Preparation of $CeSiO_4$ from aqueous precursors under soft hydrothermal conditions

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SUPPORTING INFORMATION

Table S1 Synthesis parameters for the presented $CeSiO_4$ hydrothermal syntheses.

Label	C_{Ce} ($mol \cdot L^{-1}$)	Reactive media	$C_{carb.\ tot.}$ ($mol \cdot L^{-1}$)	$pH_{initial}$	T (°C)	Δt (days)	Final phase
(1)	4.2×10^{-2}	HNO_3	---	**10.5**	250	7	CeO_2
(2)				**8.7**			
(3)				**6.9**			
(4)				**4.1**			
(5)				**3.9**			
(6)				**2.4**			
---	0.21	---	**0.10**	8.6	150	10	CeO_2
(7)			**0.21**	8.7			
(8)			**0.42**	8.6			
(9)			**1.0**	8.6			
(10)			**2.1**	8.6			
(11)	0.21	HNO_3	---	**12.3**	150	10	CeO_2
(12)				**10.1**			CeO_2
(13)				**9.0**			$CeSiO_4 + CeO_2$
(14)				**8.4**			$CeSiO_4 + CeO_2$
(15)				**7.0**			$CeSiO_4 + CeO_2$

Label	C_{Ce} ($mol \cdot L^{-1}$)	Reactive media	$C_{carb.\ tot.}$ ($mol \cdot L^{-1}$)	$pH_{initial}$	T (°C)	Δt (days)	Final phase
(16)				**5.9**			CeO_2
(17)				**3.1**			CeO_2
(18)				**1.3**			---
(19)				**8.7**			
(20)				**8.6**			
(21)	1.0	HNO_3	**---**	**8.2**	150	10	$CeSiO_4 + CeO_2$
(22)				**7.8**			
(23)				**7.4**			
(24)				**7.0**			
(25)				7.0	**90**		$CeSiO_4 + CeO_2$
(26)				7.9	**130**		$CeSiO_4 + CeO_2$
(27)	0.21	HNO_3	---	7.8	**170**	10	CeO_2
(28)				7.5	**210**		CeO_2
(29)				7.4	**250**		CeO_2
(30)	1.0	HNO_3	---	8.0	**40**	210	$CeSiO_4 + CeO_2$
(31)				7.0	**60**	52	$CeSiO_4$
(32) (33)	1.0	HCl	**---**	8.5	150	10	$CeSiO_4 + CeO_2$ + $Ce(OH)_2Cl$
---			**0.10**	8.8			$Ce_2O(CO_3)_2 + CeO_2$
(34)			**0.21**	8.7			$Ce_2O(CO_3)_2$
---	0.21	**---**	**0.42**	8.6	150	10	$Ce_2O(CO_3)_2$ + $Na_4Ce_2(CO_3)_5$
(35)			**1.0**	8.6			$Na_4Ce_2(CO_3)_5$
---			**2.1**	8.6			$Na_4Ce_2(CO_3)_5$
(36)	**1.0**	**HNO_3**	**-**	**8.0**	**150**	**20**	**$CeSiO_4$**

Table S2. Thermodynamic data for the main reactions involving Ce(III), Ce(IV), hydroxide, carbonate and silicate complexes in the considered system at I = 0 (25°C).

