Formation of CeSiO$_4$ from cerium(III) silicate precursors

Paul Estevenon[a,b], Thibault Kaczmarek[a,b], Fabien Vadot[a,b], Thomas Dumas[a], Pier Lorenzo Solari[c], Eleonore Welcomme[a], Stephanie Szenknect[b], Adel Mesbah*[b], Philippe Moisy[a], Christophe Poinssot[a], Nicolas Dacheux*[b]

[a] CEA, Nuclear Energy Division, CEA Marcoule Research Department of Mining and Fuel Recycling Processes, DMRC, BP 17171, 30207 Bagnols-sur-Cèze, France

[b] ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Site de Marcoule – Bât. 426, BP 17171, 30207 Bagnols-sur-Cèze, France

[c] Synchrotron SOLEIL L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex France

SUPPORTING INFORMATION

Table S1. Synthesis parameters of the hydrothermal syntheses, final phases identified by PXRD and CeSiO$_4$ wt.% determined by Rietveld refinement.

Label	Precursor	Reactive media	C_{Ce} (mol·L^{-1})	$pH_{initial}$	T (°C)	Δt (days)	pH_{final}	Final phases	CeSiO$_4$ wt.%
(1)				11.0			9.3	Ce$_{4.67}$(SiO$_4$)$_3$O	0%
(2)				7.0			1.7	**CeSiO$_4$**	**100%**
(3)				6.1			1.4		92%
(4)				4.3			1.4		66%
(5)	Ce$_{4.67}$(SiO$_4$)$_3$O	HNO$_3$	0.21	2.0	150	7	1.3	CeSiO$_4$ + CeO$_2$	70%
(6)				C_{HNO_3} = 0.7 M			C_{HNO_3} = 0.7 M		9%
(7)				C_{HNO_3} = 1.3 M			C_{HNO_3} = 1.3 M	CeO$_2$	0%
(8)				11.1			6.4	Ce$_{4.67}$(SiO$_4$)$_3$O	0%
(9)				8.1			2.0	CeSiO$_4$ + CeO$_2$	37%
(10)				7.0			1.4	**CeSiO$_4$**	**100%**
(11)				4.0			1.2	CeSiO$_4$ + CeO$_2$	99%
(12)	A-Ce$_2$Si$_2$O$_7$	HNO$_3$	0.21	2.0	150	7	1.2		99%
(13)				C_{HNO_3} = 0.7 M			C_{HNO_3} = 0.7 M	CeSiO$_4$ + CeO$_2$	44%
(14)				C_{HNO_3} = 1.3 M			C_{HNO_3} = 1.3 M		43%

