

How hydrothermal synthesis improves the synthesis of (Zr,Ce)SiO₄ solid solutions

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SUPPORTING INFORMATION

Table SI 1. Synthesis parameters for the presented (Zr,Ce)SiO₄ hydrothermal syntheses.

Label	Zr:Ce mol ratio	C _{Zr} (mol·L ⁻¹)	C _{Ce} (mol·L ⁻¹)	pH _{initial}	T (°C)	Δt (days)	Final phase
(1)				[H ₃ O ⁺] = 1 mol·L ⁻¹			ZrSiO ₄
(2)				1.0			ZrSiO ₄
(3)				2.0			ZrSiO ₄ + ε ZrO ₂
(4)				3.1			ZrSiO ₄ + ε ZrO ₂
(5)				4.1			ZrSiO ₄
(6)	100:0	0.20	0	4.9	250	20	ZrSiO ₄
(7)				6.0			ZrSiO ₄
(8)				7.0			ZrSiO ₄
(9)				8.0			ZrSiO ₄
(10)				9.0			ZrSiO ₄
(11)				10.0			ZrSiO ₄ + another phase
(12)				11.7			another phase
(13)	100:0	0.20	0	1.0	250	1	ZrSiO ₄
(14)						7	ZrSiO ₄
(15)	100:0	1.0	0	1.0	250	7	ZrSiO ₄
(16)		0.05					ZrSiO ₄ + ZrO ₂
(17)	95:5	0.19	0.01				(Zr,Ce)SiO ₄
(18)	90:10	0.18	0.02				(Zr,Ce)SiO ₄
(19)	80:20	0.16	0.04				(Zr,Ce)SiO ₄
(20)	60:40	0.12	0.08				(Zr,Ce)SiO ₄ + ZrO ₂
(21)	50:50	0.10	0.10	1.0	250	7	(Zr,Ce)SiO ₄ + ZrO ₂ + CeO ₂
(22)	40:60	0.08	0.12				(Zr,Ce)SiO ₄ + ZrO ₂ + CeO ₂
(23)	30:70	0.06	0.14				ZrO ₂ + CeO ₂
(24)	0:100	0	0.20	6.5	150	7	CeSiO ₄

Table SI 2. Unit cell parameters and volume obtained by Rietveld refinements made from the PXRD patterns of pristine ZrSiO₄ samples prepared under hydrothermal conditions ($\Delta t = 20$ days, $T = 250^\circ\text{C}$) with starting zirconium and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$ and with various initial pH values.

Synthesis	pH _{ini}	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
(1)	[HNO ₃] = $1.0 \text{ mol}\cdot\text{L}^{-1}$	6.612(5)	5.973 (6)	261.1(7)
(2)	1.0	6.627(4)	5.979(4)	262.6(5)
(3)	2.0	6.627(3)	5.982(4)	262.7(4)
(4)	3.1	6.628(5)	5.980(6)	262.7(7)
(5)	4.1	6.623(4)	5.972(5)	262.0(5)
(6)	4.9	6.625(7)	5.972(8)	262.1(9)
(7)	6.0	6.625(5)	5.975(6)	262.2(7)
(8)	7.0	6.621(7)	5.968(8)	261.6(9)
(9)	8.0	6.618(7)	5.970(8)	261.5(9)
(10)	9.0	6.614(6)	5.974(7)	261.3(8)

