Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information for Paper

Towards the sustainable synthesis of microporous and layered titanosilicates: mechanochemical pre-treatment reduces the water amount

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ETS-10

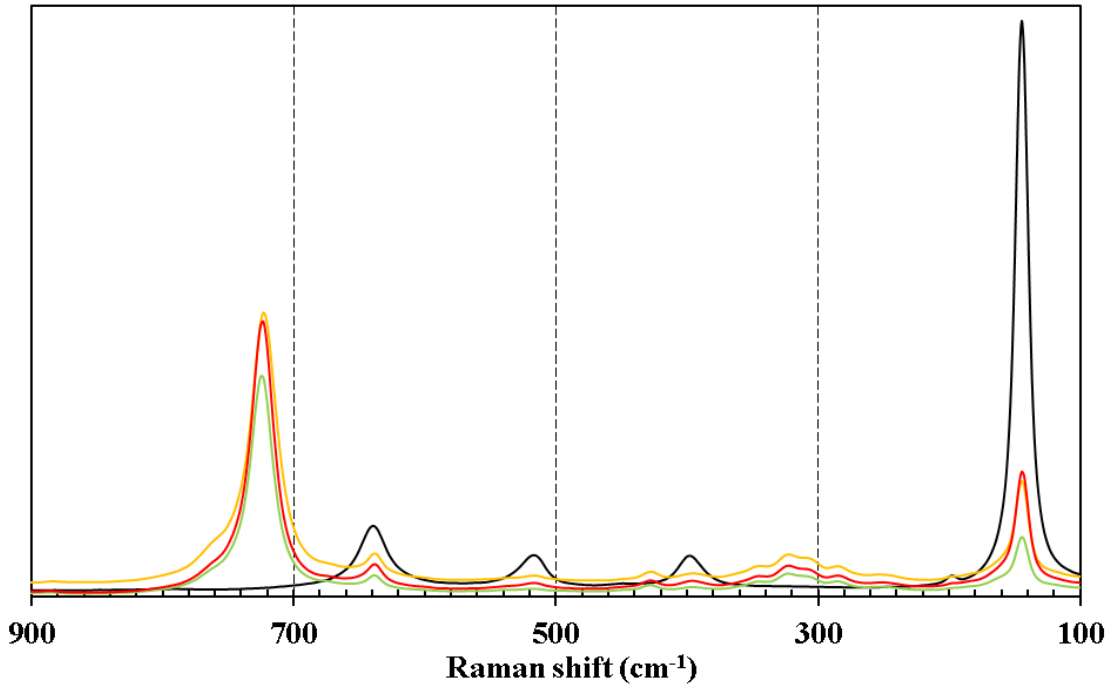

Fig. S1 FT Raman spectra of ETS-10 after crystallization at 230 °C for 12 H_2O and 1D (yellow), 7 H_2O and 3 D (red) and 3.5 H_2O and 3D (green), and the spectrum of P25 (black).

