Hydrothermal synthesis of $(Zr,U)SiO_4$, an efficient pathway to incorporate uranium in zircon

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SUPPORTING INFORMATION

Table SI 1. Synthesis parameters for the presented $(Zr,U)SiO_4$ hydrothermal syntheses (starting pH = 3.0, T = 250°C and t = 7 days).

Label	Zr:U mol ratio	C_{Zr} ($mol \cdot L^{-1}$)	C_U ($mol \cdot L^{-1}$)	Final phase
(1)	**100:0**	**0.20**	**0.00**	$ZrSiO_4$
(2)	**90:10**	**0.18**	**0.02**	$(Zr,U)SiO_4$
(3)	**80:20**	**0.16**	**0.04**	$(Zr,U)SiO_4 + UO_2$
(4)	**70:30**	**0.14**	**0.06**	$(Zr,U)SiO_4 + UO_2$
(5)	**60:40**	**0.12**	**0.08**	$(Zr,U)SiO_4 + UO_2$
(6)	**50:50**	**0.10**	**0.10**	$(Zr,U)SiO_4 + UO_2$
(7)	**40:60**	**0.08**	**0.12**	$(Zr,U)SiO_4 + UO_2$
(8)	**30:70**	**0.06**	**0.14**	$(Zr,U)O_2$
(9)	**20:80**	**0.04**	**0.16**	$(Zr,U)O_2$
(10)	**90:10**	**0.02**	**0.18**	$(Zr,U)O_2$

Table SI 2. Unit cell and volume of the zircon-type phase obtained by Rietveld refinements performed from PXRD patterns of pristine $(Zr,U)SiO_4$ solid solutions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 mol·L^{-1} with different chemical compositions.

		Pristine samples			Purified samples			Annealed at 1200°C		
	$\frac{U}{Zr+U}$	a (Å)	c (Å)	V (Å^3)	a (Å)	c (Å)	V (Å^3)	a (Å)	c (Å)	V (Å^3)
(1)	0	6.6103(5)	5.9768(4)	261.16(6)	6.6103(5)	5.9768(4)	261.16(6)	6.6025(5)	5.9770(5)	260.55(6)
(2)	0.1	6.6306(6)	5.9927 (6)	263.47(8)	6.6306(6)	5.9927 (6)	263.47(8)	6.631(1)	5.999(1)	263.8(2)
(3)	0.2	6.7341(5)	6.0556(6)	274.61(7)	6.725(2)	6.049(2)	273.6(2)	6.677(2)	6.033(2)	268.9(3)
(4)	0.3	6.7468(7)	6.0648(7)	276.06(9)	6.740(2)	6.063(2)	275.4(2)	6.723(1)	6.063(1)	274.0(1)
(5)	0.4	6.7697(5)	6.0796(5)	278.62(7)	6.761(1)	6.078(1)	277.8(1)	6.753(1)	6.085(1)	277.5(2)
(6)	0.5	6.7997(9)	6.099(1)	282.0(1)	6.793(3)	6.098(3)	281.4(4)	6.782(1)	6.105(1)	280.8(1)
(7)	0.6	6.8343(7)	6.1174(7)	285.73(9)	6.827(2)	6.117(2)	285.1(3)	6.807(1)	6.122(1)	283.6(1)

Table SI 3. Unit cell and volume of oxide phases obtained from PXRD patterns of pristine $(Zr,U)SiO_4$ solid solutions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 mol·L^{-1} with different chemical compositions.

		UO_{2+x}		$(Zr,U)O_{2+x}$	
	$\frac{U}{Zr+U}$	a (Å)	V (Å^3)	a (Å)	V (Å^3)
(3)	0.2	5.4703(3)	163.69(3)	-	-
(4)	0.3	5.467(1)	163.4(1)	-	-
(5)	0.4	5.4698(5)	163.65(4)	5.437(1)	160.7(1)
(6)	0.5	5.4636(7)	163.09(6)	5.353(5)	153.4(5)
(7)	0.6	5.460(2)	162.8(2)	5.385(1)	156.2(1)
(8)	0.7	5.463(1)	163.06(9)	5.386(2)	156.3(2)
(9)	0.8	5.4588(5)	162.66(5)	5.419(2)	159.1(2)
(10)	0.9	5.464(2)	163.1(2)	5.445(1)	161.4(1)