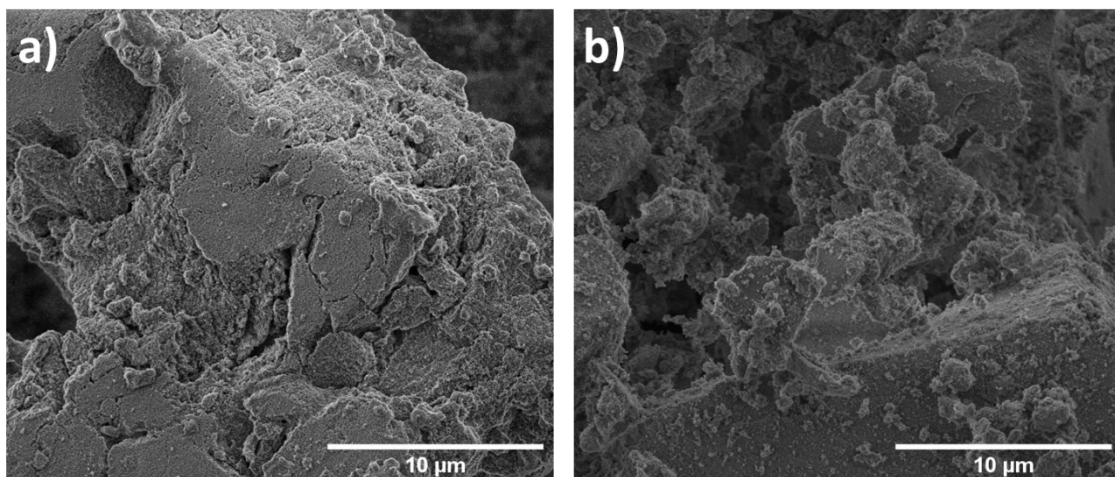


Figure SI 1. SEM micrographs recorded for **a)** pristine (14) and **b)** annealed (1000°C) ZrSiO_4 sample prepared under hydrothermal conditions ($T = 250^\circ\text{C}$, 7 days, $\text{pH} = 1.0$) starting with zirconium and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$.