Label	Precursor	Reactive media	C_{Ce} (mol·L^{-1})	pH$_{initial}$	T (°C)	Δt (days)	pH$_{final}$	Final phases	CeSiO$_4$ wt.%
(15)	A-Ce$_2$Si$_2$O$_7$	HNO$_3$	0.21	7.0	150	**1**	2.2	CeSiO$_4$ + CeO$_2$	23%
(16)				6.9		**3**	1.7	**CeSiO$_4$**	**100%**
(17)	Ce$_{4.67}$(SiO$_4$)$_3$O	HNO$_3$	0.21	7.0	**60**	**52**	3.4	CeSiO$_4$ + Ce$_{4.67}$(SiO$_4$)$_3$O	83%
(18)				6.9	**250**	**7**	0.8	CeO$_2$ + CeSiO$_4$	4%
(19)				**7.2**			4.6		55%
(20)	G-Ce$_2$Si$_2$O$_7$	HCl	0.21	**3.3**	150	7	2.4	CeSiO$_4$ + G-Ce$_2$Si$_2$O$_7$	36%
(21)				**2.2**			1.7		58%
(22)				**7.2**			4.4		56%
(23)	G-Ce$_2$Si$_2$O$_7$	HCl	0.21	**3.1**	150	21	2.3	CeSiO$_4$ + G-Ce$_2$Si$_2$O$_7$	92%
(24)				**2.1**			1.7		65%
(25)				**11.5**			11.3	Ce$_2$SiO$_5$ + CeO$_2$	0%
(26)				**8.5**			2.7		62%
(27)				**6.9**			1.9		66%
(28)	Ce$_2$SiO$_5$	HNO$_3$	0.21	**6.0**	150	7	1.7	CeSiO$_4$ + CeO$_2$	46%
(29)				**5.5**			1.5		59%
(30)				**2.1**			1.6		25%
(31)				**1.0**			1.6		13%
(32)				**11.7**			11.7	G-Ce$_2$Si$_2$O$_7$	0%
(33)				**8.2**			3.2		5%
(34)				**7.1**			2.8		34%
(35)	G-Ce$_2$Si$_2$O$_7$	HNO$_3$	0.21	**5.4**	150	7	2.5	G-Ce$_2$Si$_2$O$_7$ + CeSiO$_4$ + CeO$_2$	41%
(36)				**4.4**			1.9		54%
(37)				**2.0**			2.4		26%
(38)				**1.0**			1.4		2%
(39)	Ce$_{4.67}$(SiO$_4$)$_3$O	HNO$_3$	0.21	**7.0**	**150**	**1**	2.0	CeSiO$_4$ + CeO$_2$	44%
(40)				**7.1**		**3**	2.4		95%
(41)	A-Ce$_2$Si$_2$O$_7$	HNO$_3$	0.21	**7.0**	**60**	**52**	5.1	A-Ce$_2$Si$_2$O$_7$ + CeSiO$_4$	13%
(42)				**7.1**	**250**	**7**	0.5	CeO$_2$ + CeSiO$_4$	9%
(43)				**6.9**			5.8		45%
(44)	Ce$_{4.67}$(SiO$_4$)$_3$O	HCl	0.21	**4.6**	150	7	2.3	CeSiO$_4$ + Ce$_{4.67}$(SiO$_4$)$_3$O	51%
(45)				**2.0**			1.9		67%

Table S2. Lattice parameters determined by Rietveld refinement for Ce(III) and Ce(IV) silicate samples and literature references.

Compound	Space group	Unit cell parameters				References
		a (Å)	b (Å)	c (Å)	β (°)	
Ce_2SiO_5	$P12_1/c1$ (14)	9.2775(3)	7.3942(3)	6.9665(3)	108.33(1)	This study
		9.278	7.382	6.956	108.20	[1, 2]
$Ce_{4.67}(SiO_4)_3O$	$P6_3/m$ (176)	9.6505(4)		7.0738(3)		This study
		9.658		7.119		[2, 3]
$A\text{-}Ce_2Si_2O_7$	$P4_1$ (76)	6.7965(3)		24.7258(14)		This study
		6.792		24.700		[2, 4]
$G\text{-}Ce_2Si_2O_7$	$P2_1/n$ (14)	8.7245(4)	13.0735(6)	5.4031(3)	90.13(1)	This study
		8.727	13.080	5.405	90.13	[2, 4]
$CeSiO_4$	$I4_1/amd$ (141)	6.9523(2)		6.2036(2)		This study
		6.9603(1)		6.1946(2)		[5]
		6.9564(3)		6.1953(4)		[6]

Table S3. Assignment of the bands associated to silicate groups observed by Raman and IR spectra for $CeSiO_4$ formed from Ce(III) precursors in optimized conditions and comparison with $CeSiO_4$ prepared from aqueous solution.[30]