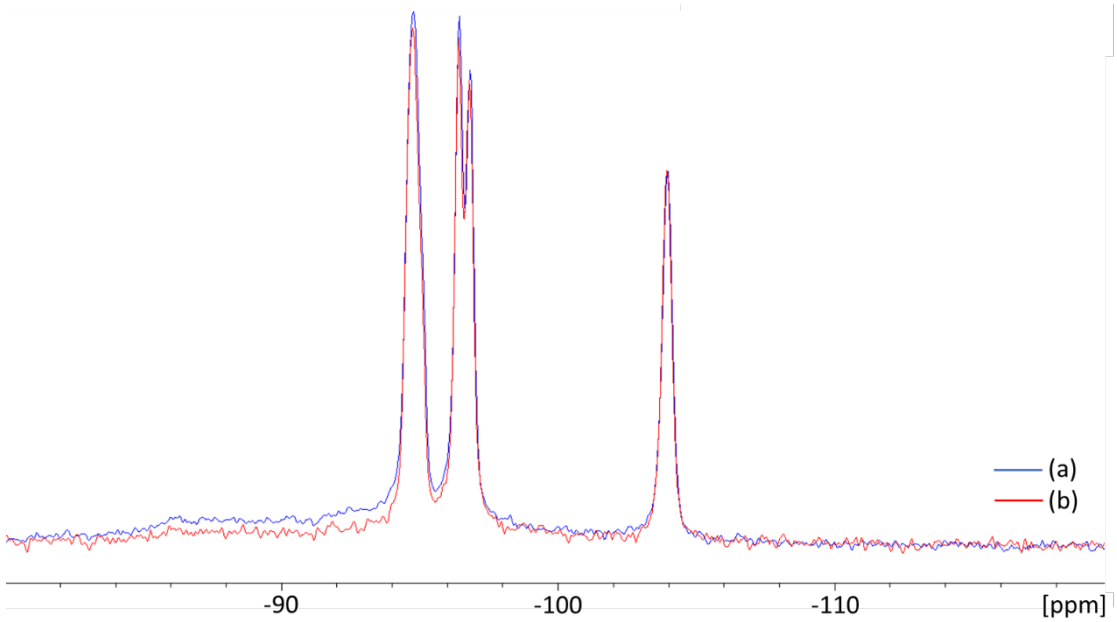

Fig. S2 ^{29}Si MAS NMR spectra of ETS-10 after crystallization at 230 °C for 12 H_2O and 1 day (a), and 3.5 H_2O and 3 days (b).

Sitinakite

Studies with different amounts of water were conducted using precipitated silica and after 8 h, showing that the minimum amount necessary to obtain pure sitinakite was 7 H_2O (Fig. S3). To understand the possibility of reducing even more the time of thermal treatment, additional experiments were performed. When using precipitated silica, the best time to obtain pure sitinakite was 6 h of thermal treatment. Shorter times did not afford pure sitinakite.

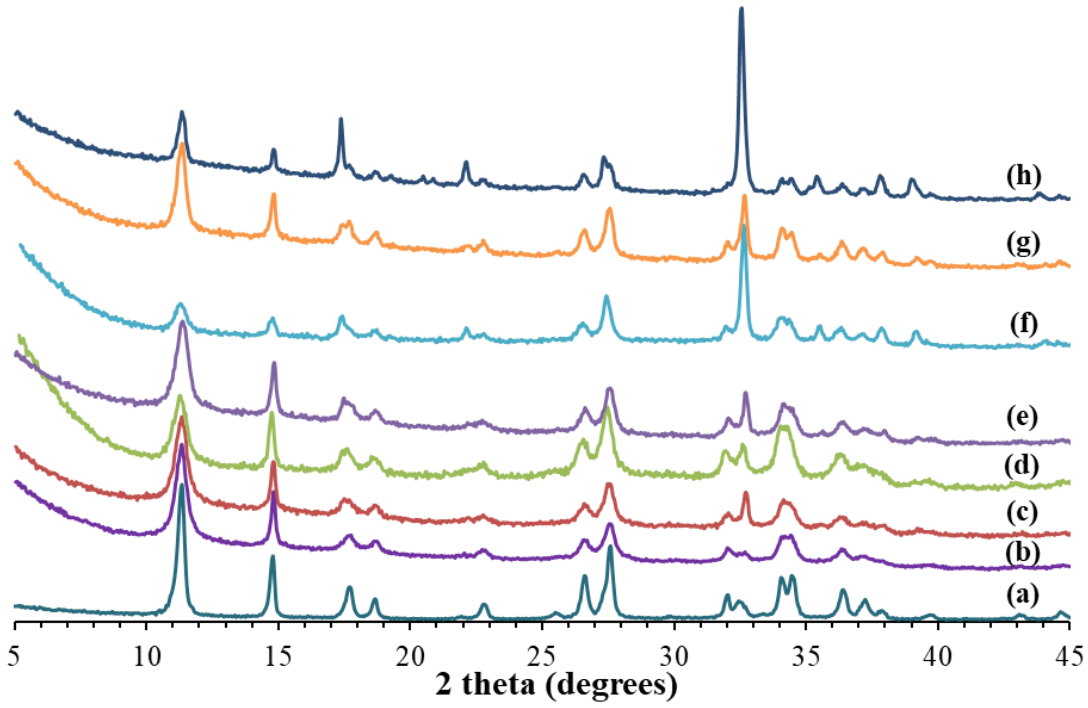

Fig. S3 PXRD patterns of sitinakite (reference sample) (a)[1], and with different amounts of H_2O prepared with ball milling and thermal treatment at 230 °C for 8 h using precipitated silica and 30 min. ball milling at 400 rpm, 7 H_2O (b), 6 H_2O (c), 5 H_2O (d), 4 H_2O (e), 3 H_2O (f), 2 H_2O (g) and 1 H_2O (h).