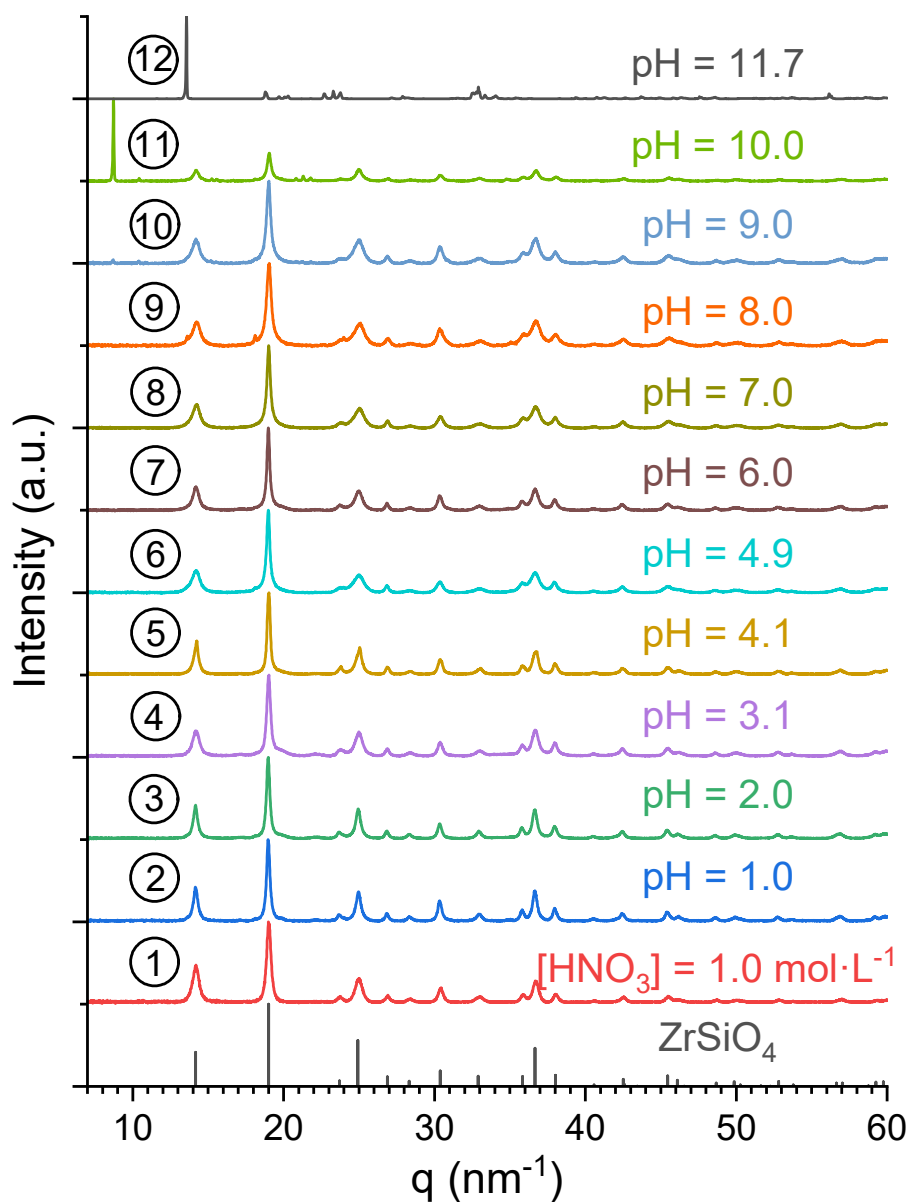


Figure SI 2. PXRD patterns obtained for ZrSiO_4 samples prepared under hydrothermal conditions (20 days, $T = 250^\circ\text{C}$) starting with zirconium and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$ and for various initial pH values: $1.0 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 (1), pH = 1.0 (2), pH = 2.0 (3), pH = 3.1 (4), pH = 4.1 (5), pH = 4.9 (6), pH = 6.0 (7), pH = 7.0 (8), pH = 8.0 (9), pH = 9.0 (10), pH = 10.0 (11) and pH = 11.7 (12), plotted in scattering vector.

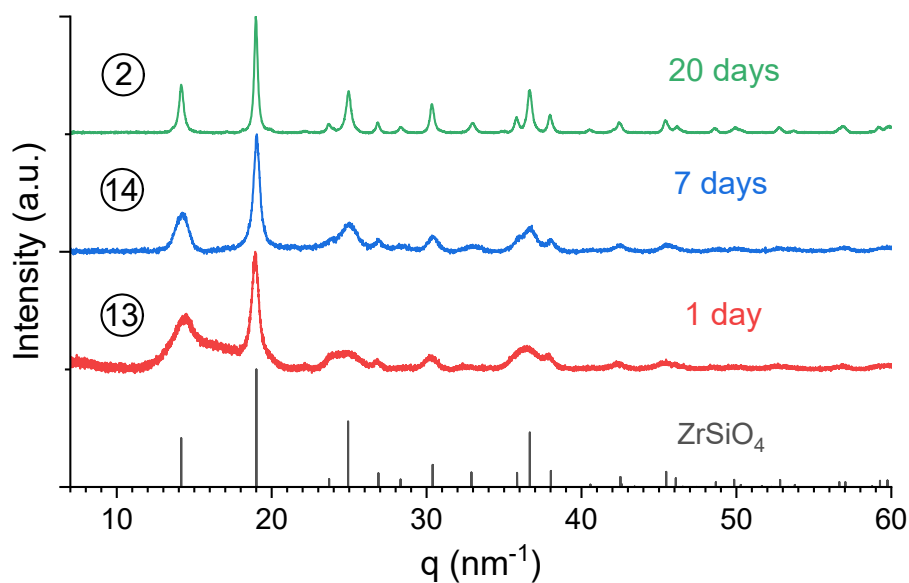


Figure SI 3. PXRD patterns obtained for ZrSiO₄ samples prepared under hydrothermal conditions ($T = 250^\circ\text{C}$, $\text{pH} = 1$) starting with zirconium and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$ and for holding time of 1 day (13), 7 days (14) and 20 days (2), plotted in scattering vector.