	Raman spectroscopy				Infrared spectroscopy			
	v_2	v_4	v_1	v_3	v_2	v_4	v_1	v_3
[5]	416 cm^{-1}	592 cm^{-1}	903 cm^{-1}	919 cm^{-1}	431 cm^{-1}	572 cm^{-1}	800 cm^{-1}	984 cm^{-1}
This study	416 cm^{-1}	592 cm^{-1}	902 cm^{-1}	919 cm^{-1}	431 cm^{-1}	570 cm^{-1}	802 cm^{-1}	980 cm^{-1}
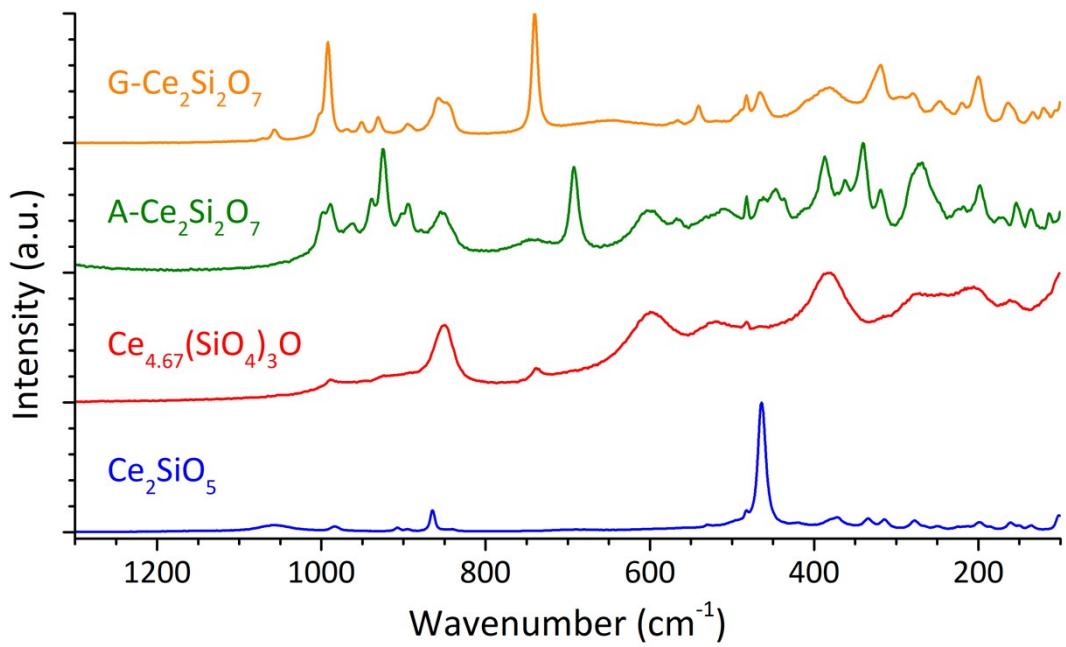
Figure S1. Raman spectra recorded for Ce_2SiO_5, $Ce_{4.67}(SiO_4)_3O$, $A-Ce_2Si_2O_7$ and $G-Ce_2Si_2O_7$.
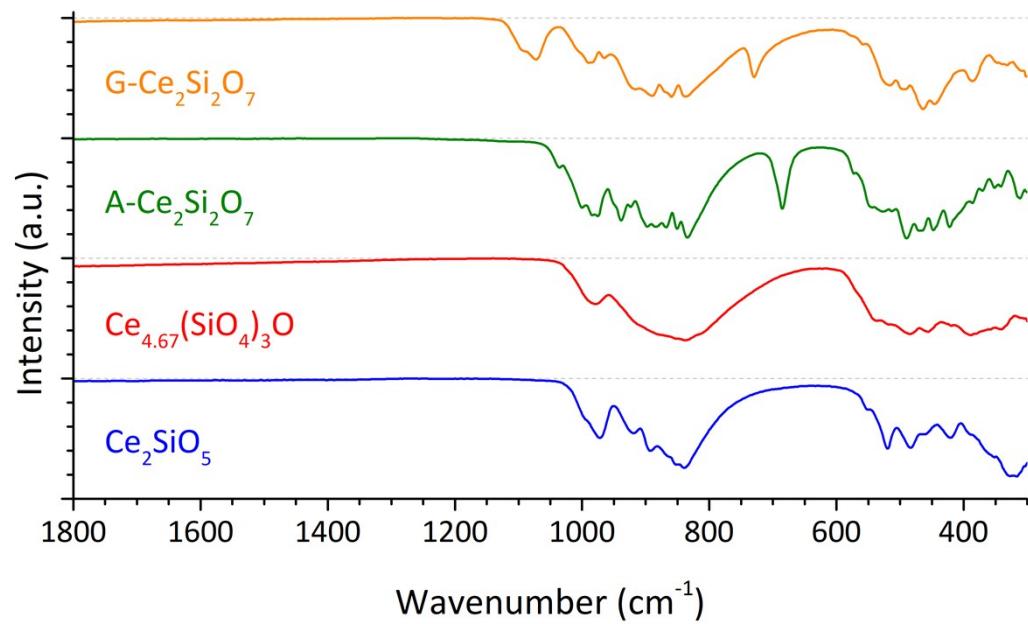
Figure S2. FTIR spectra recorded for Ce_2SiO_5, $Ce_{4.67}(SiO_4)_3O$, $A-Ce_2Si_2O_7$ and $G-Ce_2Si_2O_7$.