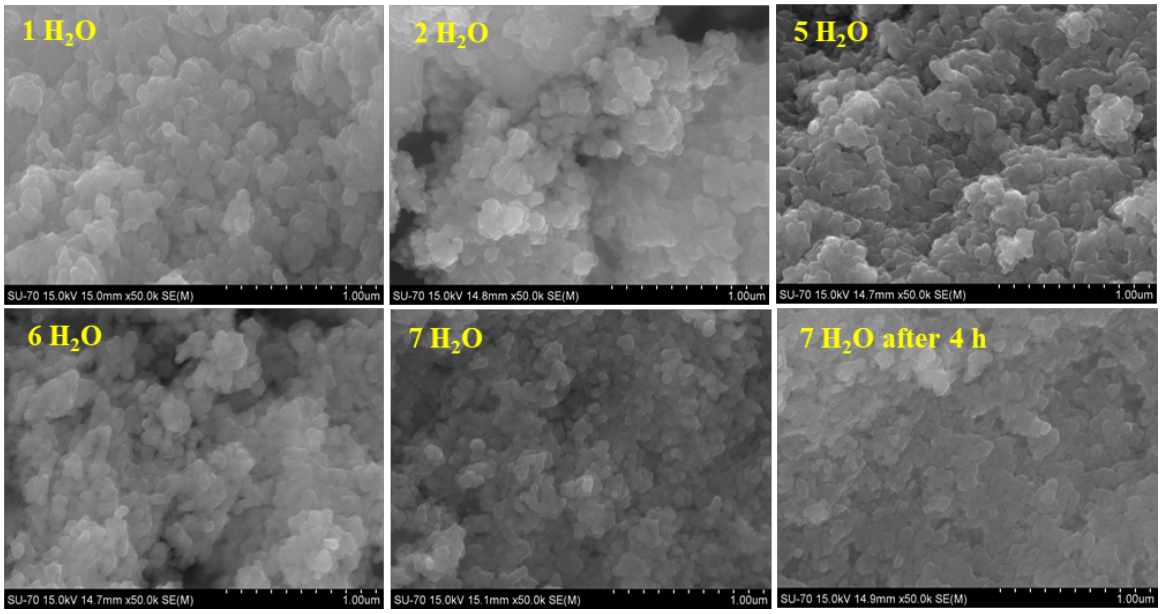

Fig. S4 SEM images of the synthesized sitinakite samples prepared by mixing sources by ball milling and after crystallization at 230 °C for 4 h (fumed silica) and 8 h (precipitated silica) (if not mentioned in the figure).