Reaction	log K°
$H_4SiO_4 \leftrightharpoons H_2SiO_4^{2-} + 2\ H^+$	– 23.14 [1]
$H_4SiO_4 \leftrightharpoons H_3SiO_4^- + H^+$	– 9.84 [1]
$2\ H_4SiO_4 \leftrightharpoons Si_2O_2(OH)_5^- + H^+ + H_2O$	– 8.50 [1]
$2\ H_4SiO_4 \leftrightharpoons Si_2O_3(OH)_4^{2-} + 2\ H^+ + H_2O$	– 19.40 [1]
$3\ H_4SiO_4 \leftrightharpoons Si_3O_5(OH)_5^{3-} + 3\ H^+ + 2H_2O$	– 29.40 [1]
$3\ H_4SiO_4 \leftrightharpoons Si_3O_6(OH)_3^{3-} + 3\ H^+ + 3\ H_2O$	– 29.30 [1]
$4\ H_4SiO_4 \leftrightharpoons Si_4O_6(OH)_6^{2-} + 2\ H^+ + 4\ H_2O$	– 15.60 [1]
$4\ H_4SiO_4 \leftrightharpoons Si_4O_7(OH)_6^{4-} + 4\ H^+ + 3\ H_2O$	– 39.10 [1]
$4\ H_4SiO_4 \leftrightharpoons Si_4O_8(OH)_4^{4-} + 4\ H^+ + 4\ H_2O$	– 39.20 [1]
$6\ H_4SiO_4 \leftrightharpoons Si_6O_{15}^{6-} + 6\ H^+ + 9\ H_2O$	– 61.80 [1]
$CO_3^{2-} + 2\ H^+ \leftrightharpoons CO_2 + H_2O$	16.68 [1]
$CO_3^{2-} + H^+ \leftrightharpoons HCO_3^-$	10.33 [1]
$Ce^{3+} + H_2O \leftrightharpoons Ce(OH)^{2+} + H^+$	– 8.4 [2]
$Ce^{3+} + 2\ H_2O \leftrightharpoons Ce(OH)_2^+ + 2\ H^+$	– 17.6 [2]
$Ce^{3+} + 3\ H_2O \leftrightharpoons Ce(OH)_3 + 3\ H^+$	– 27.2 [2]
$Ce^{3+} + CO_3^{2-} \leftrightharpoons CeCO_3^+$	5.4 [3]
$Ce^{3+} + 2\ CO_3^{2-} \leftrightharpoons Ce(CO_3)_2^-$	9.3 [3]
$Ce^{3+} + 3\ CO_3^{2-} \leftrightharpoons Ce(CO_3)_3^{3-}$	12.6 [3]
$Ce^{3+} + 4\ CO_3^{2-} \leftrightharpoons Ce(CO_3)_4^{5-}$	13.7 [3]
$Ce^{4+} + H_2O \leftrightharpoons Ce(OH)^{3+} + H^+$	0.76 [2]
$Ce^{4+} + 2\ H_2O \leftrightharpoons Ce(OH)_2^{2+} + 2\ H^+$	0.05 [2]
$Ce^{4+} + 3\ H_2O \leftrightharpoons Ce(OH)_3^+ + 3\ H^+$	– 1.49 [2]
$Ce^{4+} + 4\ H_2O \leftrightharpoons Ce(OH)_4 + 4\ H^+$	– 4.12 [2]
$Ce^{3+} + H_4SiO_4 \leftrightharpoons Ce(OSi(OH)_3)^{2+} + H^+$	– 2.0 (this study)
$Ce^{4+} + H_4SiO_4 \leftrightharpoons Ce(OSi(OH)_3)^{3+} + H^+$	1.9 (this study)

Table S3 Unit cell parameters determined by Rietveld refinement.

Conditions	*a* parameter	*c* parameter	Volume V

Ref.[4]	6.9564(3) Å	6.1953(4) Å	299.80(5) Å^3
Hydrothermal - HNO_3 (36)	6.9606(1) Å	6.1951(1) Å	300.16(1) Å^3
Hydrothermal – HCl (32)	6.9480(1) Å	6.1993(1) Å	299.27(1) Å^3
1000°C annealing	6.9446(1) Å	6.1975(2) Å	298.89(1) Å^3

