

Formation of PuSiO₄ under hydrothermal conditions

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SUPPORTING INFORMATION

Experimental procedures

Syntheses in ligand free reactive media

Syntheses were carried out by adapting the protocol we recently described for the ThSiO₄ synthesis.¹ An aqueous silicate solution was prepared by dissolving Na₂SiO₃ into water, then a volume of Pu(IV) nitric acid solution was added to obtain a solution with C_{Pu} = 0.21 mol·L⁻¹ and a silicate excess of 3 mol.% in the reacting mixture (synthesis pathway A1 in **Table S2**). The pH was then adjusted to the final expected value with 8 mol·L⁻¹ NaOH.

All of the mixtures were prepared under aerated conditions and put into 23 mL Teflon lined reactors in Parr autoclaves and then treated in hydrothermal conditions for 7 to 15 days at a temperature ranging from 60°C to 237°C under autogenous pressure (under air atmosphere). Thus, the precipitates obtained were separated from the supernatant by centrifugation for 1 min at 14 000 rpm, washed twice with deionized water and once with ethanol, and then finally dried overnight under the glovebox atmosphere.

Syntheses in carbonate ion rich reactive media

Syntheses were carried out by adapting the protocol we recently described for the ThSiO_4 synthesis² and the conditions defined by Mesbah et al. for the USiO_4 synthesis.³ An aqueous silicate solution was prepared by dissolving Na_2SiO_3 into water, then a volume of Pu(IV) nitric acid solution was added to obtain a solution with $C_{\text{Pu}} = 0.21 \text{ mol}\cdot\text{L}^{-1}$ and a silicate excess of 3 mol.% in the reacting mixture. The pH was then adjusted with $8 \text{ mol}\cdot\text{L}^{-1}$ NaOH to be close to pH = 8 (synthesis pathway B2 in **Table S2**) or in order to obtain a pH value between pH = 10 and pH = 12 (synthesis pathway B3 in **Table S2**). Controlled amounts of NaHCO_3 were then added to obtain a pH close to pH = 8.7.

Additional experiments were performed starting from Pu(IV) stabilized in a carbonate ions rich aqueous solution. Then this solution was put in contact with an aqueous silicate solution in order to obtain a solution with $C_{\text{Pu}} = 0.21 \text{ mol}\cdot\text{L}^{-1}$ and a silicate excess of 3 mol.% in the reacting mixture (synthesis pathway B4 in **Table S2**).

All of the mixtures were prepared under air atmosphere and put into 23 mL Teflon lined reactors in Parr autoclaves and then treated in hydrothermal conditions for 10 to 15 days at a temperature ranging from 150°C to 237°C under autogenous pressure (under air atmosphere). Thus, the precipitates obtained were separated from the supernatant by centrifugation for 1 min at 14 000 rpm, washed twice with deionized water and once with ethanol, and then finally dried overnight under the glovebox atmosphere.

Table S1 Unit cell parameters determined by Rietveld refinement.

Silicate Phase	Space group	Lattice parameters				
		a	b	c	β	V
Pu _{4.67} (SiO ₄) ₃ O 4, 5	P6 ₃ /m	9.572(1) Å		7.005(2) Å		555.8(1) Å ³
		9.589 Å		7.019 Å		
		9.599 Å		7.020 Å		
Pu ₂ Si ₂ O ₇ 6	P2 ₁ /n	8.646(1) Å	12.913(2) Å	5.390(1) Å	90.14(1)°	601.8(1) Å ³
		8.664 Å	12.96 Å	5.397 Å		
PuSiO ₄ 7, 8	I4 ₁ /amd	6.9676(9) Å		6.2007(9) Å		301.05(7) Å ³
		6.906(6) Å		6.221(6) Å		296.6(5) Å ³

Table S2 Constants of complexation of An(IV)/Ce(IV) limit complexes with carbonates ions at I = 0 (25 °C).

Ln/An	Ionic radii _{viii} M ⁴⁺ (Å) ⁹	Log(β°_5) ^a	Log(β°_6) ^a	Reference
Pu	0.96	35.7 ± 1.1	—	10
Ce	0.97	≤ 41.8 ± 0.5	42.2 ± 0.5	11
U	1.00	34.0 ± 0.9	—	10
Th	1.05	31.0 ± 0.7	—	12

^a β°_n is associated with the reaction $An^{4+} + nCO_3^{2-} = An(CO_3)_n^{(2n-4)-}$.

Table S3. Thermodynamic data for the main reactions involving Pu(III), Pu(IV), hydroxide and silicate complexes in the considered system at I = 0 (25°C).

Reaction	log K°
$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_2\text{SiO}_4^{2-} + 2 \text{H}^+$	- 23.14 ¹³
$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+$	- 9.84 ¹³
$2 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_2\text{O}_2(\text{OH})_5^- + \text{H}^+ + \text{H}_2\text{O}$	- 8.50 ¹³
$2 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_2\text{O}_3(\text{OH})_4^{2-} + 2 \text{H}^+ + \text{H}_2\text{O}$	- 19.40 ¹³
$3 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_3\text{O}_5(\text{OH})_5^{3-} + 3 \text{H}^+ + 2\text{H}_2\text{O}$	- 29.40 ¹³
$3 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_3\text{O}_6(\text{OH})_3^{3-} + 3 \text{H}^+ + 3 \text{H}_2\text{O}$	- 29.30 ¹³
$4 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_4\text{O}_6(\text{OH})_6^{2-} + 2 \text{H}^+ + 4 \text{H}_2\text{O}$	- 15.60 ¹³
$4 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_4\text{O}_7(\text{OH})_6^{4-} + 4 \text{H}^+ + 3 \text{H}_2\text{O}$	- 39.10 ¹³
$4 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_4\text{O}_8(\text{OH})_4^{4-} + 4 \text{H}^+ + 4 \text{H}_2\text{O}$	- 39.20 ¹³
$6 \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Si}_6\text{O}_{15}^{6-} + 6 \text{H}^+ + 9 \text{H}_2\text{O}$	- 61.80 ¹³
$\text{Pu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})^{2+} + \text{H}^+$	- 6.9 ¹⁴
$\text{Pu}^{3+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})_2^+ + 2 \text{H}^+$	- 15.1 ¹⁴
$\text{Pu}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})_3 + 3 \text{H}^+$	- 25.3 ¹⁴
$\text{Pu}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})^{3+} + \text{H}^+$	0.6 ¹⁴
$\text{Pu}^{4+} + 2 \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})_2^{2+} + 2 \text{H}^+$	0.6 ¹⁴
$\text{Pu}^{4+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})_3^+ + 3 \text{H}^+$	- 2.3 ¹⁴
$\text{Pu}^{4+} + 4 \text{H}_2\text{O} \rightleftharpoons \text{Pu}(\text{OH})_4 + 4 \text{H}^+$	- 4.1 ¹⁴
$\text{Pu}^{3+} + \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Pu}(\text{OSi}(\text{OH})_3)_2^+ + \text{H}^+$	- 1.7 (this study – Figure S16)
$\text{Pu}^{4+} + \text{H}_4\text{SiO}_4 \rightleftharpoons \text{Pu}(\text{OSi}(\text{OH})_3)_3^+ + \text{H}^+$	2.0 ¹⁵
$\text{Pu}(\text{OH})_3, \text{solid} + 3 \text{H}^+ = \text{Pu}^{3+} + 3 \text{H}_2\text{O}$	15.8 ¹⁴
$\text{PuO}_2 \cdot x\text{H}_2\text{O}_{\text{solid}} + (2-x) \text{H}_2\text{O} = \text{Pu}^{4+} + 4 \text{HO}^-$	- 58.5 ¹⁶

Table S4. Equilibrium constants of M(III)- and M(IV)-hydroxide and silicate complexes at I = 0 (25°C).