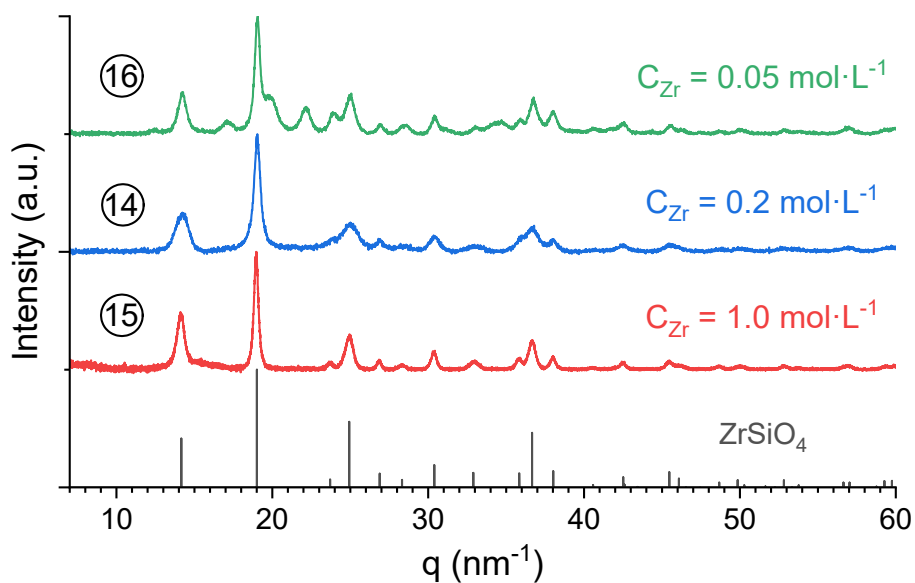


Figure SI 4. PXRD patterns obtained for ZrSiO₄ samples prepared under hydrothermal conditions ($T = 250^\circ\text{C}$, 7 days) at $\text{pH} = 1.0$ starting with zirconium and silicate concentrations of $1.0 \text{ mol}\cdot\text{L}^{-1}$ (15), $0.2 \text{ mol}\cdot\text{L}^{-1}$ (14) and $0.05 \text{ mol}\cdot\text{L}^{-1}$ (16), plotted in scattering vector.

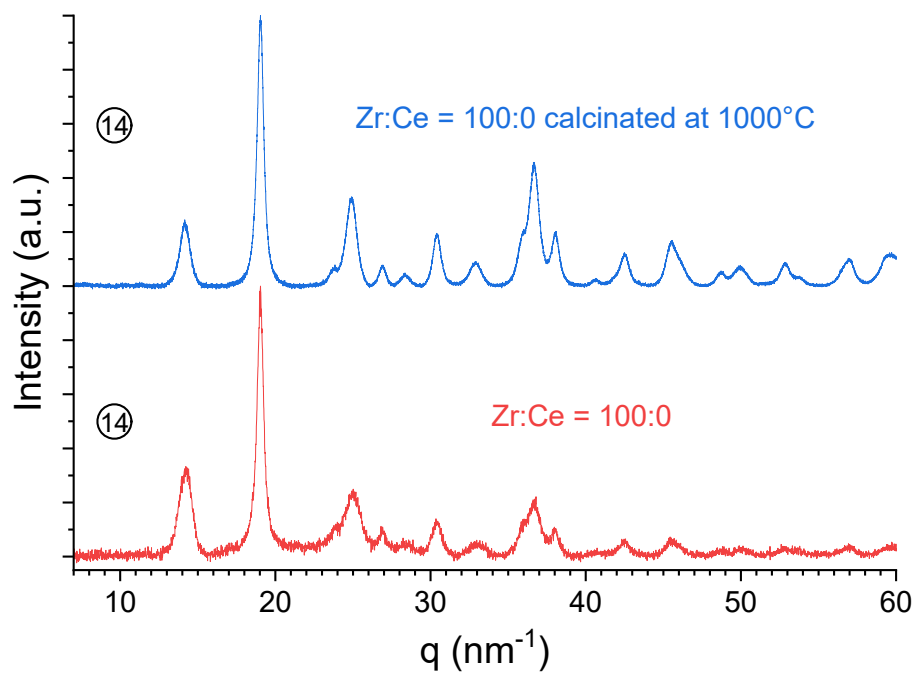


Figure SI 5. PXRD patterns recorded for a pristine and annealed (after TGA, 1000°C) ZrSiO₄ sample (14) prepared under hydrothermal conditions (T = 250°C, 7 days) at pH = 1.0 starting with zirconium and silicate concentrations of 0.2 mol·L⁻¹, plotted in scattering vector.