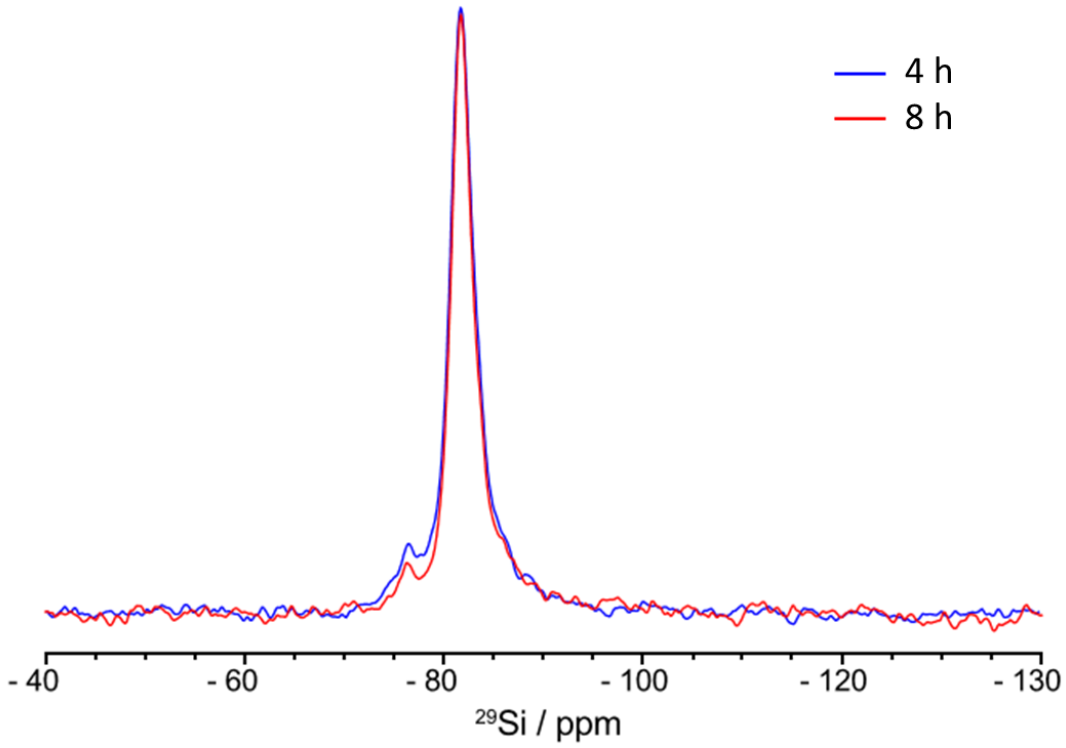

Fig. S5 ^{29}Si MAS NMR spectra of sitinakite prepared at 230 °C for 4 h (from fumed silica) and 8 h (from precipitated silica).

Table S1 Experimental conditions used to prepare sitinakite in this work and reported in the literature.

Entry	Temperature (°C)	Time	Mixture/Gel composition	Ref.
1	230	4 h – 8 h	0.75 Na_2O : 0.60 SiO_2 : 1 TiO_2 : 1-7 H_2O	This work
2	170	8 days	5.1 Na_2O : 1 SiO_2 : 1 TiO_2 : 142 H_2O	2
3	200	10 days	10 Na_2O : 1.5 SiO_2 : 1 TiO_2 : 829 H_2O	3,4
4	170	3.5 days	y Na_2O : x SiO_2 : 1 TiO_2 : 146 H_2O y Na_2O : 1.98 SiO_2 : 1 TiO_2 : 218 H_2O	5,6
5	200	5-10 days	3.70 Na_2O 0.2 SiO_2 : 1 TiO_2 : 82 H_2O	7–10
6	210	10 days	6.77 Na_2O : 1.98 SiO_2 : 1 TiO_2 : 218 H_2O	11,12
7	170	6-7 days	1.60 Na_2O : 1 SiO_2 : 0.78 TiO_2 : 20 H_2O	1
8*	200	24 h	4 Na_2O : 2n SiO_2 : 2 TiO_2 : n H_2O	13
9	200	10 days	3 Na_2O : 0.03 Si_2O : 1 TiO_2 : 160 H_2O	14
10	250	12 h	5.98 Na_2O : 1.2 SiO_2 : 1 TiO_2 : 657.7 H_2O	15