Reaction	log β°
$\text{Eu}^{3+} + \text{HO}^- \rightleftharpoons \text{Eu}(\text{OH})^{2+}$	6.2 ¹⁷
$\text{Eu}^{3+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Eu}(\text{OSi}(\text{OH})_3)^{2+}$	8.04 ± 0.08 ¹⁸
$\text{Am}^{3+} + \text{HO}^- \rightleftharpoons \text{Am}(\text{OH})^{2+}$	7.6 ± 0.7 ¹⁰
$\text{Am}^{3+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Am}(\text{OSi}(\text{OH})_3)^{2+}$	8.23 ± 0.09 ¹⁸
$\text{Cm}^{3+} + \text{HO}^- \rightleftharpoons \text{Cm}(\text{OH})^{2+}$	6.4 ± 0.1 ¹⁰
$\text{Cm}^{3+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Cm}(\text{OSi}(\text{OH})_3)^{2+}$	7.94 ± 0.06 ¹⁸
$\text{Al}^{3+} + \text{HO}^- \rightleftharpoons \text{Al}(\text{OH})^{2+}$	9.05 ¹³
$\text{Al}^{3+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Al}(\text{OSi}(\text{OH})_3)^{2+}$	8.73 ± 0.06 ¹⁹
$\text{Fe}^{3+} + \text{HO}^- \rightleftharpoons \text{Fe}(\text{OH})^{2+}$	11.81 ¹³
$\text{Fe}^{3+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Fe}(\text{OSi}(\text{OH})_3)^{2+}$	9.33 ± 0.26 ²⁰
$\text{Pu}^{3+} + \text{HO}^- \rightleftharpoons \text{Pu}(\text{OH})^{2+}$	7.1 ± 0.3 ¹⁴
$\text{Pu}^{3+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Pu}(\text{OSi}(\text{OH})_3)^{2+}$	8.2 (this study – Figure S16)
$\text{Pu}^{4+} + \text{H}_3\text{SiO}_4^- \rightleftharpoons \text{Pu}(\text{OSi}(\text{OH})_3)^{3+}$	11.8 ¹⁵

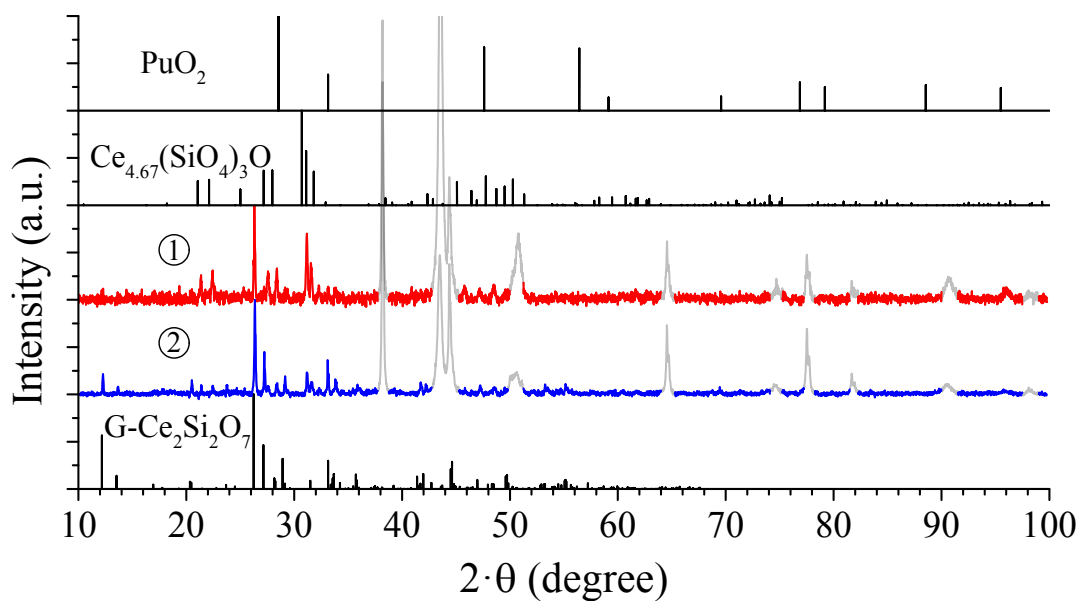


Figure S1 PXRD patterns obtained for $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$ (1) and $\text{Pu}_2\text{Si}_2\text{O}_7$ (2) prepared after a 9 hour-long heat treatment at 1350°C under Ar-H_2 (4%) atmosphere. Characteristic XRD lines of PuO_2 , $\text{G-Ce}_2\text{Si}_2\text{O}_7$ and $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ were extracted from references 21, 22 and 22, respectively.

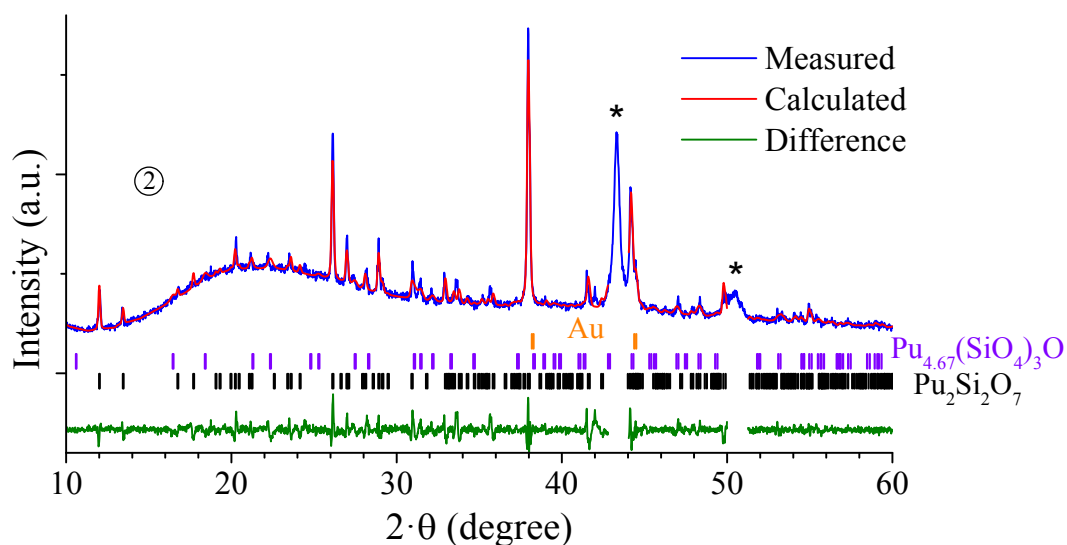


Figure S2 X-ray powder diffraction profile, calculated and difference profile after Rietveld refinement for a $\text{Pu}_2\text{Si}_2\text{O}_7$ sample (2) prepared after a 9 hour-long heat treatment at 1350°C under Ar-H_2 (4%) atmosphere. XRD lines of sample holder are pointed out by an asterisk.