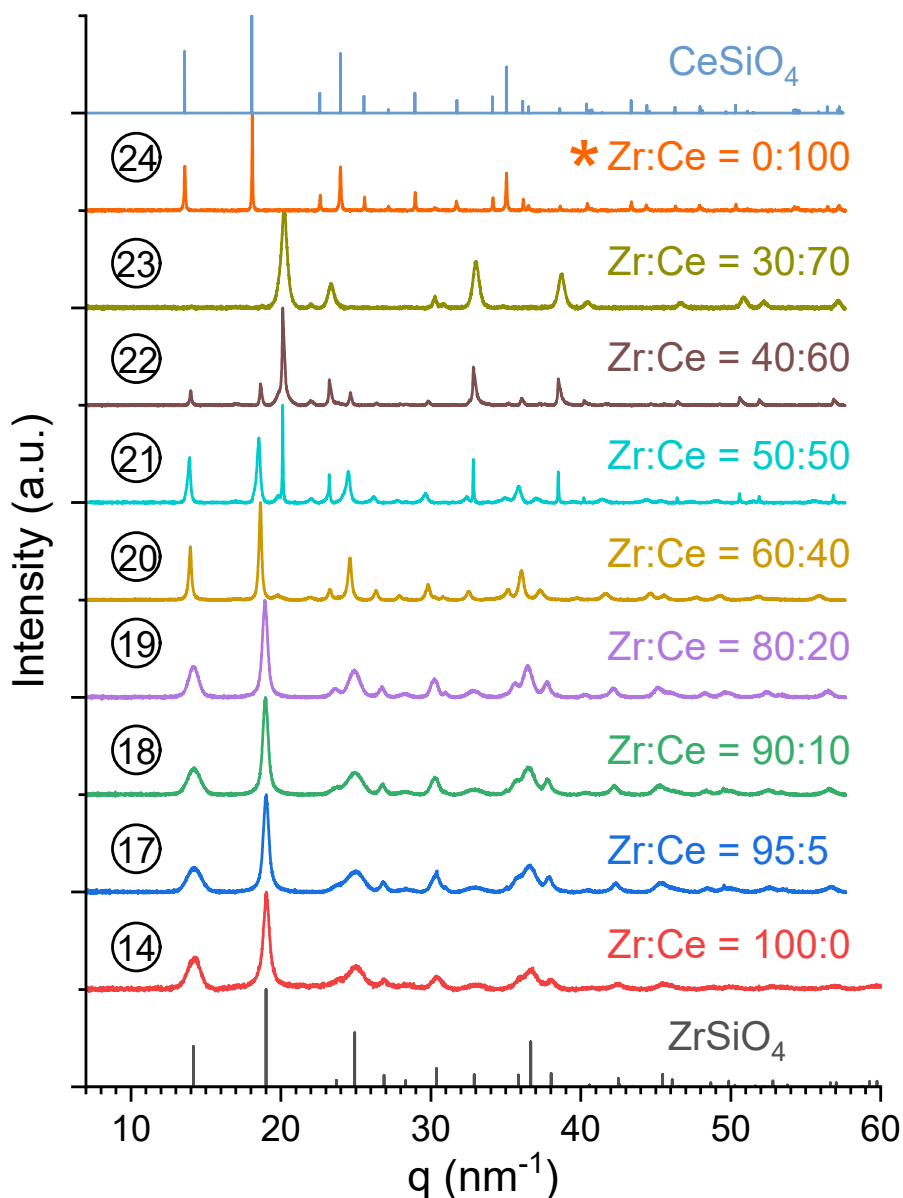


Figure SI 6. PXRD patterns recorded for pristine $(\text{Zr,Ce})\text{SiO}_4$ solid solutions with various chemical compositions prepared under hydrothermal conditions ($T = 250^\circ\text{C}$, 7 days, $\text{pH} = 1.0$) starting with Zr + Ce and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$ for Zr:Ce = 100:0 (14), 95:5 (17), 90:10 (18), 80:20 (19), 60:40 (20), 50:50 (21), 40:60 (22), 30:70 (23). * Reference CeSiO_4 sample ($T = 150^\circ\text{C}$, 7 days, $\text{pH} = 6.5$) starting with cerium and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$ (24), plotted in scattering vector.