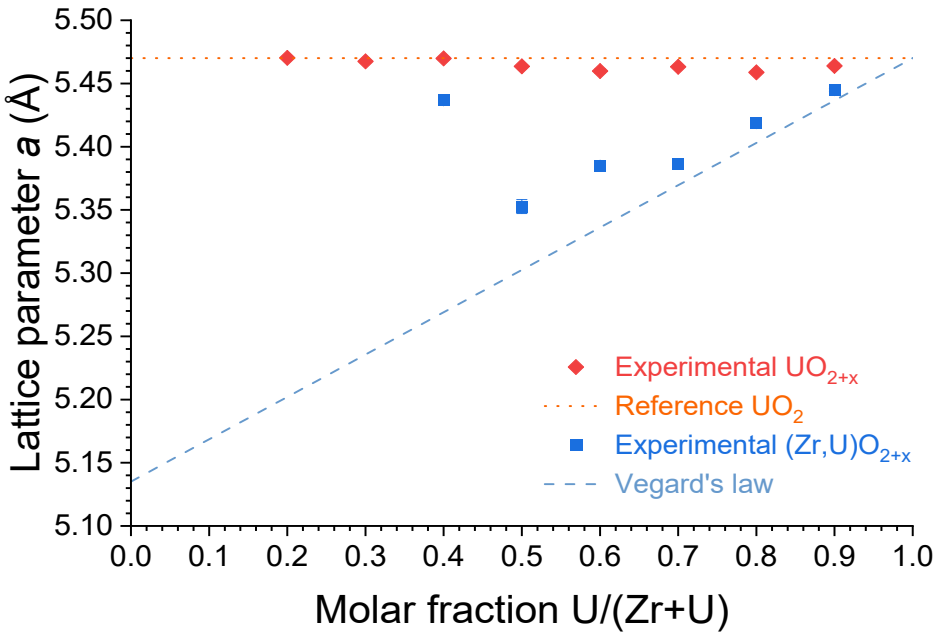

Figure SI 1. Unit cell parameters *a* obtained by Rietveld refinements for the oxide phases performed from PXRD patterns of pristine (Zr,U)SiO_4 solid solutions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 mol·L^{-1} with different chemical compositions.

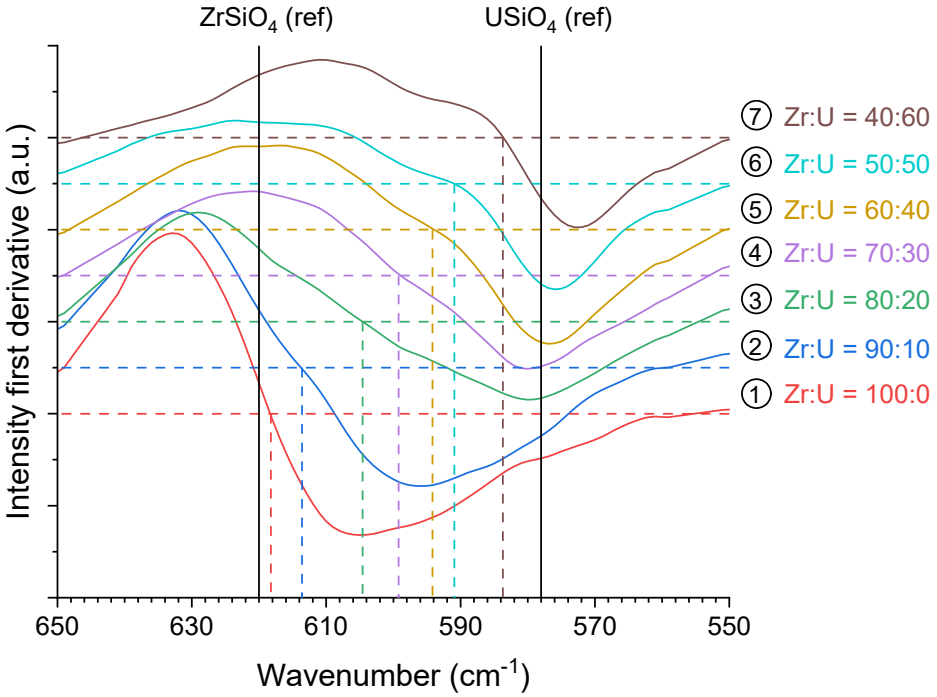

Figure SI 2. First derivative of the infrared spectra, focussed on the SiO_4 group ν_4 band, recorded for pristine (Zr,U)SiO_4 solid solutions with different chemical compositions prepared under hydrothermal conditions without purification (T = 250°C, 7 days, pH = 3.0) from Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 100:0 (1), 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6), 40:60 (7), 30:70 (8), 20:80 (9) and 10:90 (10). The reference $ZrSiO_4$ ν_4 band position has been taken from ref. [91]