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

Reaction	**log β°**
$Eu^{3+} + HO^- \leftrightharpoons Eu(OH)^{2+}$	6.2 [5]
$Eu^{3+} + H_3SiO_4^- \leftrightharpoons Eu(OSi(OH)_3)^{2+}$	8.04 ± 0.08 [6]
$Am^{3+} + HO^- \leftrightharpoons Am(OH)^{2+}$	7.6 ± 0.7 [7]
$Am^{3+} + H_3SiO_4^- \leftrightharpoons Am(OSi(OH)_3)^{2+}$	8.23 ± 0.09 [6]
$Cm^{3+} + HO^- \leftrightharpoons Cm(OH)^{2+}$	6.4 ± 0.1 [7]
$Cm^{3+} + H_3SiO_4^- \leftrightharpoons Cm(OSi(OH)_3)^{2+}$	7.94 ± 0.06 [6]
$Al^{3+} + HO^- \leftrightharpoons Al(OH)^{2+}$	9.05 [1]
$Al^{3+} + H_3SiO_4^- \leftrightharpoons Al(OSi(OH)_3)^{2+}$	8.73 ± 0.06 [8]
$Fe^{3+} + HO^- \leftrightharpoons Fe(OH)^{2+}$	11.81 [1]
$Fe^{3+} + H_3SiO_4^- \leftrightharpoons Fe(OSi(OH)_3)^{2+}$	9.33 ± 0.26 [9]
$Ce^{3+} + HO^- \leftrightharpoons Ce(OH)^{2+}$	5.6 ± 0.1 [2]
$Ce^{3+} + H_3SiO_4^- \leftrightharpoons Ce(OSi(OH)_3)^{2+}$	7.8 (this study)
$Th^{4+} + HO^- \leftrightharpoons Th(OH)^{3+}$	11.8 ± 0.2 [10]
$Th^{4+} + H_3SiO_4^- \leftrightharpoons Th(OSi(OH)_3)^{3+}$	8.7 – 9.2 [8]
$Np^{4+} + HO^- \leftrightharpoons Np(OH)^{3+}$	14.5 ± 0.2 [10]
$Np^{4+} + H_3SiO_4^- \leftrightharpoons Np(OSi(OH)_3)^{3+}$	11.2 [11]
$Pu^{4+} + HO^- \leftrightharpoons Pu(OH)^{3+}$	14.6 ± 0.2 [10]
$Pu^{4+} + H_3SiO_4^- \leftrightharpoons Pu(OSi(OH)_3)^{3+}$	11.8 [11]
$Ce^{4+} + HO^- \leftrightharpoons Ce(OH)^{3+}$	14.8 [2]
$Ce^{4+} + H_3SiO_4^- \leftrightharpoons Ce(OSi(OH)_3)^{3+}$	11.7 (this study)

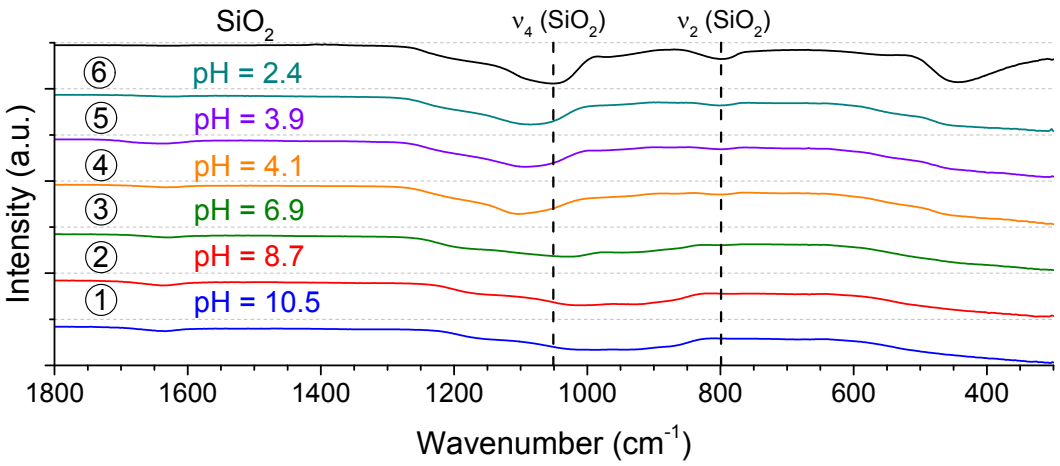

Figure S1 Infrared spectra obtained for samples prepared under hydrothermal conditions (7 days, T = 250°C) with starting silicate and cerium(IV) concentrations of 4.2×10^{-2} mol·L^{-1} and initial pH value equal to 10.5 (1), 8.7 (2), 6.9 (3), 4.1 (4), 3.9 (5) and 2.4 (6).