* Ultrasonic for 1 h

Ivanyukite-K

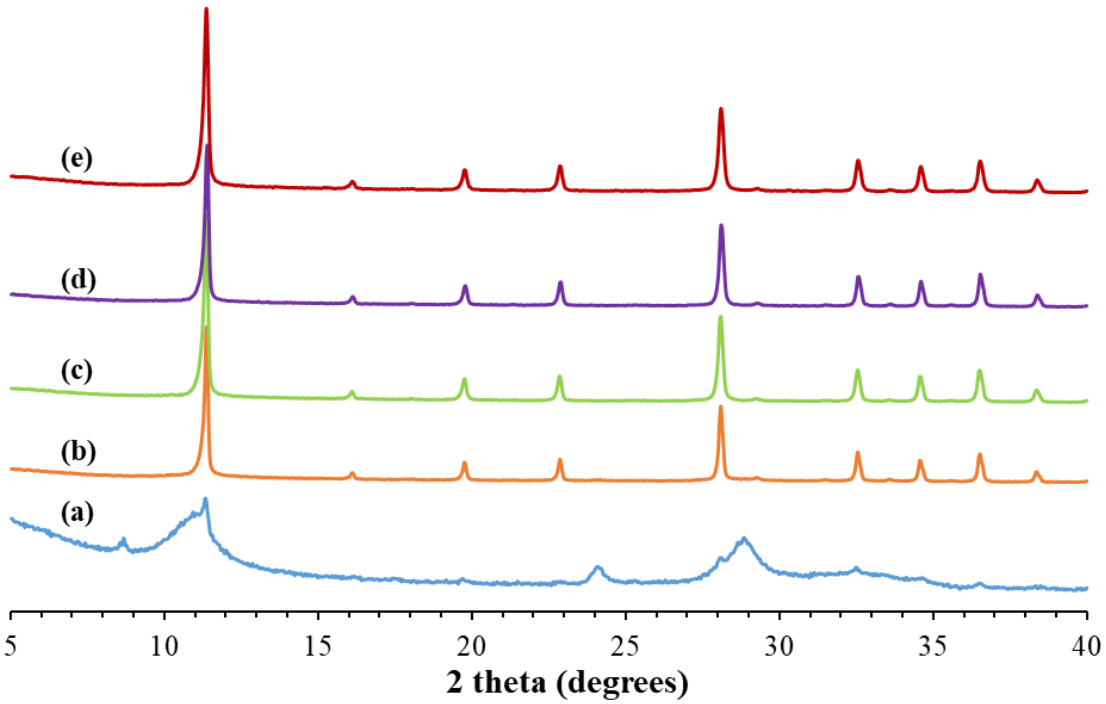

Fig. S6 PXRD patterns of ivanyukite-K prepared without additional H_2O, 1 day (a), 2 days (b), 3 days (c), 4 days (d) and 6 days (e) of hydrothermal treatment at 230 ºC.