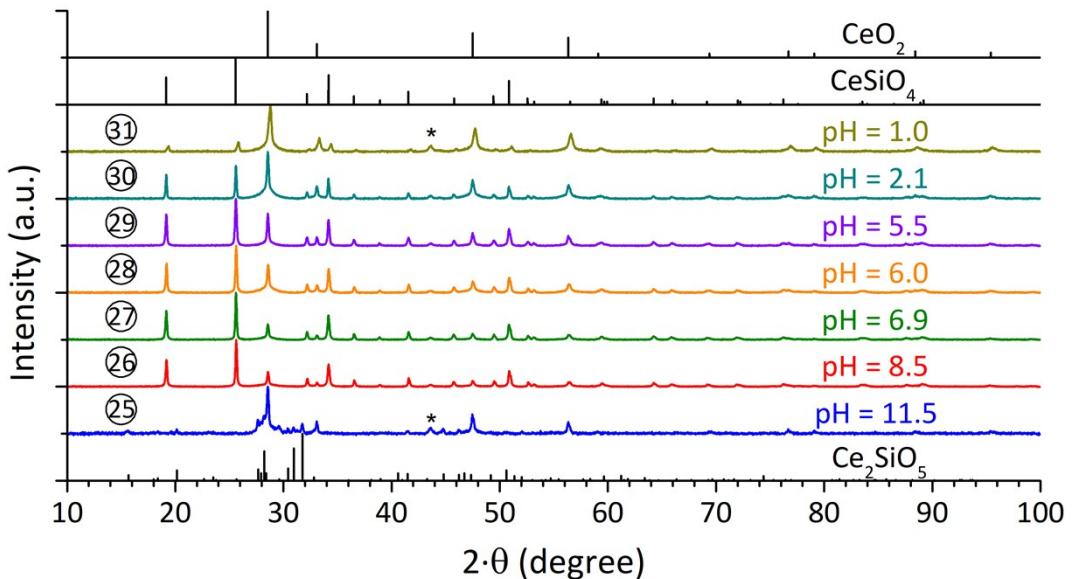
**Figure S3.** PXRD patterns obtained after hydrothermal treatment (7 days, T = 150°C) under air atmosphere starting from Ce_2SiO_5 precursor, in nitric medium and with pH value equal to 11.5 (25), 8.5 (26), 6.9 (27), 6.0 (28), 5.5 (29), 2.1 (30) and 1.0 (31). XRD lines of the sample holder are pointed out by an asterisk. Characteristic XRD lines of CeO_2, $CeSiO_4$ and Ce_2SiO_5 were extracted from references **7**, **6** and **1**, respectively.
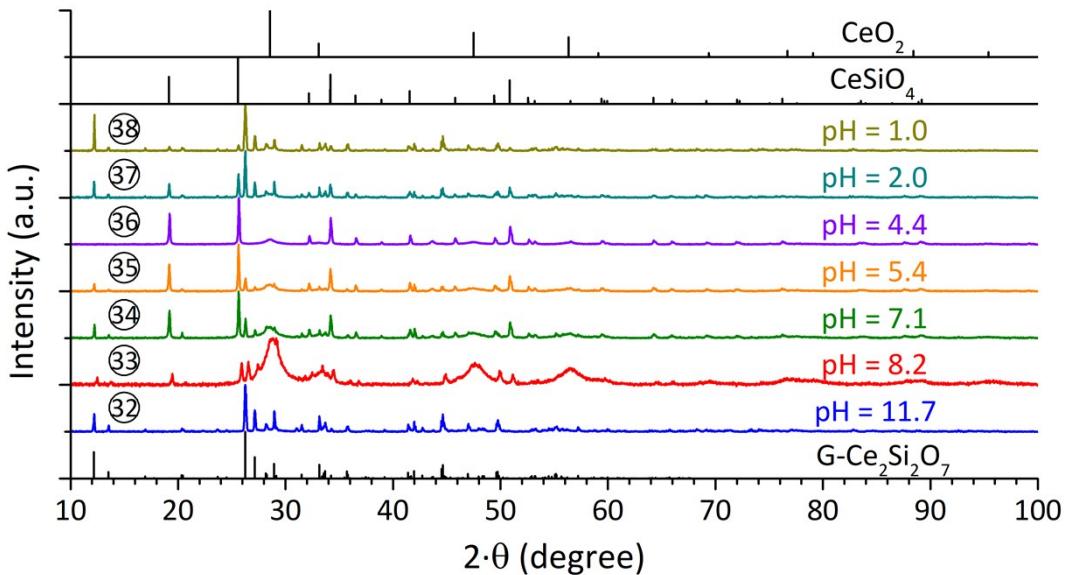