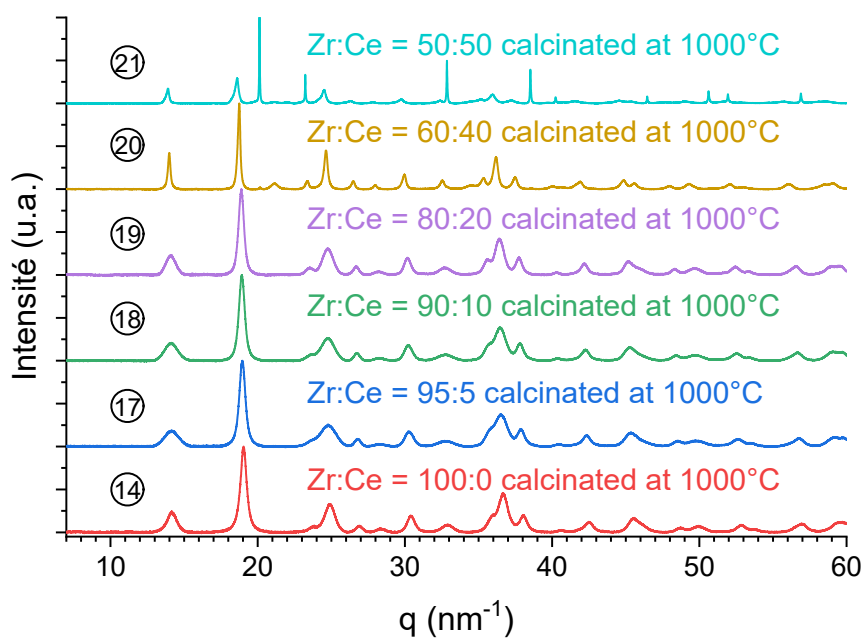


Figure SI 7. Synchrotron PXRD patterns recorded for $(\text{Zr,Ce})\text{SiO}_4$ solid solutions annealed at 1000°C with Zr:Ce = 100:0 (14), Zr:Ce = 95:5 (17), Zr:Ce = 90:10 (18), Zr:Ce = 80:20 (19), Zr:Ce = 60:40 (20) and Zr:Ce = 50:50 (21) prepared under hydrothermal conditions ($T = 250^\circ\text{C}$, 7 days, $\text{pH} = 1.0$) starting with Zr + Ce and silicate concentrations of $0.2 \text{ mol}\cdot\text{L}^{-1}$, plotted in scattering vector.