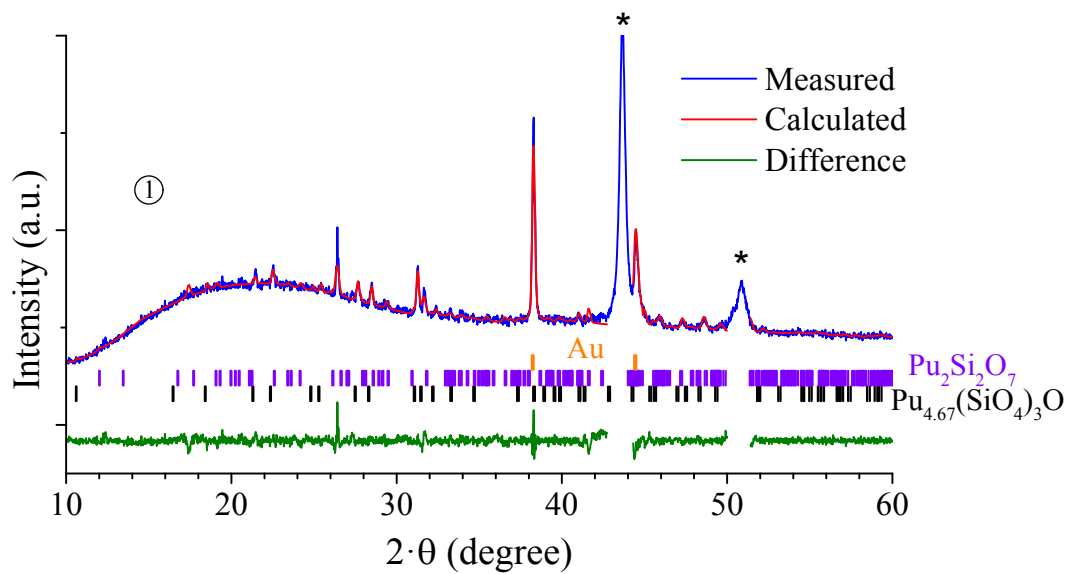
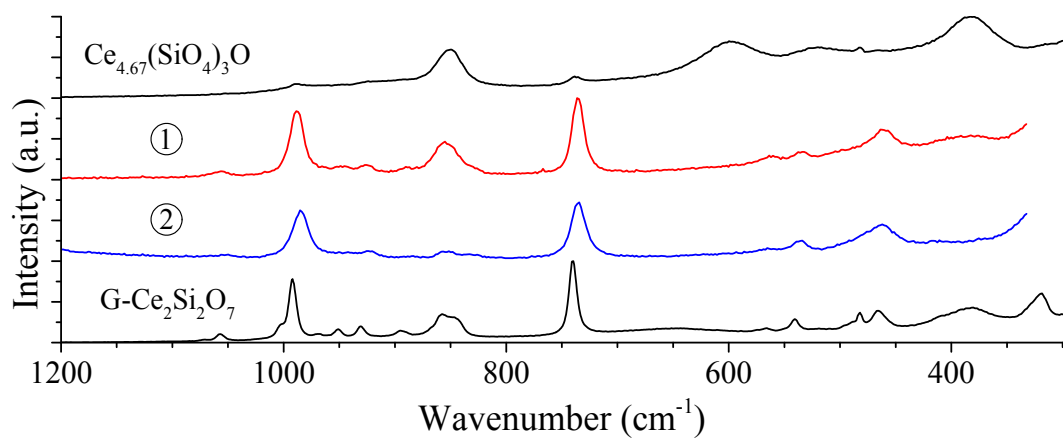


Figure S3 X-ray powder diffraction profile, calculated and difference profile after Rietveld refinement for a Pu_{4.67}(SiO₄)₃O sample (1) prepared after a 9 hour-long heat treatment at 1350°C under Ar-H₂ (4%) atmosphere. XRD lines of sample holder are pointed out by an asterisk.



(b)

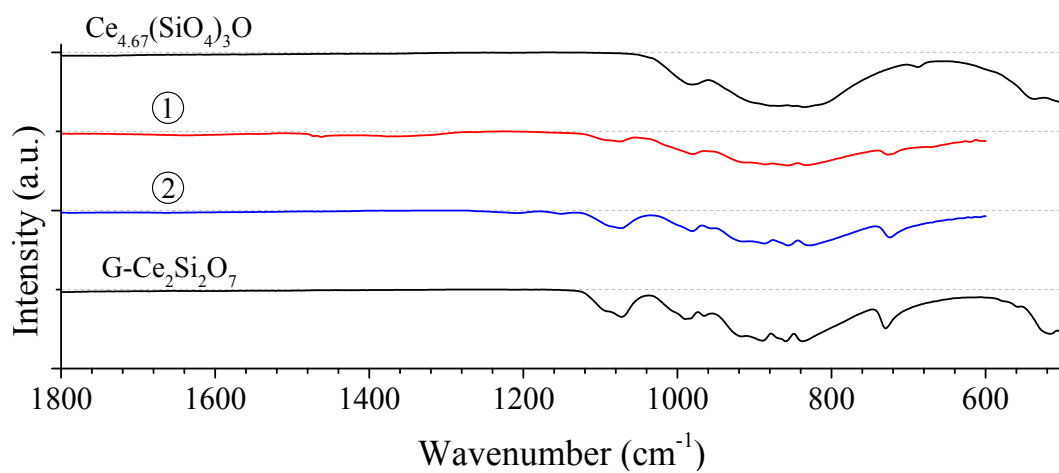


Figure S4 Raman (a) and infrared (b) spectra obtained for $Pu_{4.67}(SiO_4)_3O$ (1) and $Pu_2Si_2O_7$ (2) prepared after a 9 hour-long heat treatment at 1350°C under Ar-H₂ (4%) atmosphere. $G-Ce_2Si_2O_7$ and $Ce_{4.67}(SiO_4)_3O$ were extracted from reference 23.