Figure S4. PXRD patterns obtained after hydrothermal treatment (7 days, T = 150°C) under air atmosphere starting from $G-Ce_2Si_2O_7$ precursor, in nitric medium and with pH value equal to 11.7 (32), 8.2 (33), 7.1 (34), 5.4 (35), 4.4 (36), 2.0 (37) and 1.0 (38). Characteristic XRD lines of CeO_2, $CeSiO_4$ and $G-Ce_2Si_2O_7$ were extracted from references **7**, **6** and **8**, respectively.
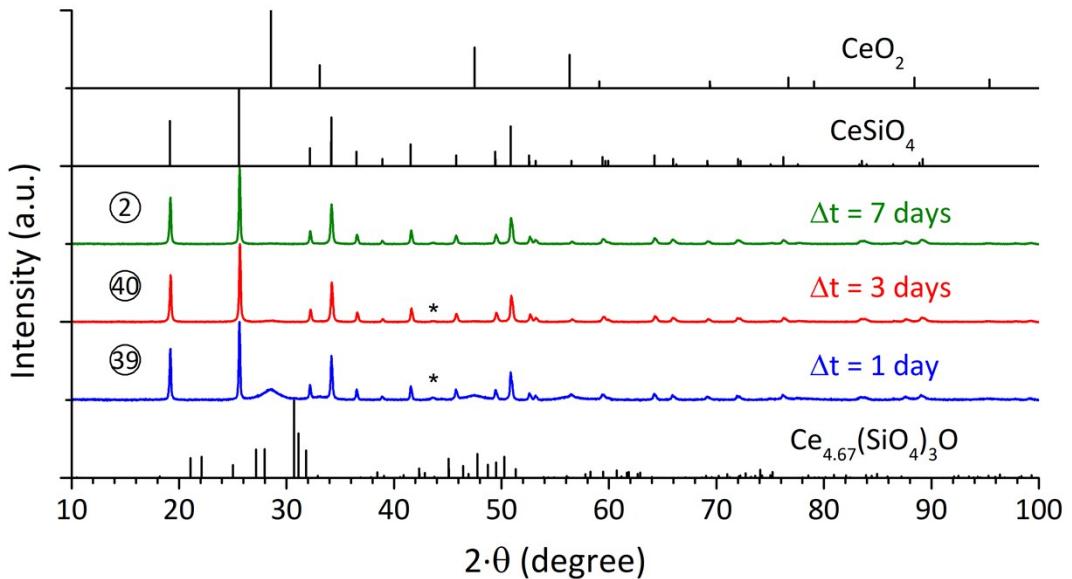
Figure S5. PXRD patterns obtained when using $Ce_{4.67}(SiO_4)_3O$ as starting precursor, after hydrothermal treatment performed at 150°C under air atmosphere in nitric media and pH = 7 for 1 day (39), 3 days (40) and 7 days (2). XRD lines of sample holder are pointed out by an asterisk. Characteristic XRD lines of CeO_2, $CeSiO_4$ and $Ce_{4.67}(SiO_4)_3O$ were extracted from references **7**, **6** and **3**, respectively.
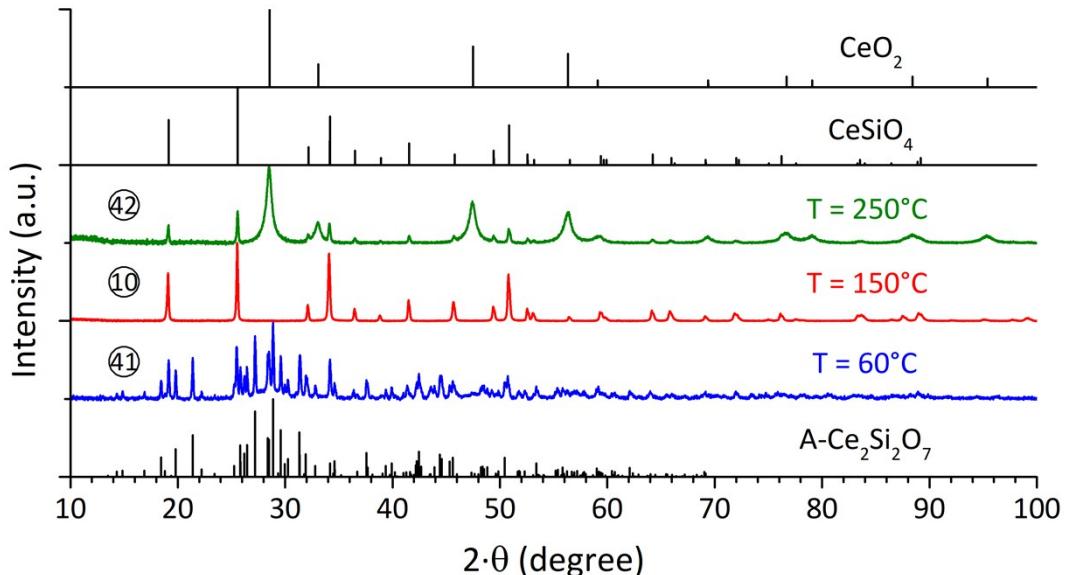