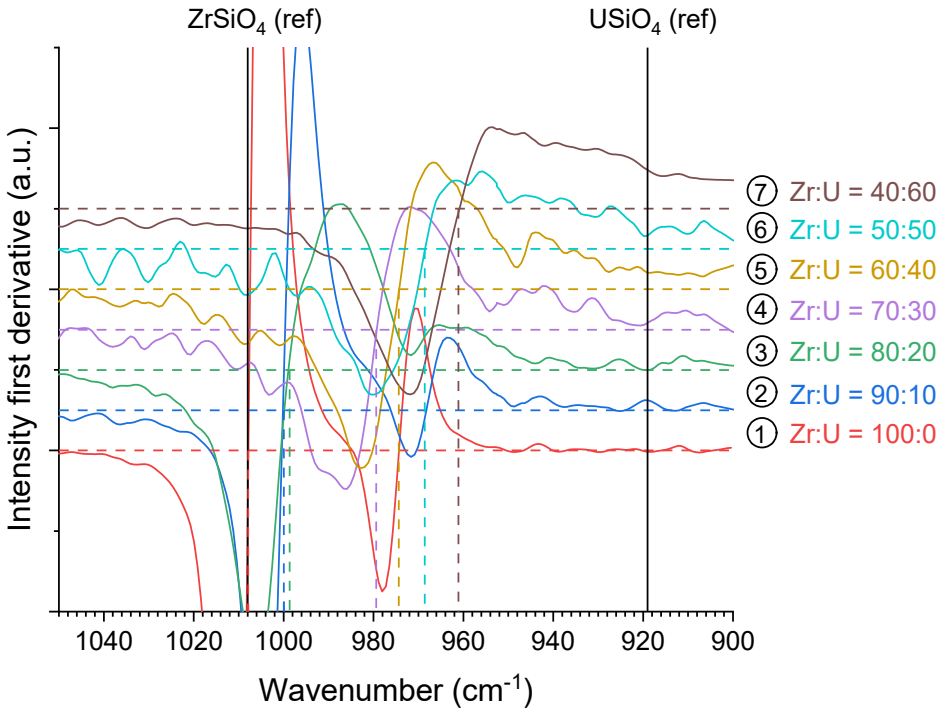

Figure SI 3. First derivative of the Raman spectra, focussed on the SiO_4 group ν_3 band, recorded for pristine (Zr,U)SiO_4 solid solutions with different chemical compositions prepared under hydrothermal conditions without purification (T = 250°C, 7 days, pH = 3.0) from Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 100:0 (1), 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6), 40:60 (7), 30:70 (8), 20:80 (9) and 10:90 (10). Reference $ZrSiO_4$ and $USiO_4$ ν_3 band positions taken from ref [93].

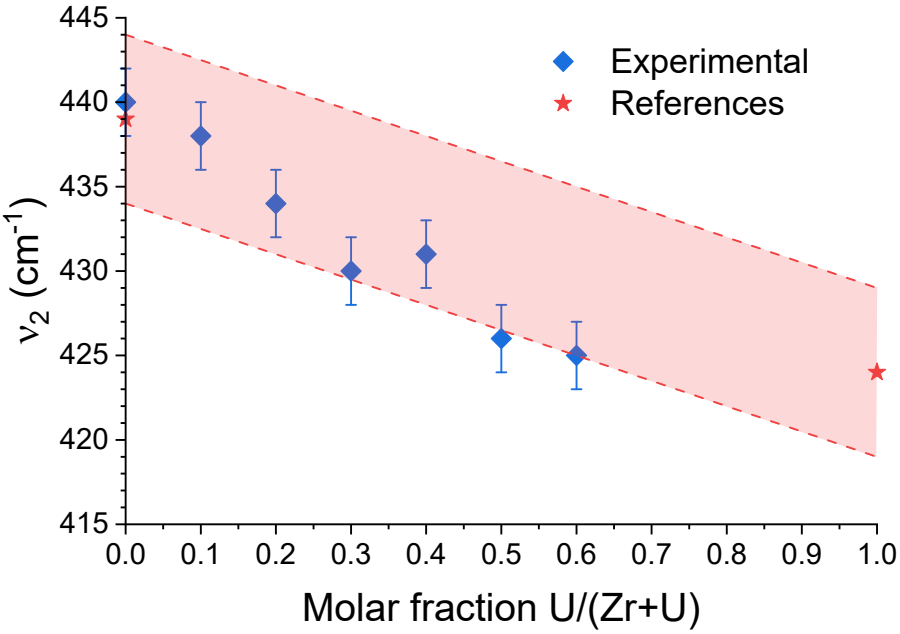

Figure SI 4. Position of the ν_2 band in Raman spectroscopy plotted as a function of the expected U/(Zr+U) molar fraction for pristine (Zr,U)SiO_4 solid solutions with different chemical compositions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting from Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 100:0 (1), 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6) and 40:60 (7). Reference $ZrSiO_4$ and $USiO_4$ ν_2 band positions taken from ref [93]. The shaded area corresponds to the expected linear variation of the ν_2 band of the SiO_4 group in Raman spectroscopy, based on reference values reported in the literature, with a confidence interval of 5 cm^{-1}.