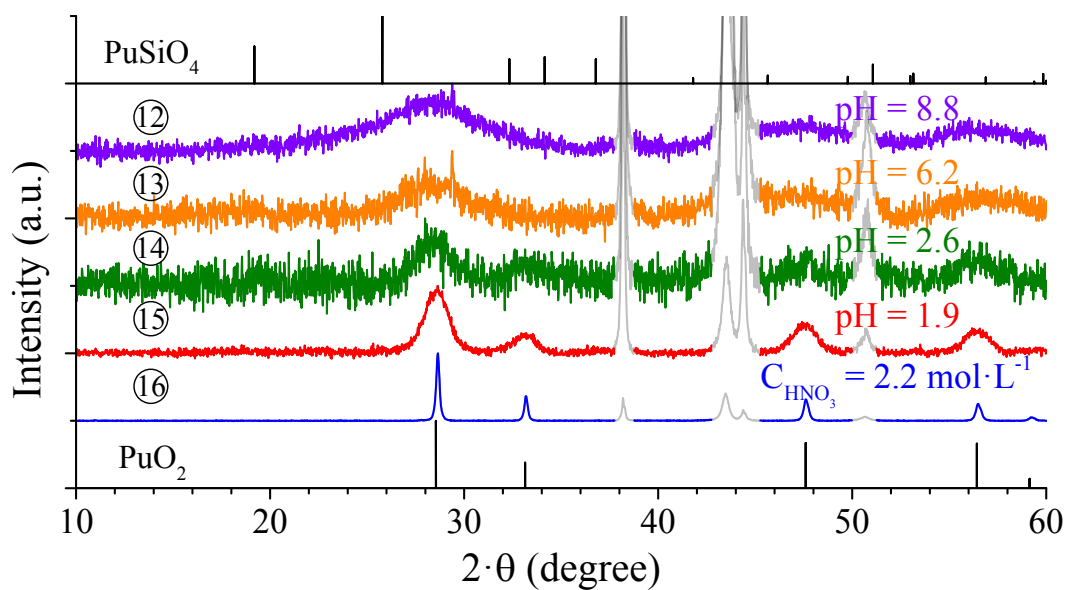


Figure S5 PXRD patterns obtained for samples prepared under hydrothermal conditions ($T = 150^{\circ}\text{C}$) with starting silicate and plutonium(IV) concentrations of $0.21 \text{ mol}\cdot\text{L}^{-1}$ and for starting pH values of 8.8 (12), 6.2 (13), 2.6 (14), 1.9 (15) and $[\text{H}_3\text{O}^+] = 2.2 \text{ mol}\cdot\text{L}^{-1}$ (16). Characteristic XRD lines of PuO_2 and PuSiO_4 were extracted from references 21 and 7, respectively.

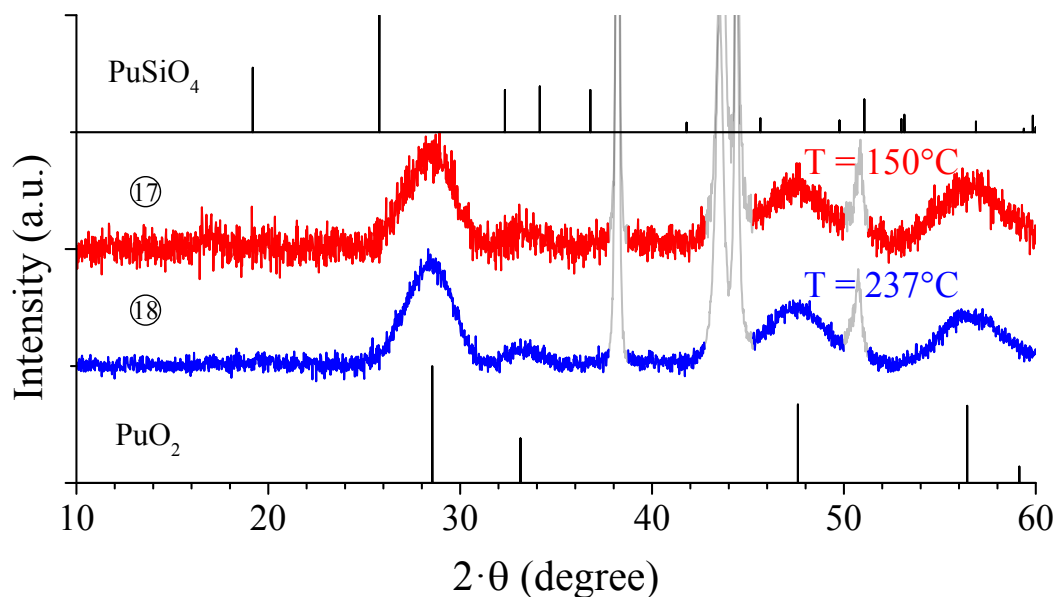


Figure S6 PXRD patterns obtained for samples prepared according to the protocol described by Keller⁷ with starting silicate and plutonium(IV) concentrations of $0.21 \text{ mol}\cdot\text{L}^{-1}$ at $T = 150^{\circ}\text{C}$ (17) and $T = 237^{\circ}\text{C}$ (18). Characteristic XRD lines of PuO_2 and PuSiO_4 were extracted from references 21 and 7, respectively.

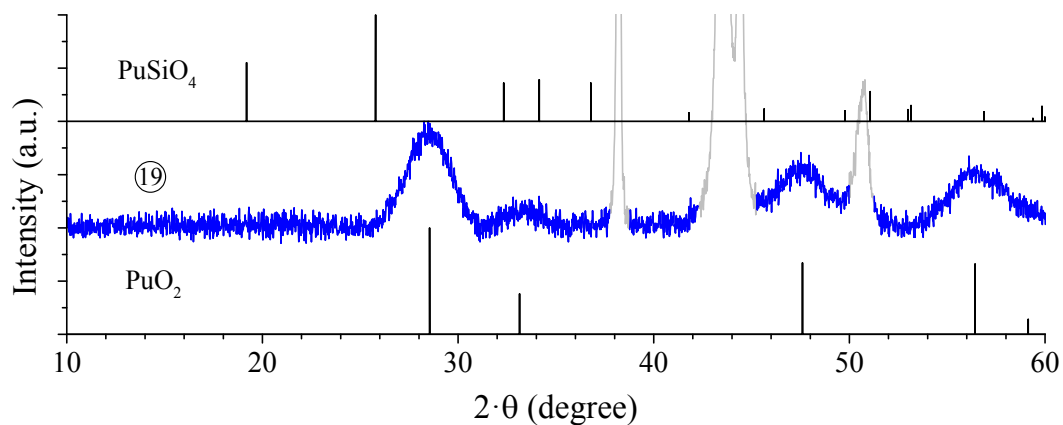


Figure S7 PXRD patterns obtained for a sample prepared according to the protocol identified for ThSiO_4 synthesis² with starting silicate and plutonium(IV) concentrations of $0.21 \text{ mol}\cdot\text{L}^{-1}$ at $T = 237^\circ\text{C}$ (19). Characteristic XRD lines of PuO_2 and PuSiO_4 were extracted from references 21 and 7, respectively.

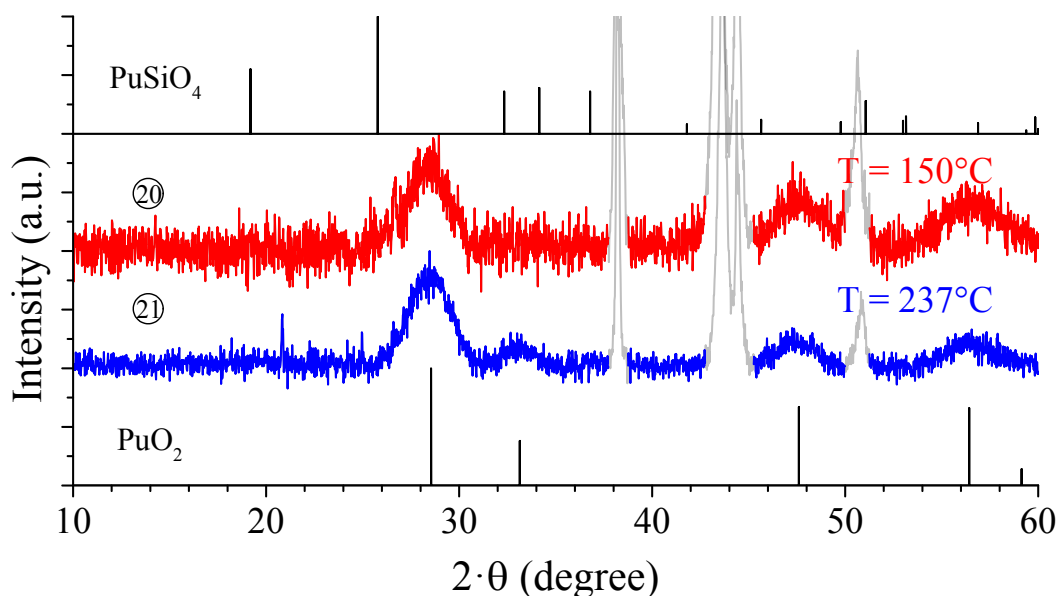


Figure S8 PXRD patterns obtained for samples prepared according to the protocol identified for USiO_4 syntheses³ with starting silicate and plutonium(IV) concentrations of $0.21 \text{ mol}\cdot\text{L}^{-1}$ at $T = 150^\circ\text{C}$ (20) and $T = 237^\circ\text{C}$ (21). Characteristic XRD lines of PuO_2 and PuSiO_4 were extracted from references 21 and 7, respectively.