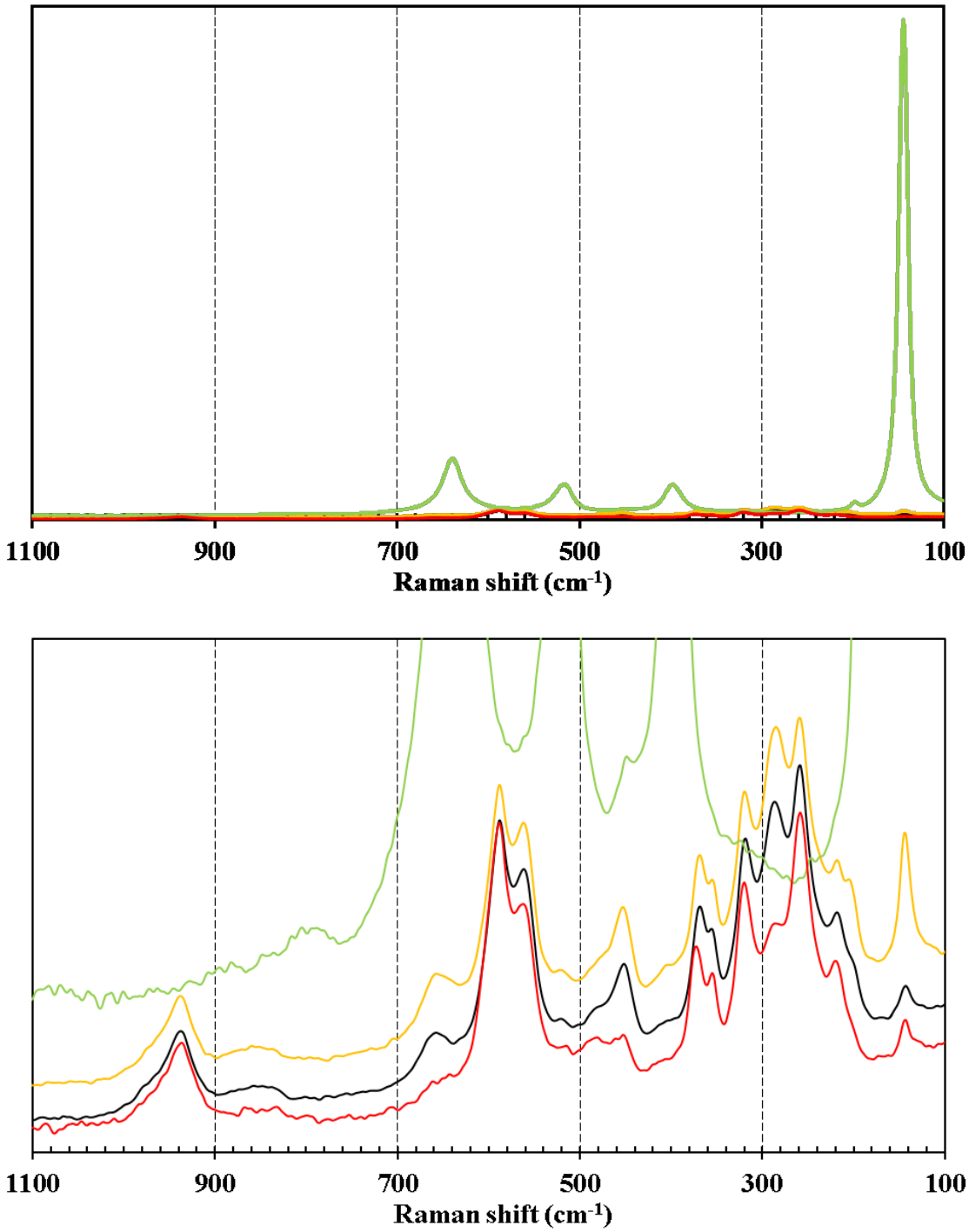

Fig. S7 FT Raman spectra of synthetic ivanyukite-K samples 3 H_2O, 2D (black), 6.5 H_2O, 1D (red) and 6.5 H_2O, 6D (yellow), and TiO_2 (P25) (green), measured in same conditions.

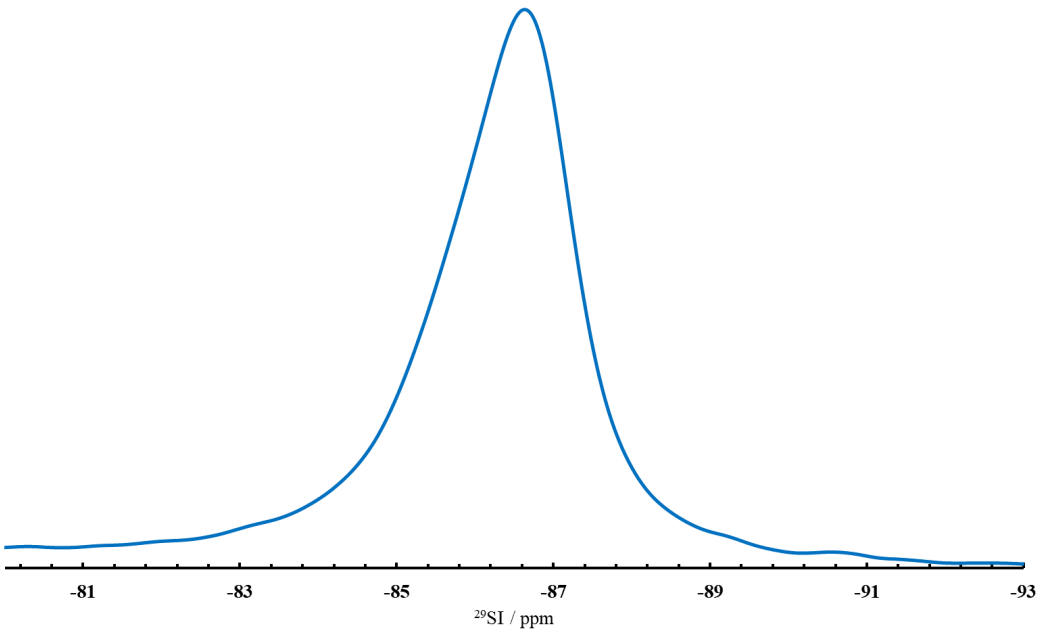

Fig. S8 ^{29}Si MAS NMR spectrum of synthetic ivanyukite-K prepared with 6.5 H_2O and 1 day at 230º C.