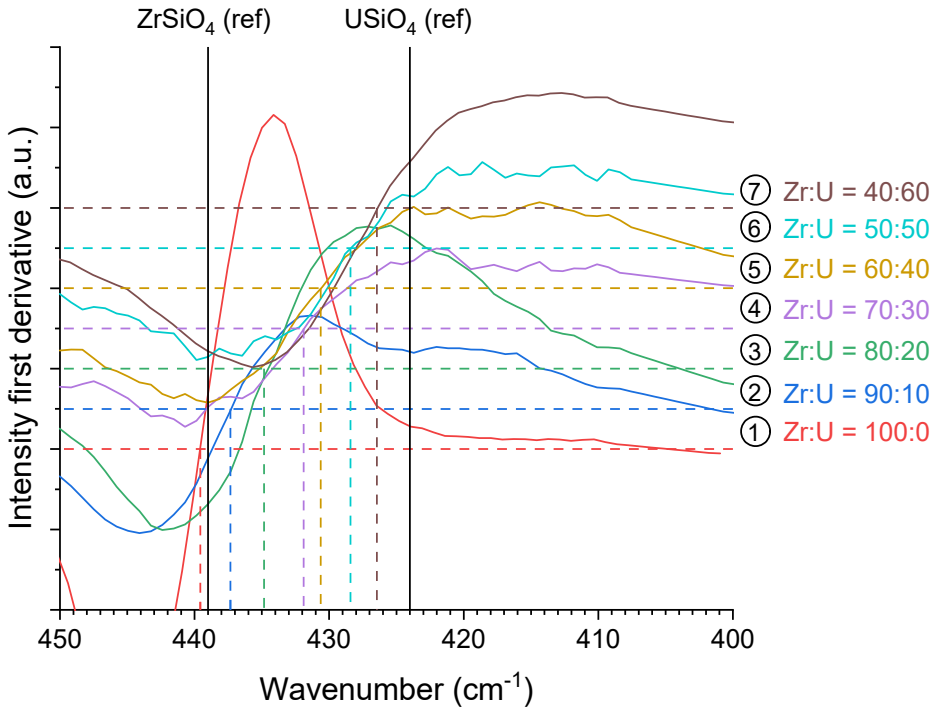

Figure SI 5. First derivative of the Raman spectra, focussed on the SiO_4 group ν_2 band, recorded for pristine (Zr,U)SiO_4 solid solutions with different chemical compositions prepared under hydrothermal conditions without purification (T = 250°C, 7 days, pH = 3.0) from Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 100:0 (1), 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6), 40:60 (7), 30:70 (8), 20:80 (9) and 10:90 (10). Reference $ZrSiO_4$ and $USiO_4$ ν_2 band positions taken from ref [93].

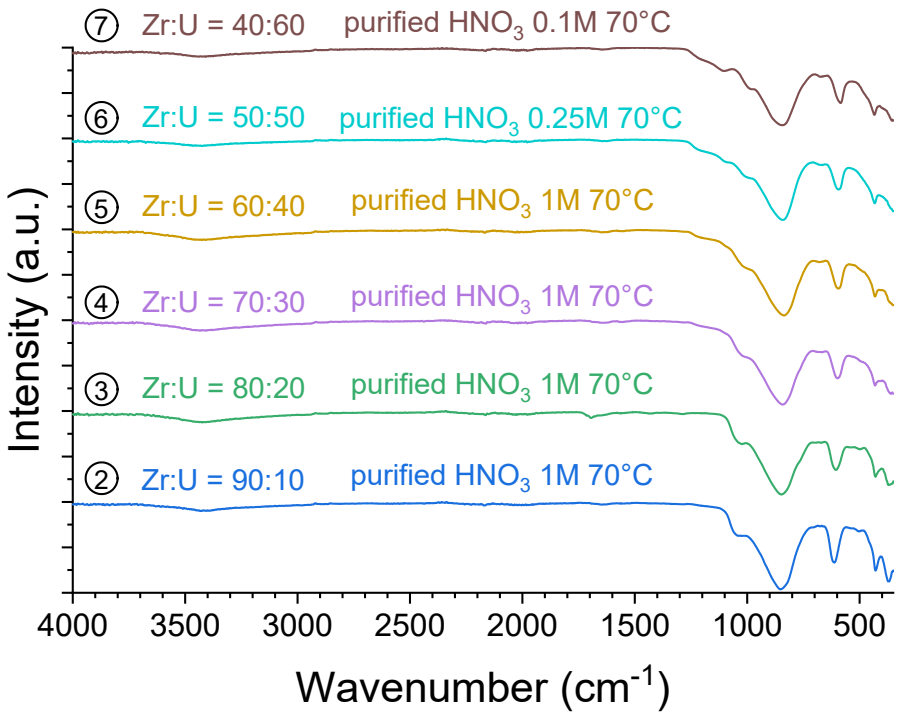

Figure SI 6. Infrared spectra recorded for purified (Zr,U)SiO_4 solid solutions of different chemical compositions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6), 40:60 (7) and washed in nitric media.