Figure S6. PXRD patterns obtained from $A-Ce_2Si_2O_7$ starting precursor after hydrothermal treatment performed under air atmosphere in nitric media and pH = 7 for 52 days at 60°C (41), for 7 days at 150°C (2) and for 7 days at 250°C (42). Characteristic XRD lines of CeO_2, $CeSiO_4$ and $A-Ce_2Si_2O_7$ were extracted from ref **7**, **6** and **9**, respectively.
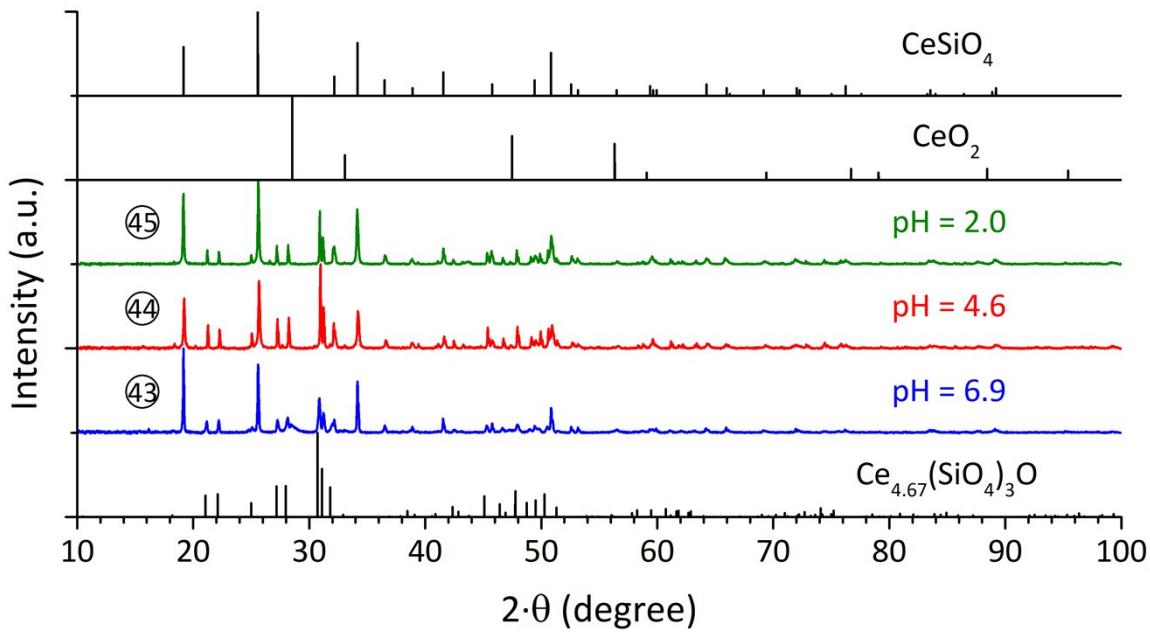
Figure S7. PXRD patterns obtained after hydrothermal treatment (7 days, T = 150°C) under air atmosphere in hydrochloric media, starting from $Ce_{4.67}(SiO_4)_3O$ precursor and with pH value equal to 6.9 (43), 4.6 (44) and 2.0 (45). Characteristic