Table S2 Experimental conditions used to prepare ivanyukite-K (GTS-1) in this work and reported in the literature.

Entry	Temperature (°C)	Time (days)	Gel composition	Ref.
1	230	1-6	2.7 K_2O : 3.0 SiO_2 : 1 TiO_2 : 0-6.5 H_2O	This work
2	200	2	5.5 K_2O : 2.0 SiO_2 : 1 TiO_2 : 155 H_2O	16,17
3	200	7	1 K_2O : 1 SiO_2 : 1 TiO_2 : 97 H_2O	18
4	200	4	0.4 Na_2O : 1.7 K_2O : 1.4 SiO_2 : 1 TiO_2 : 30 H_2O	19
5	200	1	17.9 K_2O : 10 SiO_2 : 1 TiO_2 : 675 H_2O	20

AM-2

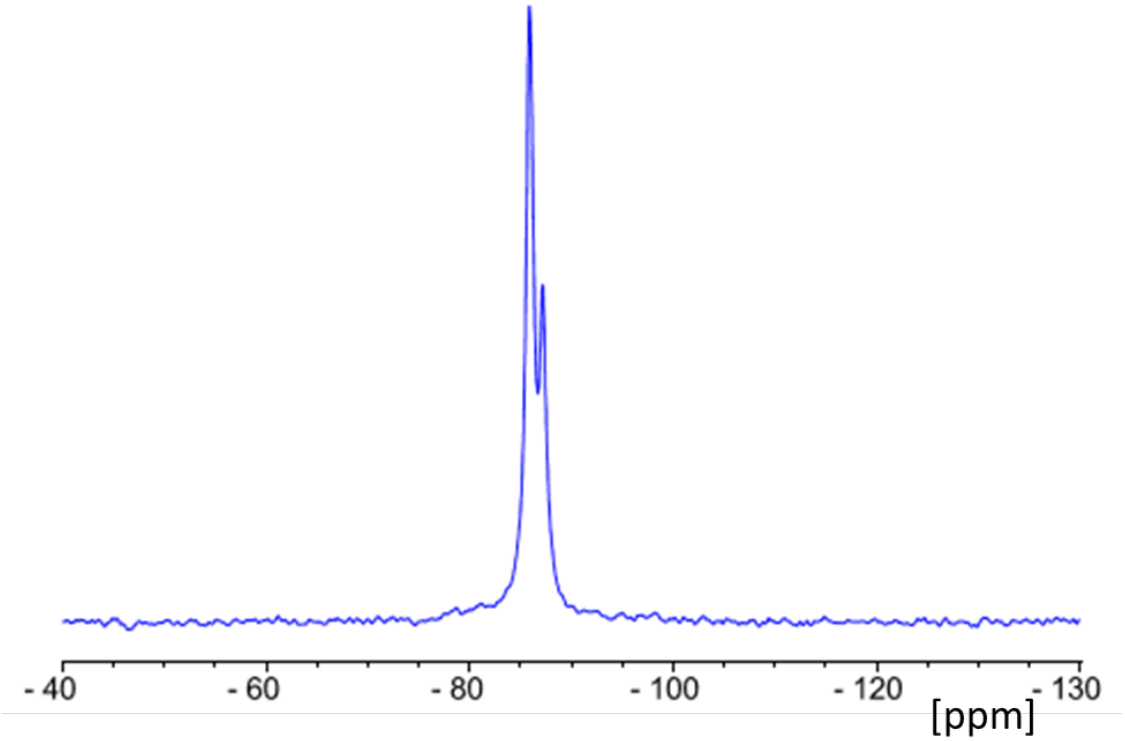

Fig. S9 ^{29}Si MAS NMR of AM-2 with 0 H_2O, after crystallization at 230 °C for 3 days.

Table S3 Experimental conditions used to prepare AM-2 in this work and reported in the literature.