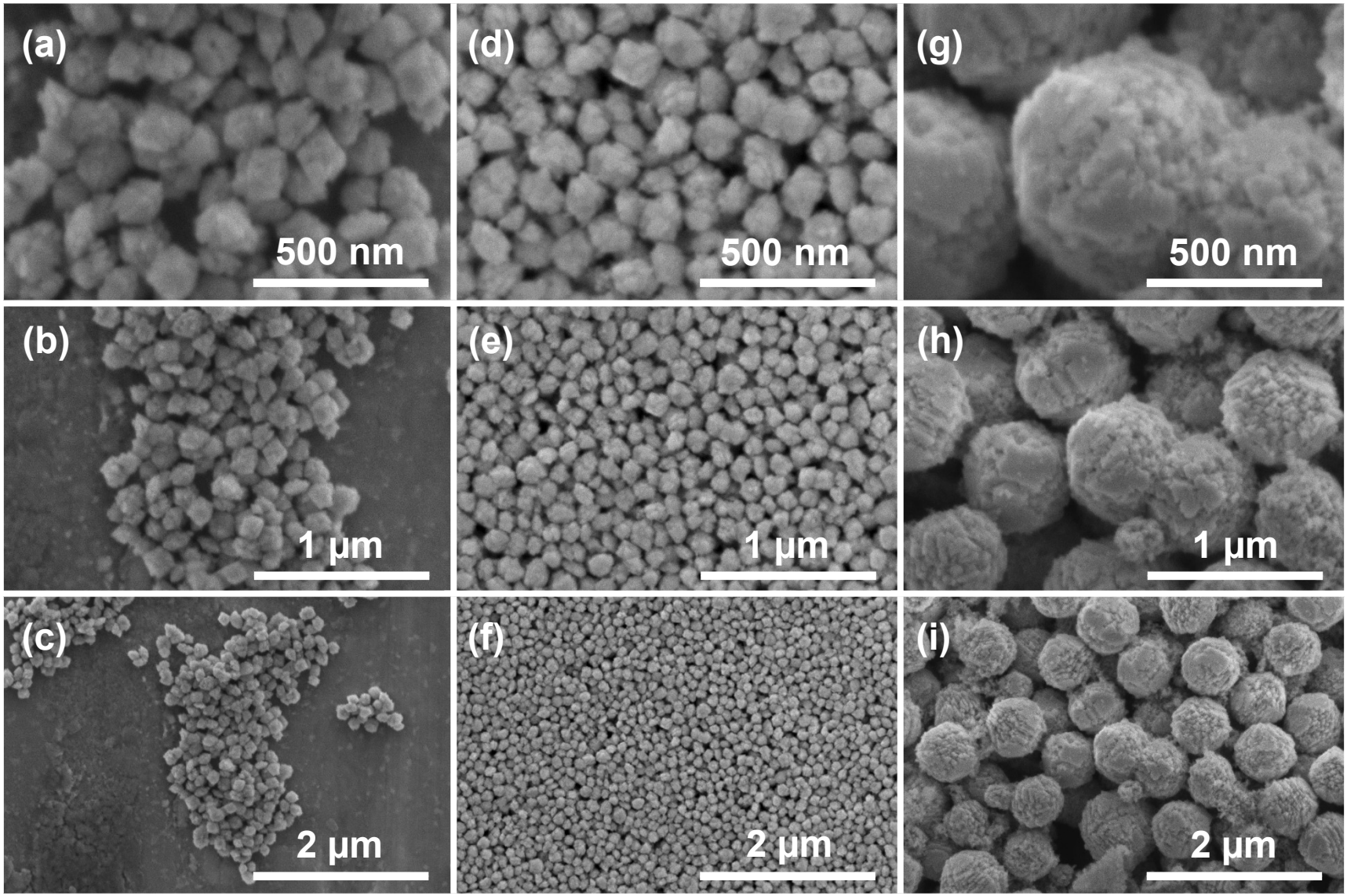

Figure SI 7. SEM micrographs of purified $(Zr,U)SiO_4$ solid solutions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 $mol \cdot L^{-1}$ for Zr:U = 80:20 (3) (a, b and c), 60:40 (5) (d, e and f) and 40:60 (7) (g, h and i) and washed in nitric media.