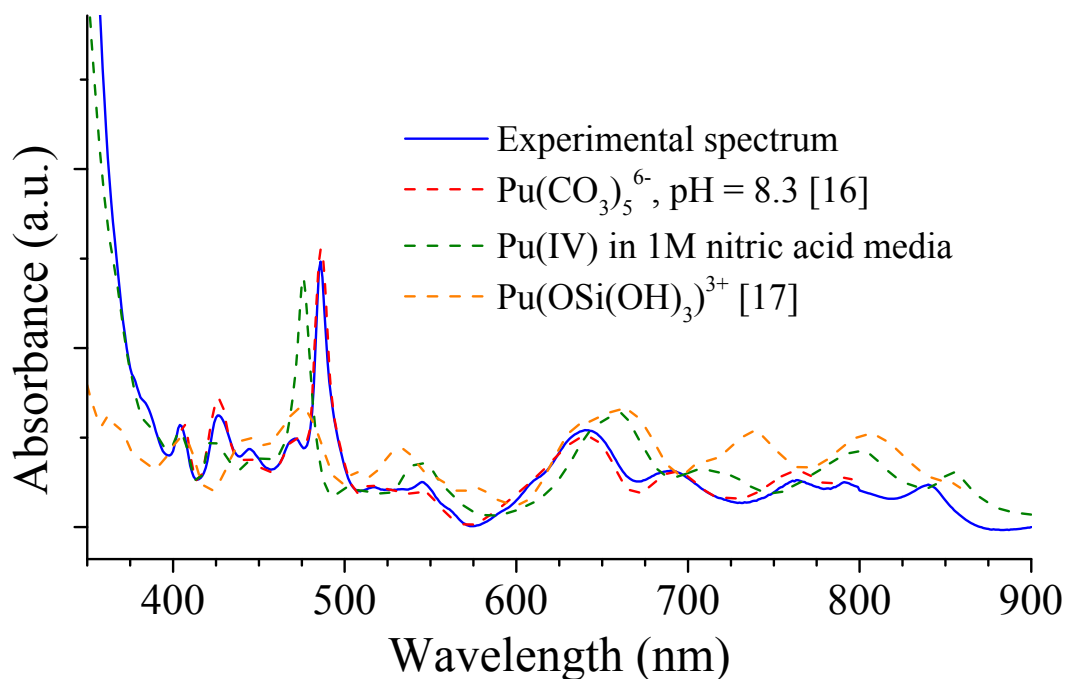


Figure S9 Visible spectrum of sample (27) reactive media prior to the hydrothermal treatment. Reference spectra for $\text{Pu}(\text{CO}_3)_5^{6-}$ at pH = 8.3 and $\text{Pu}(\text{OSi}(\text{OH})_3)^{3+}$ were respectively extracted from references 24 and 15.

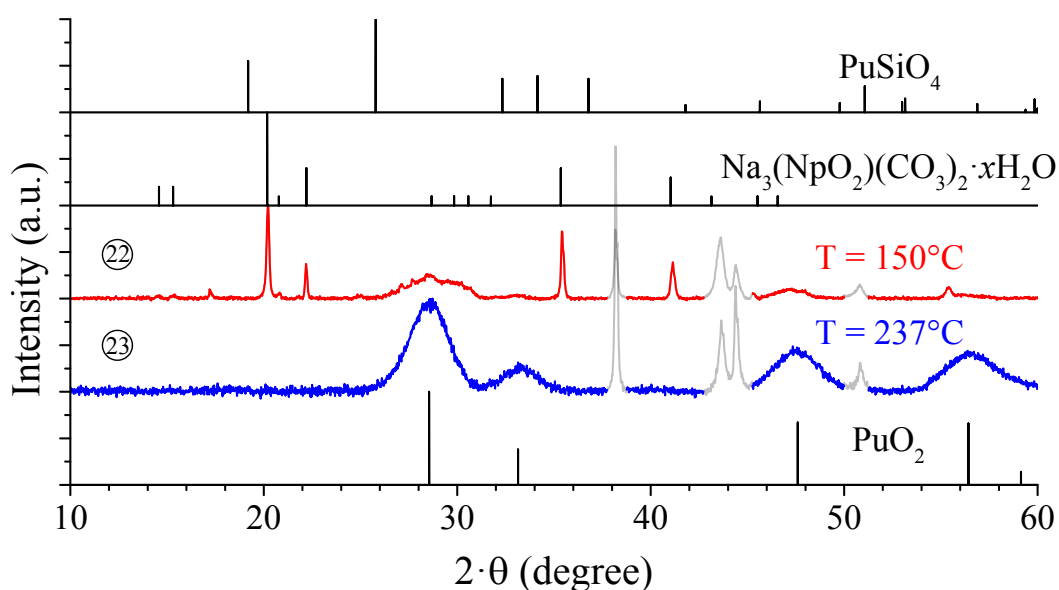


Figure S10 PXRD patterns obtained for samples prepared from the plutonium stabilized in carbonate ions rich reactive media under hydrothermal conditions with starting silicate and plutonium(IV) concentrations of $0.21 \text{ mol}\cdot\text{L}^{-1}$ at $T = 150^\circ\text{C}$ (22) and $T = 237^\circ\text{C}$ (23). Characteristic XRD lines of PuO_2 , $\text{Na}_3(\text{NpO}_2)(\text{CO}_3)_2\cdot x\text{H}_2\text{O}$ and PuSiO_4 were extracted from references 21, 25 and 7, respectively.