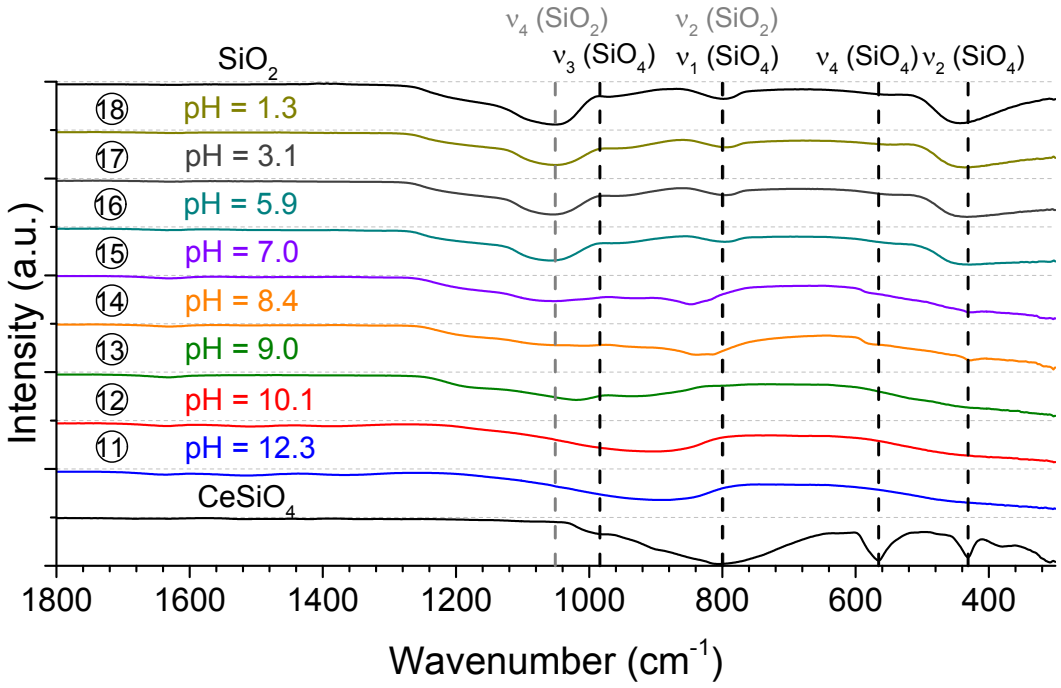

Figure S2 IR obtained for samples prepared under hydrothermal conditions (10 days, T = 150°C) with starting silicate and cerium(III) concentrations of 0.21 mol·L^{-1}, in nitric acid media and with an initial pH equal to 12.3 (11), 10.1 (12), 9.0 (13), 8.4 (14), 7.0 (15), 5.9 (16), 3.1 (17) or 1.3 (18).