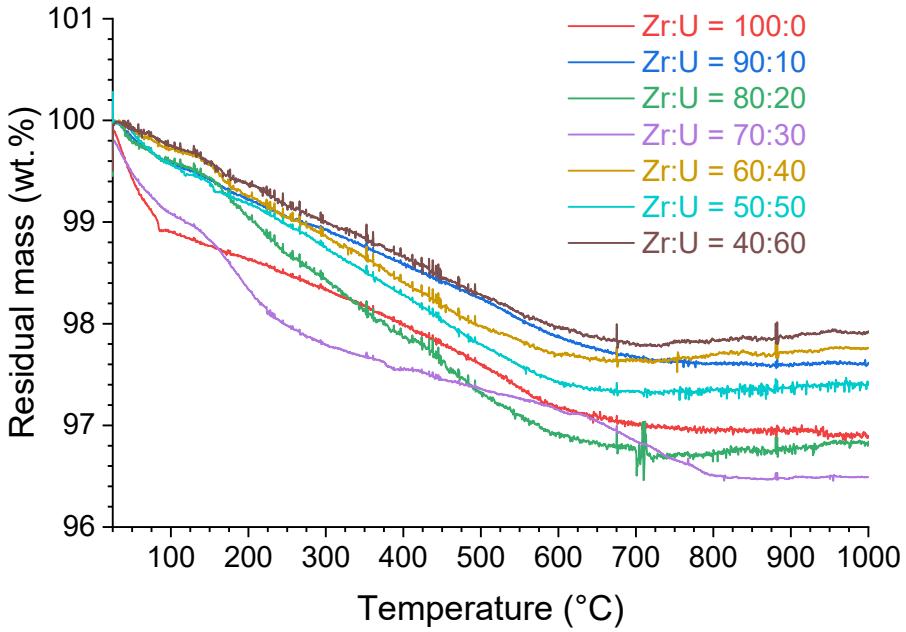

Figure SI 8. Results of Thermogravimetric analyses recorded in inert atmosphere (Ar) for purified (Zr,U)SiO_4 solid solutions of different chemical compositions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6), 40:60 (7) and after washing in nitric media.