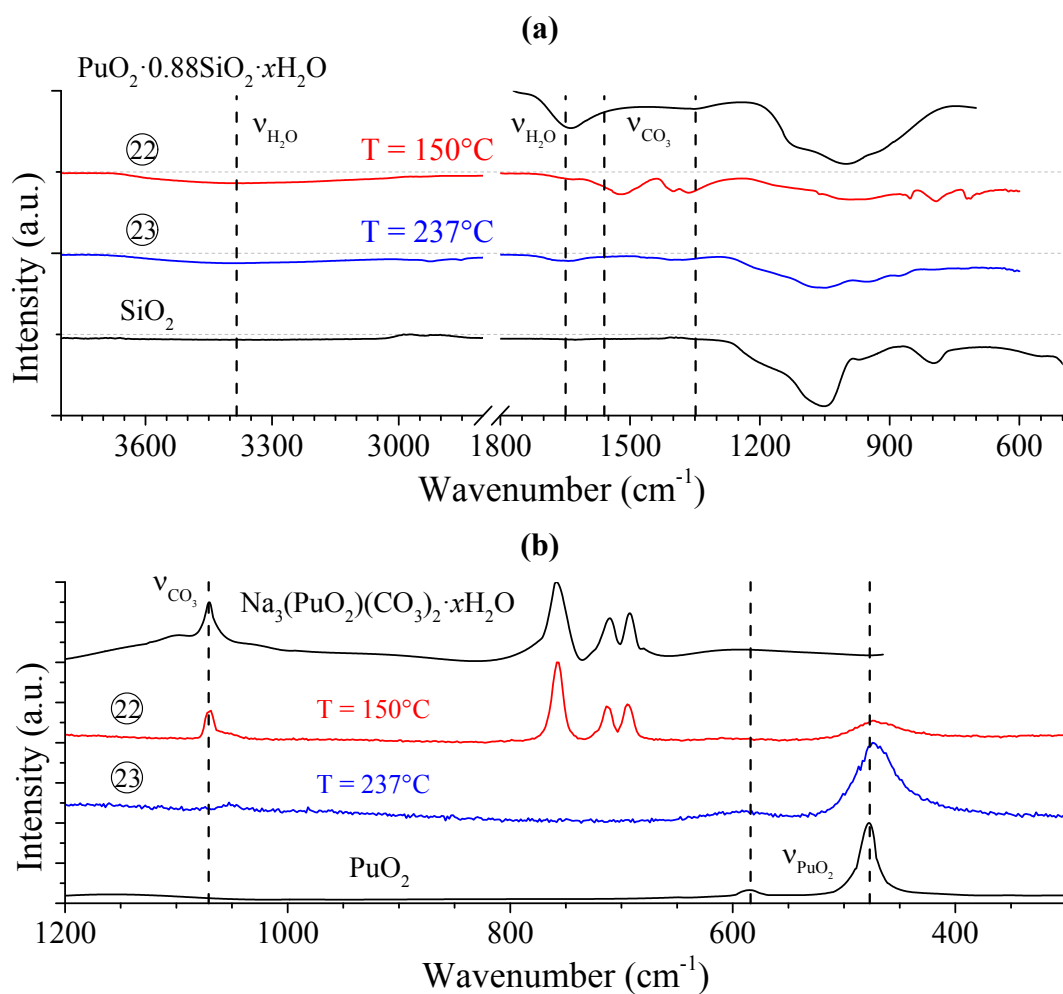


Figure S11 Infrared (a) and Raman (b) spectra obtained for samples prepared with the plutonium stabilized in carbonate ions rich reactive media under hydrothermal conditions with starting silicate and plutonium(IV) concentrations of $0.21 \text{ mol} \cdot \text{L}^{-1}$ at $T = 150^\circ\text{C}$ (22) and $T = 237^\circ\text{C}$ (23). $\text{PuO}_2 \cdot 0.88\text{SiO}_2 \cdot x\text{H}_2\text{O}$ infrared spectrum was extracted from reference 26. $\text{Na}_3(\text{PuO}_2)(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ and PuO_2 Raman spectra were respectively extracted from references 27 and 28.

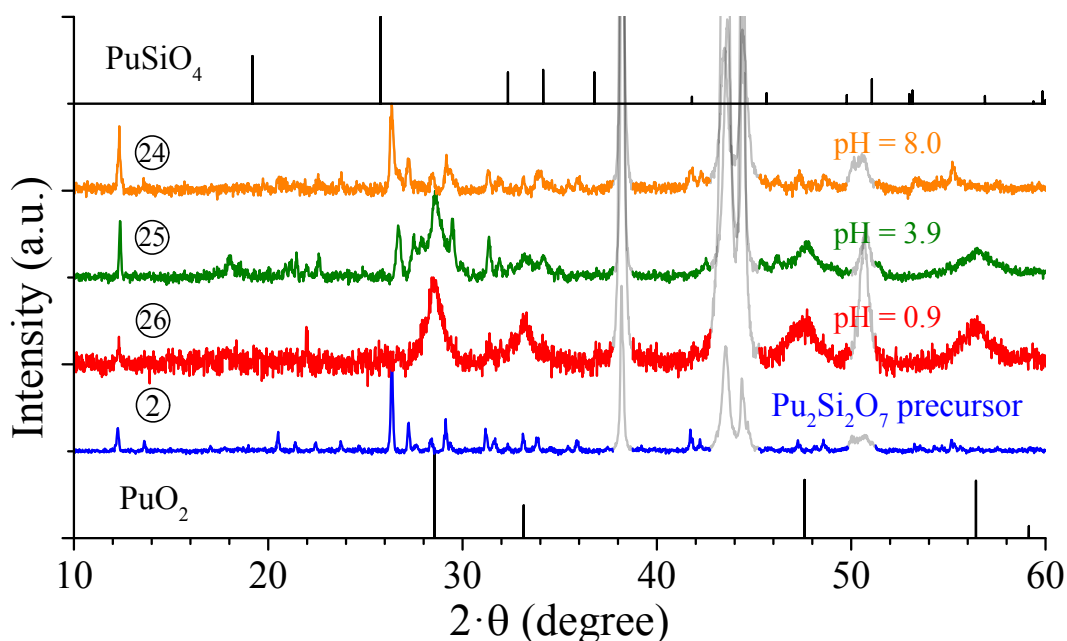


Figure S12 PXRD patterns obtained after hydrothermal treatment ($T = 150^{\circ}\text{C}$, $t = 20$ days, air atmosphere) of $\text{Pu}_2\text{Si}_2\text{O}_7$ reactant (2) with 0.84 mmol of Pu in nitric media (4mL) for starting pH values of 8.0 (24), 3.9 (25) and 0.9 (26). Characteristic XRD lines of PuO_2 and PuSiO_4 were extracted from reference 21 and 7, respectively.

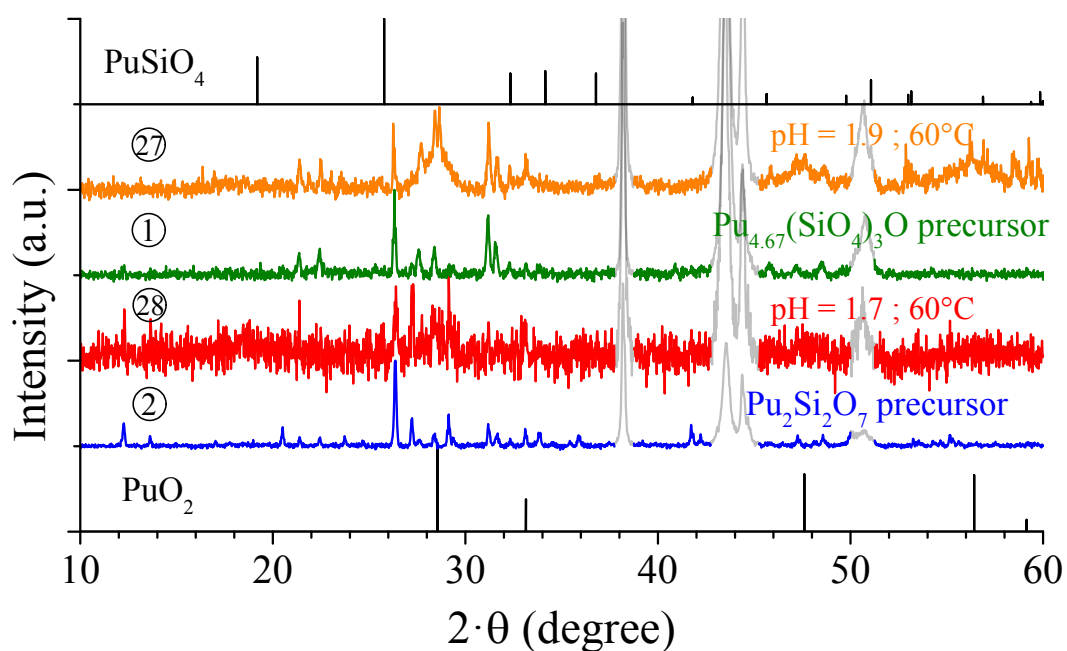


Figure S13 PXRD patterns obtained after treatment in aqueous solution ($T = 60^{\circ}\text{C}$, $t = 21$ days, air atmosphere) of $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$ (1) and $\text{Pu}_2\text{Si}_2\text{O}_7$ reactant (2) with 0.84 mmol of Pu in nitric media (4mL) for starting pH values of 1.9 (27) and 1.7 (28). Characteristic XRD lines of PuO_2 and PuSiO_4 were extracted from reference 21 and 7, respectively.

