completely reduced in Pu^{3+}. For both experiments, the incorporation of the plutonium in its tetravalent state was incomplete. This also supposes that a part of calcium, introduced in the starting mixture as a charge compensator element, was not incorporated in the monazite structure, forming a secondary phase, probably the $Ca_2P_2O_7$ phosphate which was not observable in our materials. However, higher intensity peaks of $Ca_2P_2O_7$ and the Pu-monazite phase are superimposed making the detection of a hypothetical secondary phase difficult. Nevertheless, after a 1400 °C heating, a fused bead was visually observed, possibly accounting for $Ca_2P_2O_7$ formation as its melting temperature is close to 1300 °C [13,14].

3.3. Synthesis of $Am^{3+}PO_4$ and alpha self-irradiation of the monazite structure (Exp. C)

The resulting product of the calcination of the AmO_2–$NH_4H_2PO_4$ mixture (Exp. C) at 1400 °C for 2 h under argon atmosphere is pure monazite $AmPO_4$ as expected (Fig. 5). The cell parameters are very close to those of $Pu^{3+}PO_4$ (Table 2). ^{241}Am is an alpha emitter with a sufficient activity allowing the investigation of the behaviour of the monazite structure under alpha self-irradiation over a rather short duration. The monazite structure remains intact until a cumulative dose of close to 10^{24} α decay m^{-3} which corresponds to a 20 days irradiation (Fig. 5). For a higher cumulative dose, the structure progressively turns amorphous. No more diffraction peaks could be observed after 300 days and a dose of 1.65×10^{25} α decay m^{-3}. All these results are in good accordance with those of Burakov who recently showed that $^{238}PuPO_4$ became completely amorphous at a relatively low dose of 4.2×10^{24} α decay m^{-3} [7]. This value is lower than that obtained for $^{241}AmPO_4$.

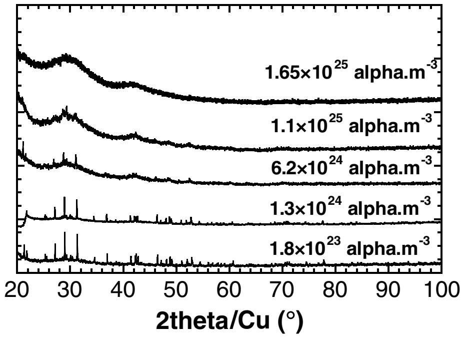

Fig. 5. X-ray diffraction diagrams of $Am^{3+}PO_4$ powders for different alpha cumulative doses.

It could be surprising to observe that monazite, a proposed nuclear waste matrix, became completely amorphous for such low cumulative alpha doses. Moreover, this observation, carried out on synthetic materials, goes against the results obtained on natural monazite. Indeed, well-crystallized 2 billions aged (U, Th)-monazite samples were found [20]. It is now well-known that the behaviour of monazite under irradiation is governed by two opposite effects: creation of structural defects by alpha particles and self-annealing at relatively low temperature [1]. Thus, the monazite structure remains crystalline as long as the creation of defects is entirely compensated by self-annealing. The behaviour of the monazite structure under irradiation is dependant on the radionuclide activity and its incorporation rate. Burakov showed that $^{238}PuPO_4$ became completely amorphous whereas $LaPO_4$ doped with 8.1 wt% of ^{238}Pu remains crystalline. This could also explain the difference observed between $^{238}PuPO_4$ and $^{241}AmPO_4$. The former becomes amorphous at a lower α dose than $^{241}AmPO_4$ due to ^{238}Pu and ^{241}Am specific decay periods (87.74 years and 432.6 years, respectively). If using monazite as a minor actinides host phase, the actinide incorporation ratio will not exceed 10 wt%. More exhaustive investigations have to be carried out on these materials to be representative of nuclear waste conditioning matrix.

4. Conclusion

This study was a straight continuation of a work on the synthesis by high-temperature solid state route of monazite powders carried out with actinides chemical analogues. The developed protocol was applied to the synthesis of monazite powders containing plutonium (III), plutonium (IV) and americium (III). The calcination of a $Pu^{4+}O_2$–$NH_4H_2PO_4$ mixture at 1400 °C for 2 h lead to a pure monazite $Pu^{3+}PO_4$ powder under argon atmosphere whereas traces of $Pu^{4+}P_2O_7$ were detected under air atmosphere. This could be explained by the slow rate of decomposition of $Pu^{4+}P_2O_7$ into $Pu^{3+}PO_4$ under these oxidizing conditions. The incorporation of the Pu^{4+}/Ca^{2+} couple in the monazite structure was investigated as a function of the atmosphere. All Pu^{4+} was reduced into Pu^{3+} under argon atmosphere whereas 40% of the plutonium remains in its tetravalent state under air, leading to a monazite with a chemical composition of $Pu^{3+}_{0.4}Pu^{4+}_{0.3}Ca^{2+}_{0.3}PO_4$. That demonstrates the existence of a strong correlation between the oxygen partial pressure (P_{O_2}) and the Pu^{4+} incorporation in the monazite structure. Complementary studies are necessary to fully apprehend this issue and determine the minimum value of P_{O_2} corresponding to a complete incorporation of Pu^{4+} in the monazite structure. The solid state synthesis was also tested on $^{241}AmPO_4$ resulting in a pure monazite. The behaviour of the monazite structure under alpha self-irradiation was investigated by XRD. We observed a complete amorphisation of the crystalline structure after 300 days and a cumulative dose of 1.65×10^{25} α decay m^{-3}. However, these results do not question the interest of the monazite material for a radionuclide conditioning matrix. It is on the other hand essential to determine the maximum amount of americium loadable in the monazite structure for which the structural defects creation is entirely compensated by self-annealing.

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