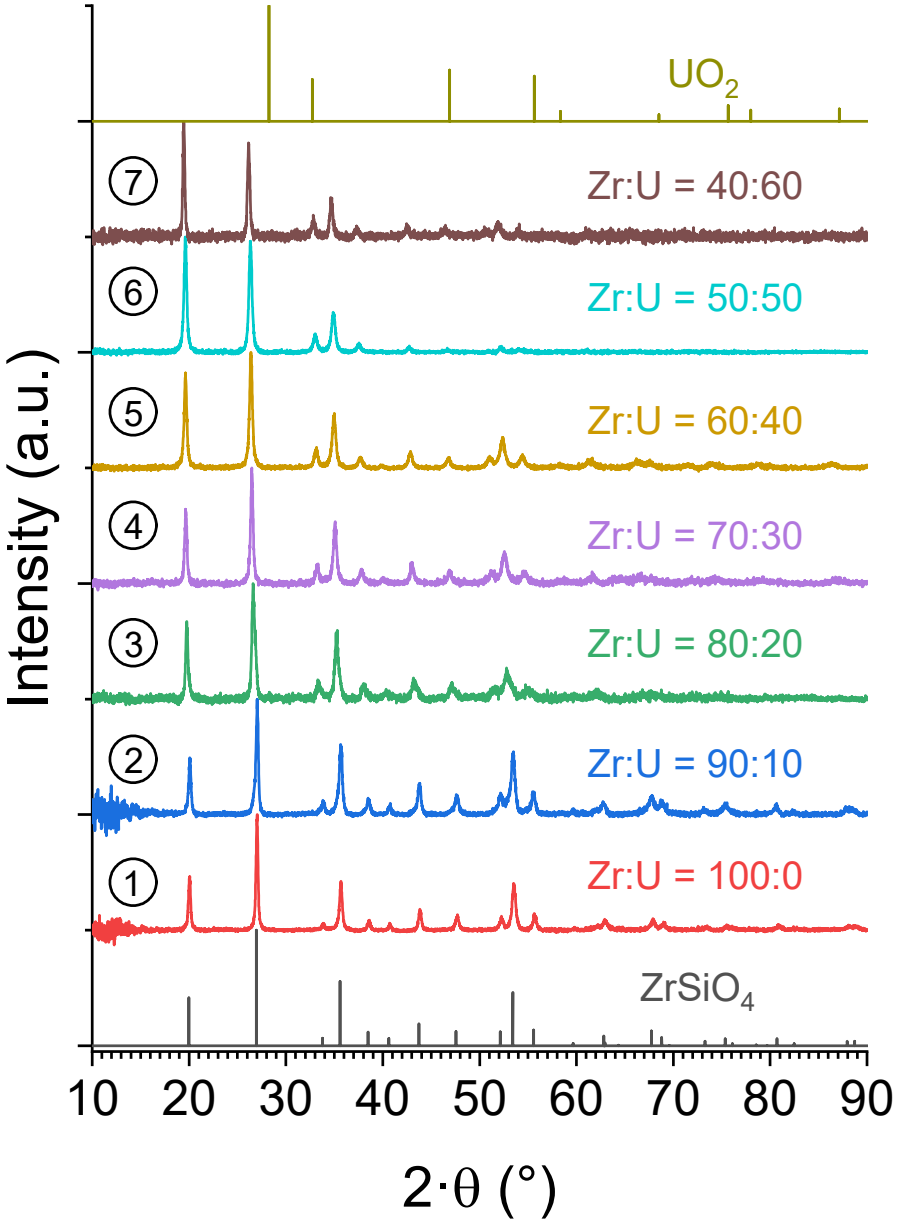

Figure SI 9. PXRD patterns recorded for purified (Zr,U)SiO_4 solid solutions heated at 1000°C under argon atmosphere with different chemical compositions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0) starting with Zr + U and silicate concentrations of 0.2 mol·L^{-1} for Zr:U = 90:10 (2), 80:20 (3), 70:30 (4), 60:40 (5), 50:50 (6), 40:60 (7). Bragg positions of the characteristic peaks of $ZrSiO_4$ and UO_2 were extracted from Refs [89] and [94].

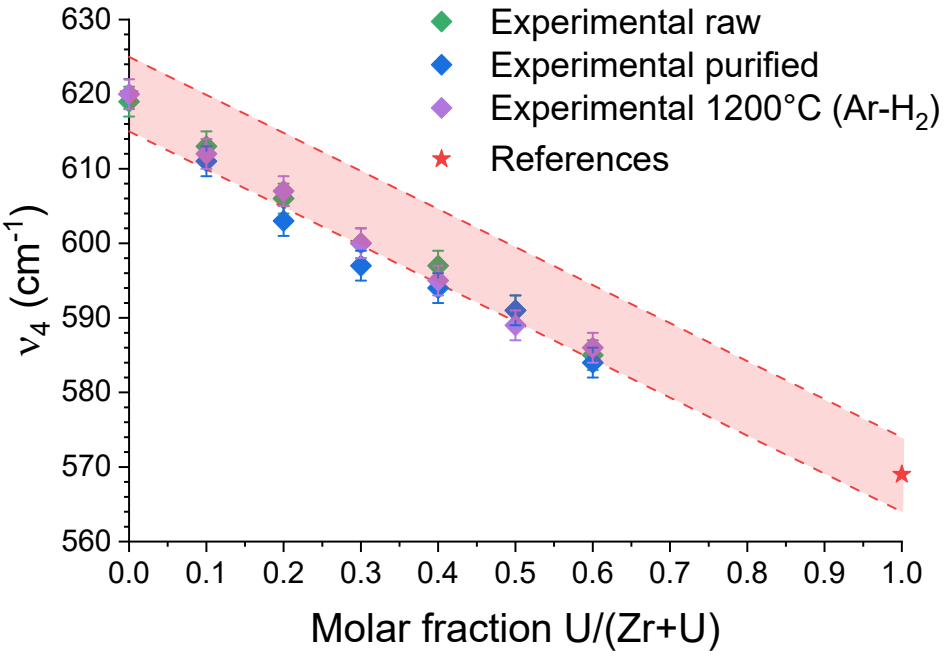

Figure SI 10. Position of the ν_4 band in infrared spectroscopy plotted as a function of the expected U/(Zr+U) molar fraction for pristine, purified and calcined $(Zr,U)SiO_4$ solid solutions $(Zr,U)SiO_4$ solid solutions with different chemical compositions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0). The reference $ZrSiO_4$ ν_4 band position has been taken from ref. [91] The shaded area corresponds to the expected linear variation of the ν_4 band of the SiO_4 group in IR spectroscopy, based on reference values reported in the literature, with a confidence interval of 5 cm^{-1}.