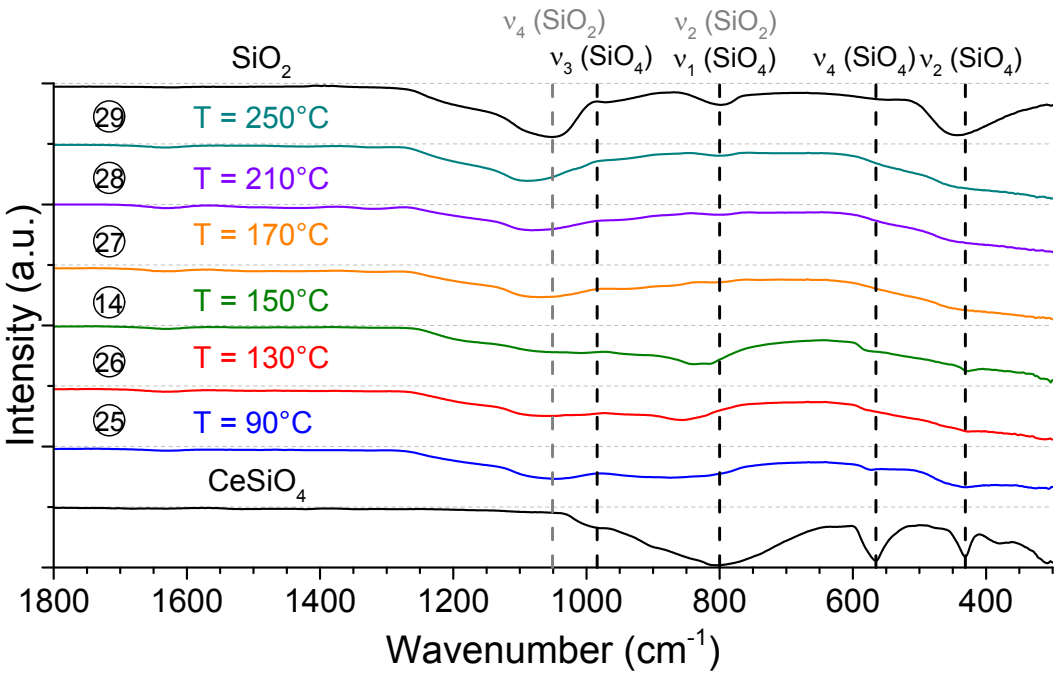

Figure S3 IR obtained for samples prepared with starting silicate and cerium(III) concentrations of 0.21 mol·L^{-1}, in nitric acid media and with an initial pH ranging from 7 to 8, after hydrothermal treatment during 10 days at 90°C (25), 130°C (26), 150°C (27), 170°C (28) and 250°C (29).

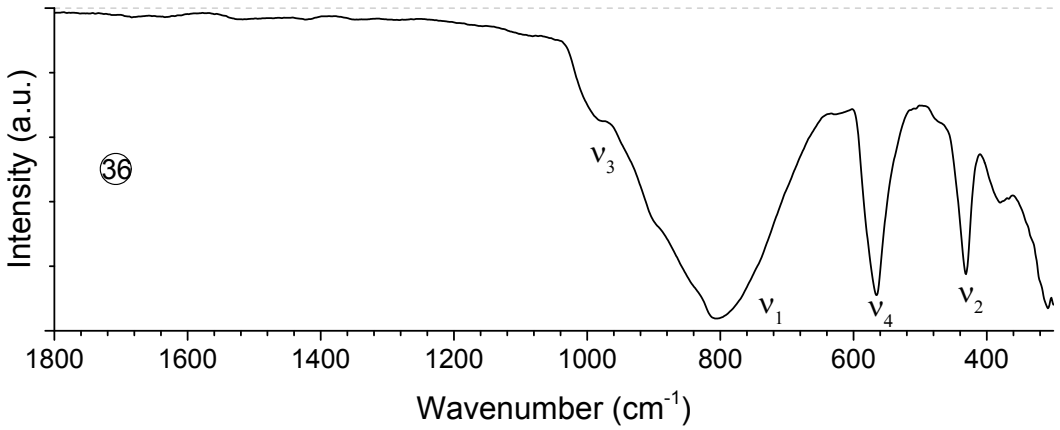

Figure S4 IR spectrum obtained for $CeSiO_4$ prepared under hydrothermal conditions (T = 150°C, t = 20 days, Ar-atmosphere), in nitric medium, with $C_{Ce(III)} \approx C_{Si} \approx$ 1 mol·L^{-1} and $pH_{initial}$ = 8.0 (36).

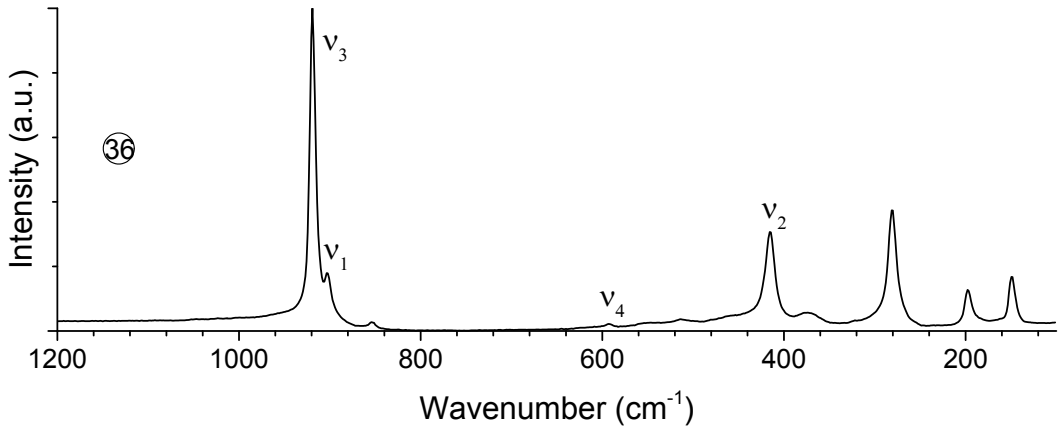

Figure S5 Raman spectrum recorded for $CeSiO_4$ prepared under hydrothermal conditions (T = 150°C, t = 20 days, Ar-atmosphere), in nitric medium, with $C_{Ce(III)} \approx C_{Si} \approx$ 1 mol·L^{-1} and $pH_{initial}$ = 8.0 (36).