XRD lines of CeO_2, $CeSiO_4$ and $Ce_{4.67}(SiO_4)_3O$ were extracted from references **7**, **6** and **3**, respectively.
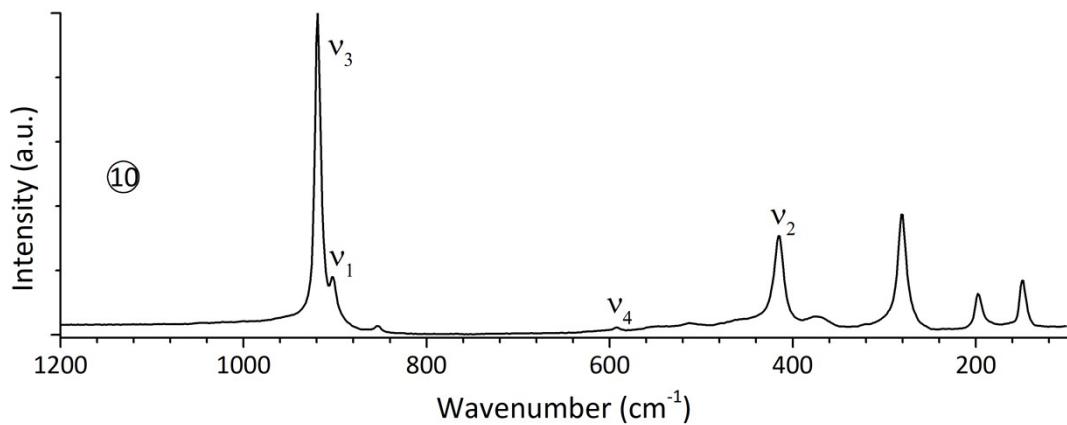
**Figure S8.** Raman spectrum obtained for $CeSiO_4$ prepared under hydrothermal conditions (T = 150°C, t = 7 days) under air atmosphere in nitric medium, starting from $A\text{-}Ce_2Si_2O_7$ precursor and with pH = 7.0 (10).
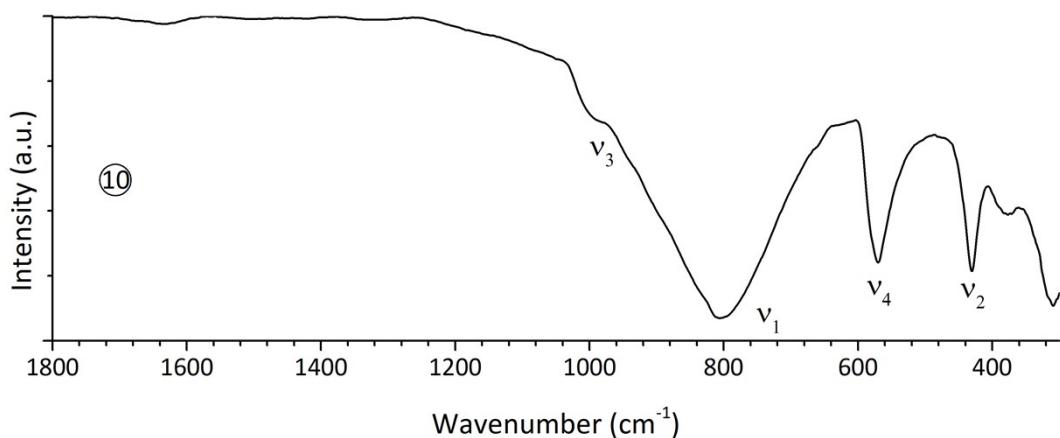
Figure S9. Infrared spectrum obtained for $CeSiO_4$ prepared under hydrothermal conditions (T = 150°C, t = 7 days) under air atmosphere in nitric medium, starting from A-$Ce_2Si_2O_7$ precursor and with pH = 7.0 (10).