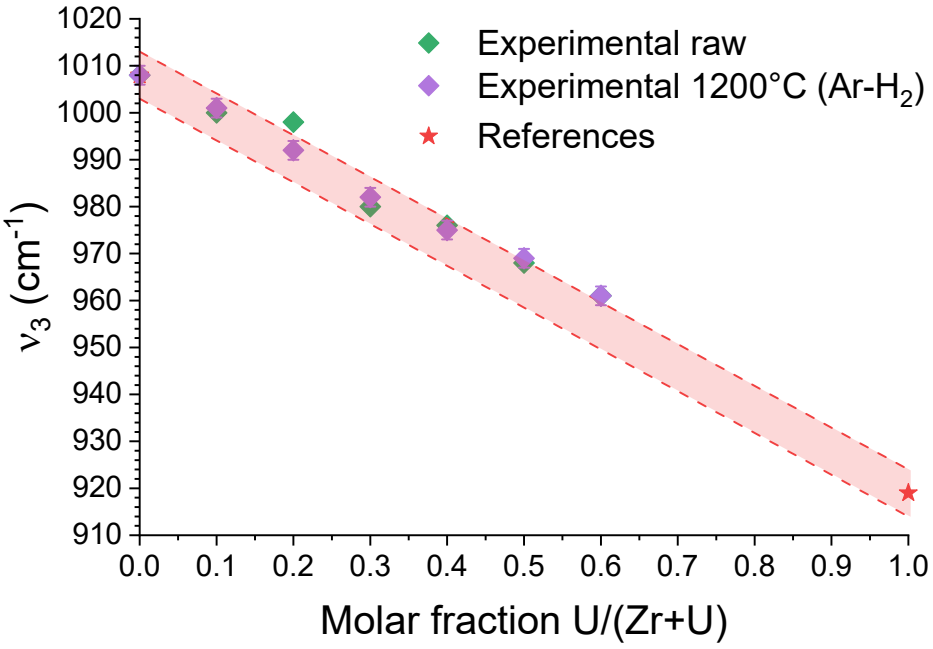

Figure SI 11. Position of the ν_3 band in Raman spectroscopy plotted as a function of the expected U/(Zr+U) molar fraction for pristine and calcined $(Zr,U)SiO_4$ solid solutions $(Zr,U)SiO_4$ solid solutions with different chemical compositions

prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0). Reference $ZrSiO_4$ and $USiO_4$ ν_3 band positions taken from ref [93]. The shaded area corresponds to the expected linear variation of the ν_3 band of the SiO_4 group in Raman spectroscopy, based on reference values reported in the literature, with a confidence interval of 5 cm^{-1}.

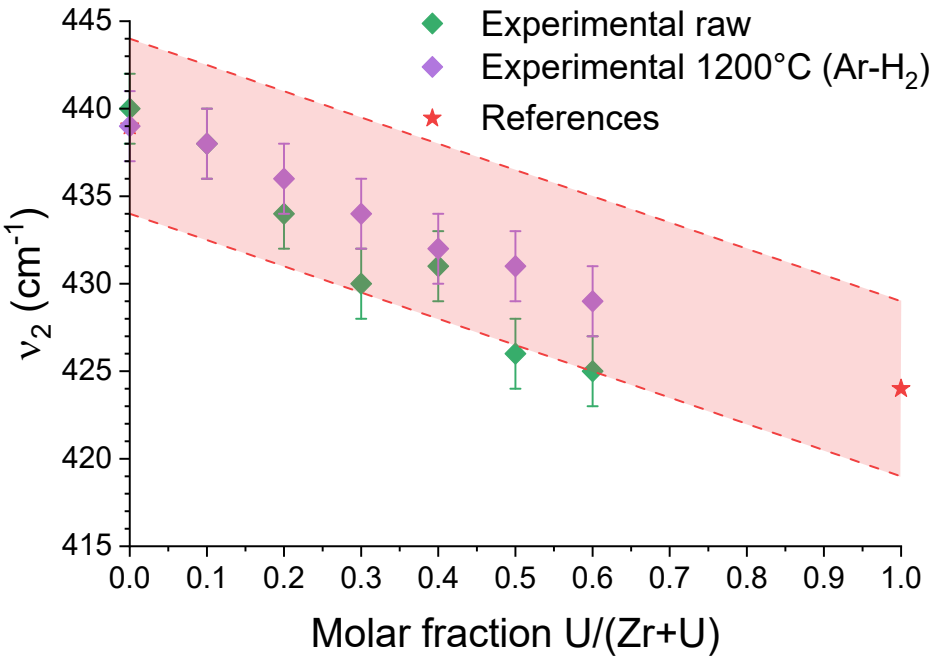

Figure SI 12. Position of the ν_2 band in Raman spectroscopy plotted as a function of the expected U/(Zr+U) molar fraction for pristine and calcined $(Zr,U)SiO_4$ solid solutions $(Zr,U)SiO_4$ solid solutions with different chemical compositions prepared under hydrothermal conditions (T = 250°C, 7 days, pH = 3.0). Reference $ZrSiO_4$ and $USiO_4$ ν_2 band positions taken from ref [93]. The shaded area corresponds to the expected linear variation of the ν_2 band of the SiO_4 group in Raman spectroscopy, based on reference values reported in the literature, with a confidence interval of 5 cm^{-1}.