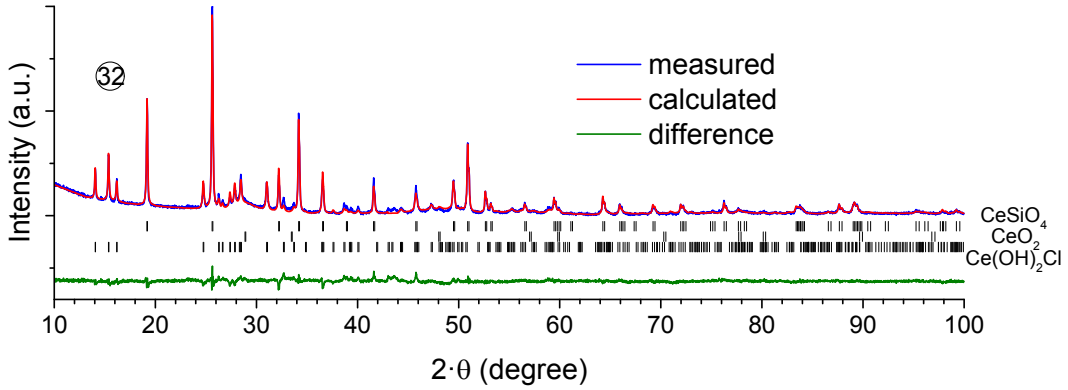

Figure S6 PXRD profile, calculated and difference profile after Rietveld refinement obtained for a sample prepared under hydrothermal conditions (T = 150°C, t = 20 days, Ar-atmosphere) in hydrochloric medium, with $C_{Ce(III)} \approx C_{Si} \approx$ 0.21 mol·L^{-1} and $pH_{initial}$ = 8.5 (32). Unit cell parameters: $CeSiO_4$: a = 6.9480(1) Å and c = 6.1993(1) Å, i.e. V = 299.27(1) Å^3.
$Ce(OH)_2Cl$: a = 6.2842(5) Å, b = 3.9476(5) Å, c = 6.8710(8) Å and β = 113.50(1)°, i.e. V = 156,31(3) Å^3.

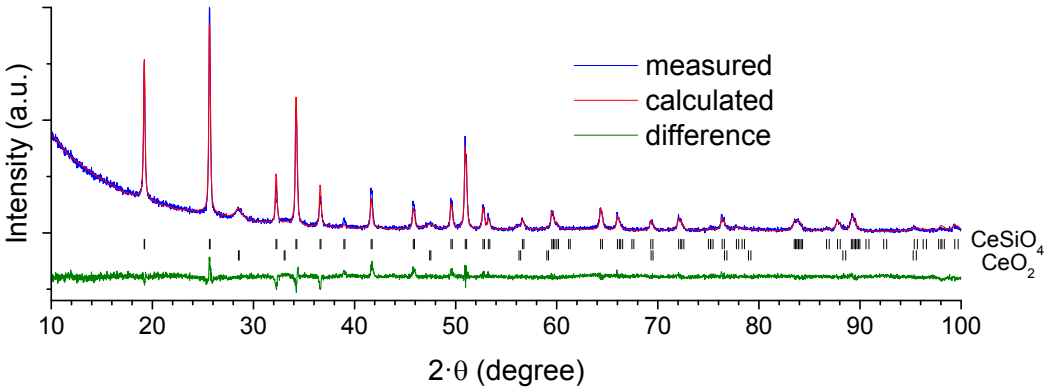

Figure S7 PXRD profile, calculated and difference profile after Rietveld refinement obtained for a $CeSiO_4$ sample prepared under hydrothermal conditions (T = 150°C, t = 20 days, Ar-atmosphere), in nitric medium, with $C_{Ce(III)} \approx C_{Si} \approx 1\ mol \cdot L^{-1}$ and $pH_{initial}$ = 8.0 then submitted to heating treatment at 1000°C under inert atmosphere (Ar). Unit cell parameters:

$CeSiO_4$: *a* = 6.9446(1) Å, *c* = 6.1975(2) Å, V = 298.89(1) Å^3.