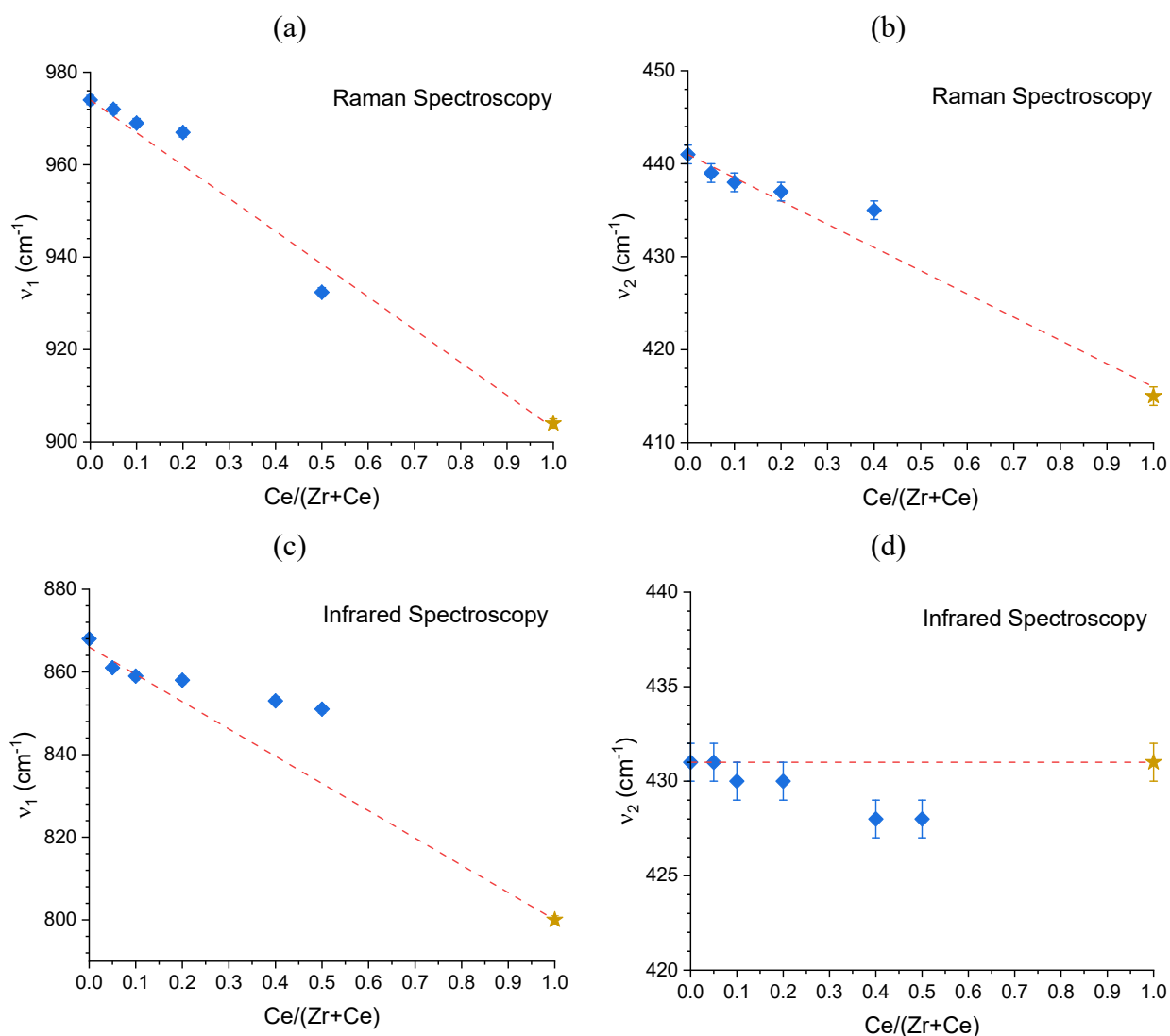


Figure SI 8. Variation of the ν_1 (a) and ν_2 (b) observed by Raman and ν_1 (c) and ν_2 (d) by IR spectroscopy for $(\text{Zr,Ce})\text{SiO}_4$ (annealed samples at 1000°C) versus the expected chemical composition. * Reference CeSiO_4 sample wasn't obtained in the same chemical conditions as the $(\text{Zr,Ce})\text{SiO}_4$ samples.

ν_4 is not observable for Raman spectroscopy, due to its low intensity. ν_3 band position was difficult to determine by IR spectroscopy was difficult to determine with a good accuracy due to its low intensity and nearness with SiO_2 characteristic band. Moreover, ν_1 band position for $\text{Zr}:\text{Ce} = 60:40$ by Raman spectroscopy was masked by ν_3 band and ν_2 band position for $\text{Zr}:\text{Ce} = 50:50$ by Raman spectroscopy masked by CeO_2 T_{2g} band.

Errors bars for ν_1 bands position are smaller than the data point size ($\pm 1 \text{ cm}^{-1}$).