References:

1. H. A. M. van Hal and H. T. Hintzen, *Journal of Alloys and Compounds*, 1992, **179**, 77-85.

2. A. C. Tas and M. Akinc, *Journal of the American Ceramic Society*, 1994, **77**, 2953-2960.

3. A. C. Tas and M. Akinc, *Powder diffraction*, 1992, **7**, 219-222.

4. A. C. Tas and M. Akinc, *Journal of American Ceramic Society*, 1993, **76**, 1595-1601.

5. P. Estevenon, E. Welcomme, S. Szenknect, A. Mesbah, P. Moisy, C. Poinssot and N. Dacheux, *Dalton Transactions*, 2019, **48**, 7551-7559.

6. J. M. S. Skakle, C. L. Dickson and F. P. Glasser, *Powder diffraction*, 2000, **15**, 234-238.

7. C. Artini, M. Pani, M. M. Carnasciali, M. T. Buscaglia, J. R. Plaisier and G. A. Costa, *Inorganic Chemistry*, 2015, **15**, 4126–4137.

8. A. C. Tas and M. Akinc, *Journal of the American Ceramic Society*, 1994, **77**, 2968-2970.

9. S. Zec, S. Bošković, Ž. Bogdanov and N. Popović, *Materials Chemistry and Physics*, 2006, **95**, 150-153.