CeO_2: *a* = 5.417(2) Å, V = 159.0(1) Å^3.

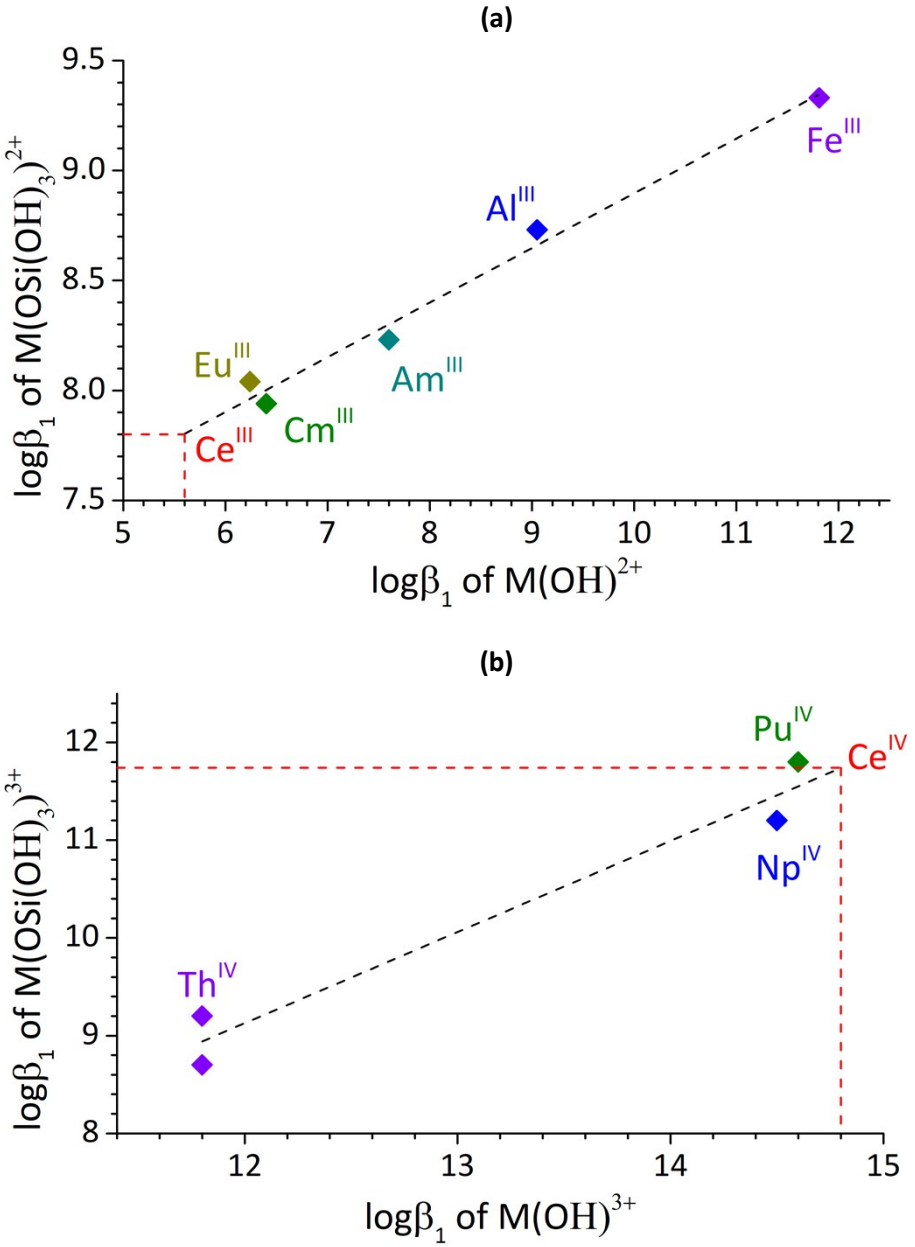

Figure S8. Comparison of the stability constants for the formation of metal-o-silicate and metal hydroxide complexes for M(III)- (a) and M(IV)-elements (b). Considered thermodynamics data available in **Table S4**.