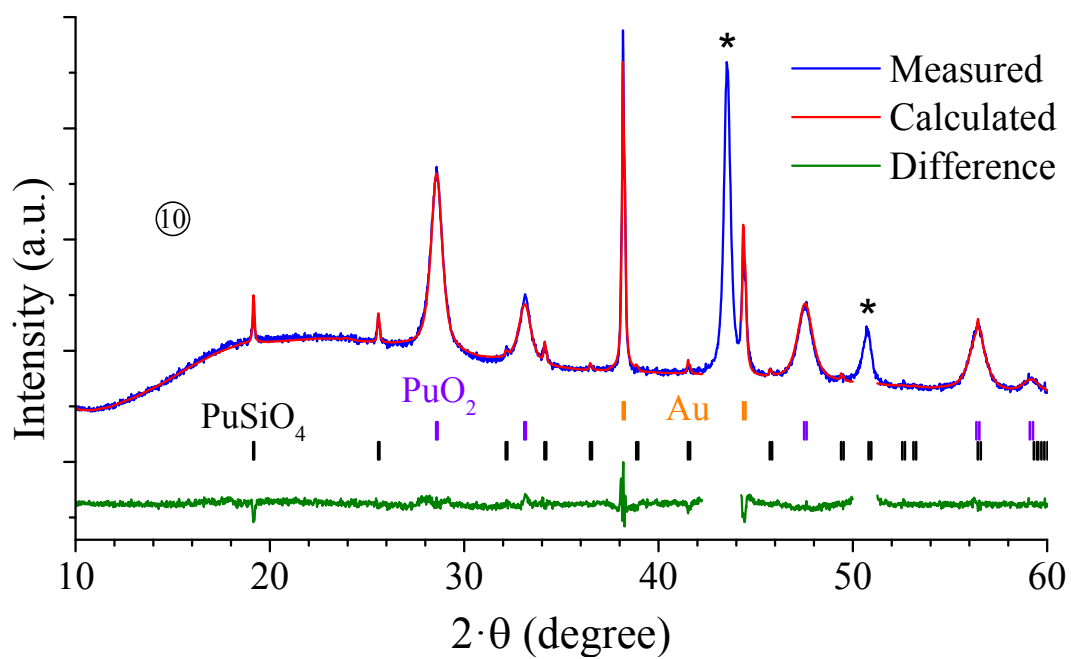


Figure S14 X-ray powder diffraction profile, calculated and difference profile after Rietveld refinement for a PuSiO_4 containing sample (10) from $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$ reactant (1) with 0.84 mmol of Pu in hydrochloric media (4mL) for starting pH values of 4.0. XRD lines of sample holder are pointed out by an asterisk.

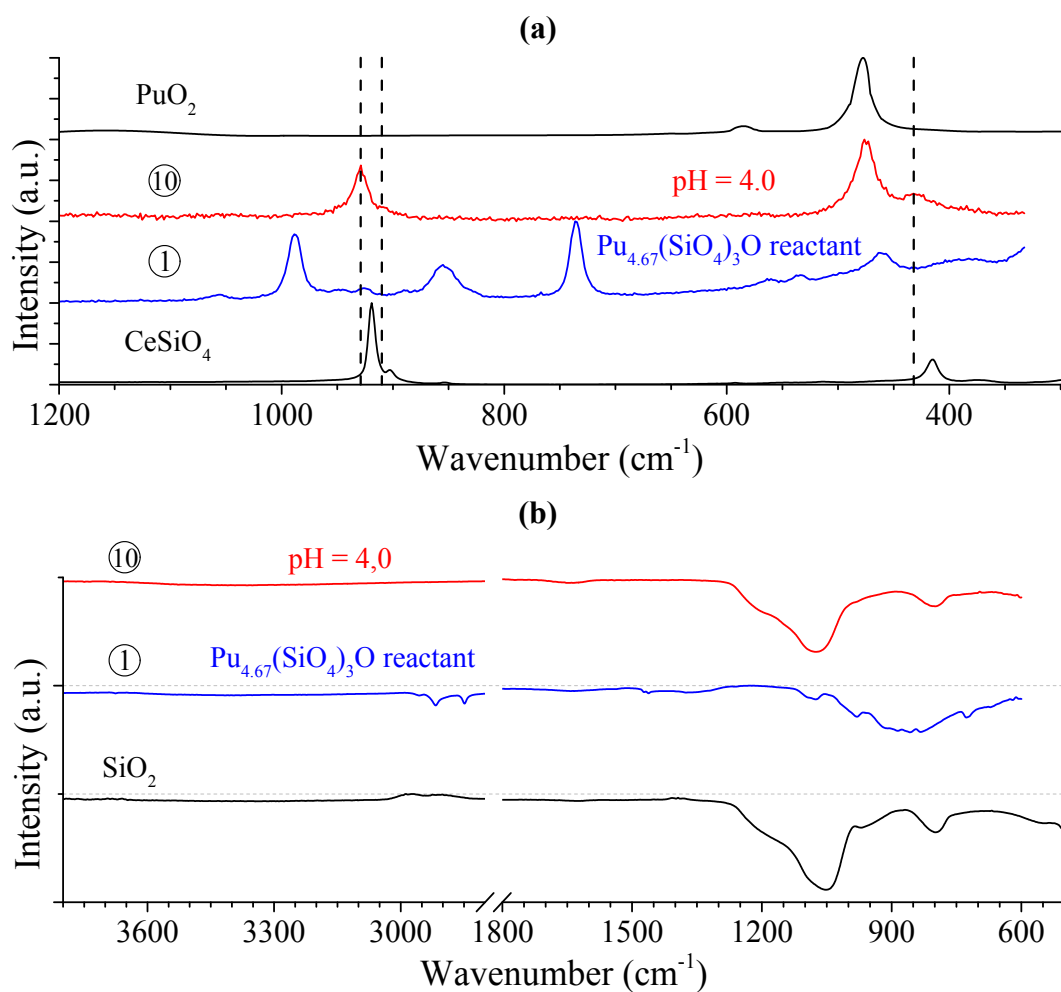


Figure S15 Raman (a) and infrared (b) spectra obtained for a PuSiO_4 containing sample (10) from $\text{Pu}_{4.67}(\text{SiO}_4)_3\text{O}$ reactant (1) with 0.84 mmol of Pu in hydrochloric media (4mL) for starting pH values of 4.0. CeSiO_4 and PuO_2 Raman spectra were respectively extracted from 29 and 28.

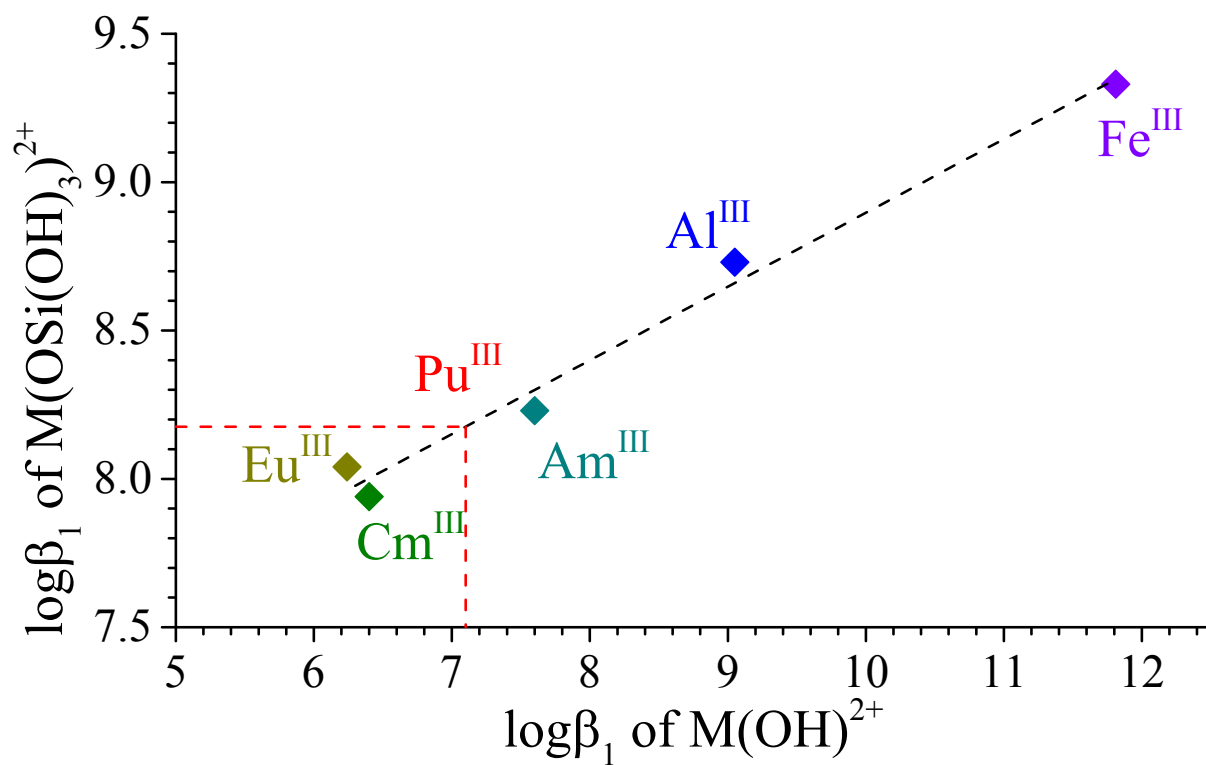


Figure S16. Comparison of the stability constants for the formation of metal-o-silicate and metal hydroxide complexes for M(III)-elements. Considered thermodynamics data available in **Table S4**.

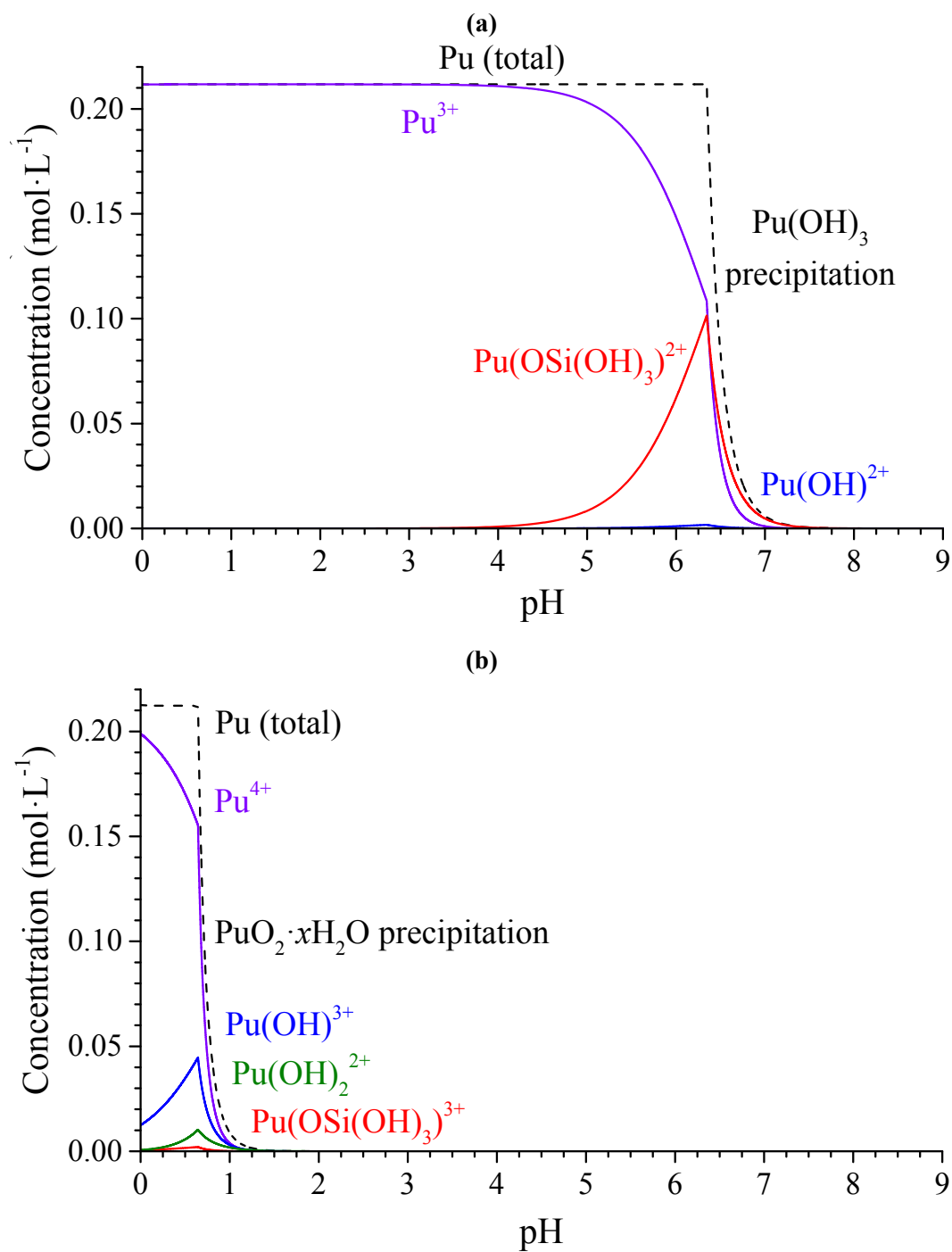


Figure S17. Speciation diagrams of Pu(III) (a) and Pu(IV) (b) determined by PhreeqC calculations³⁰ at room temperature with $C_{\text{Si total}} \approx C_{\text{Pu total}} = 0.21 \text{ mol}\cdot\text{L}^{-1}$. Thermodynamics data considered for these calculations are gathered in **Table S3**.

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