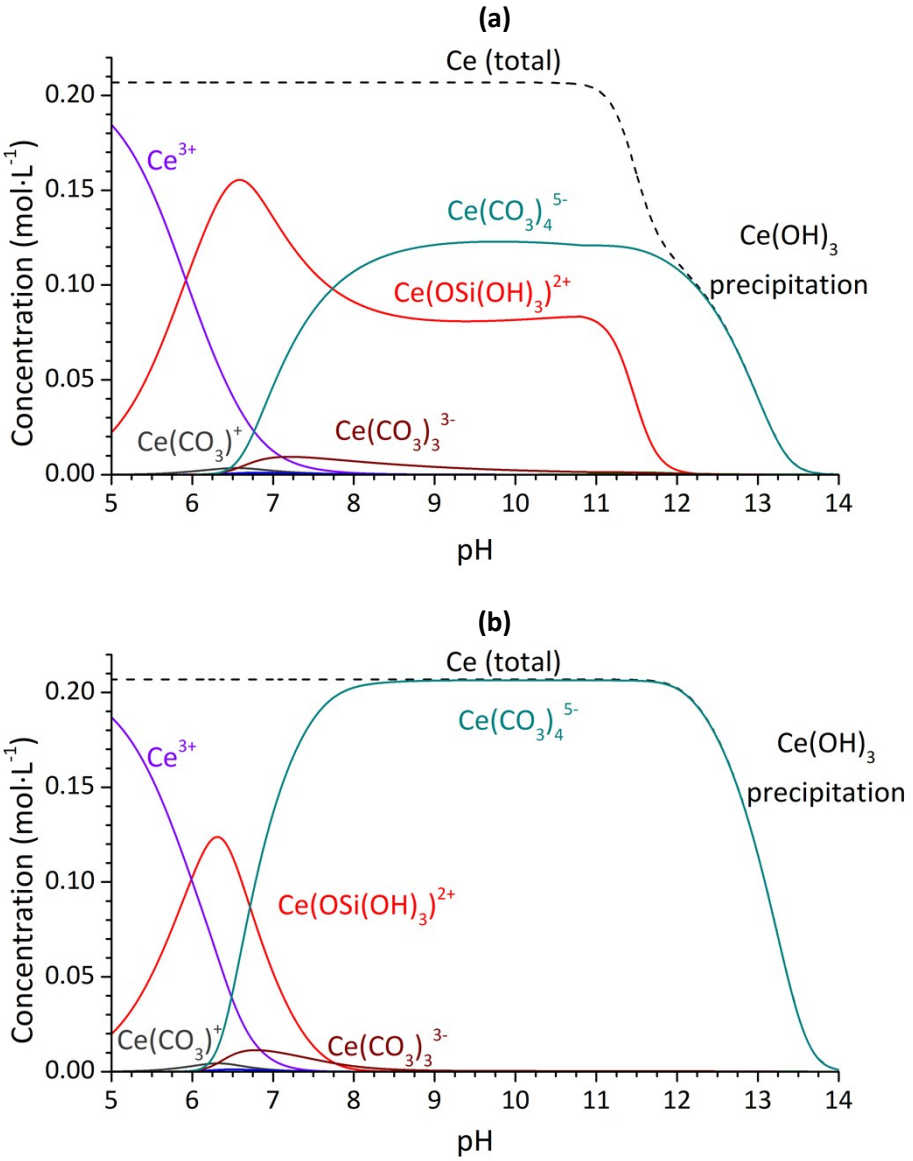

Figure S9. Cerium(III) speciation diagram of Ce(III) determined by PhreeqC calculation at room temperature with $C_{Si\ total} \approx C_{Ce\ total} = 0.21$ mol·L^{-1} and total carbonate concentration of 0.5 mol L^{-1} (a) and 1.0 mol L^{-1} (b). Considered thermodynamics data available in **Table S3**.

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