Entry	Temperature (°C)	Time (days)	Gel composition	Ref.
1	230	1-3	1.6 K_2O : 2.75 SiO_2 : 1 TiO_2 : 0 - 5 H_2O	This work
2	230	4	6.1 K_2O : 4 SiO_2 : 1 TiO_2 : 120 H_2O	21
3	230	1	14.11 K_2O : 8.34 SiO_2 : 0.84 TiO_2 : 668 H_2O	22
4	200	5	6 K_2O : 3.5 SiO_2 : 1 TiO_2 : 142 H_2O	23
5	200	10 day	28.2 K_2O : 13.9 SiO_2 : 1 TiO_2 : 426 H_2O	24
6	200	2 days	0.5 K_2O : 0.25 SiO_2 : 1 TiO_2 : 40 H_2O	25

Natisite

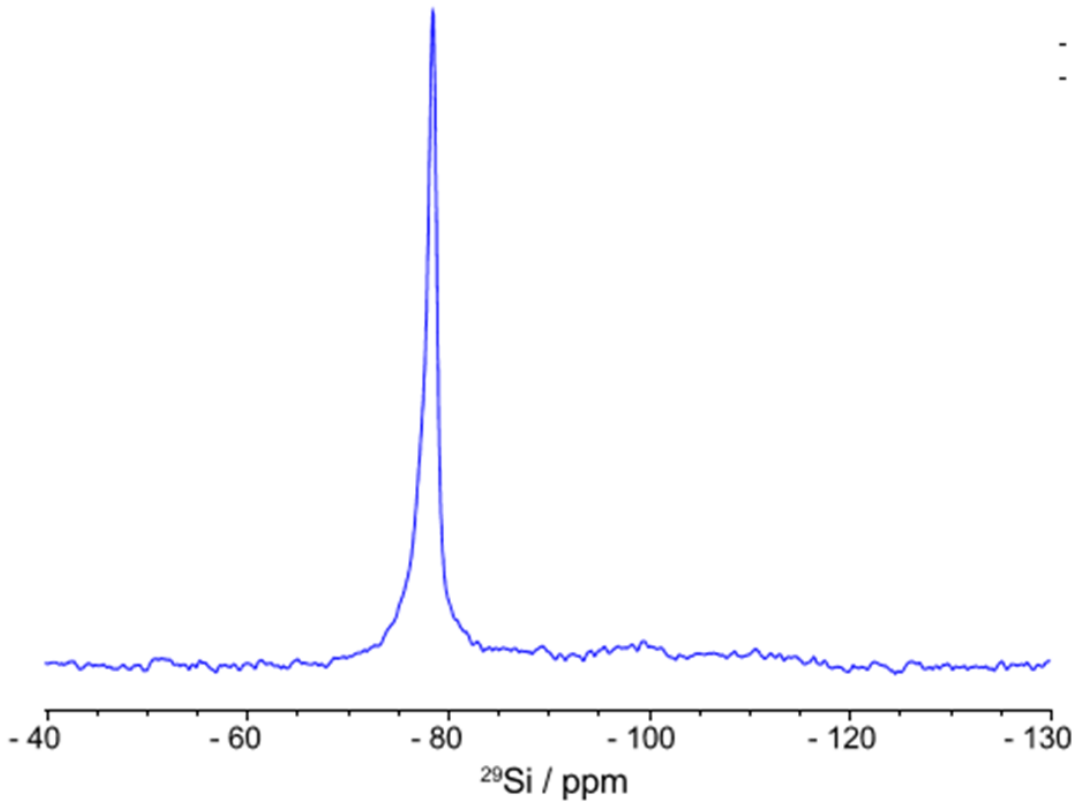

Fig. S10 ^{29}Si MAS NMR spectrum of natisite with 2.8 H_2O and 3 days crystallization at 230 °C.

Table S4 Experimental conditions used to prepare natisite in this work and reported in the literature.

Entry	Temperature (°C)	Time	Gel composition	Ref.
1	230	1-3 days	2.75 Na_2O : 3 SiO_2 : 1 TiO_2 : 0 – 9 H_2O	This work
2	200	24 h	a Na_2O : b K_2O : 10 SiO_2 : c TiO_2 : 675 H_2O	26,27
3	200	24-144 h	20-30 Na_2O : 10 SiO_2 : 1-3 TiO_2 : 370-670 H_2O	28

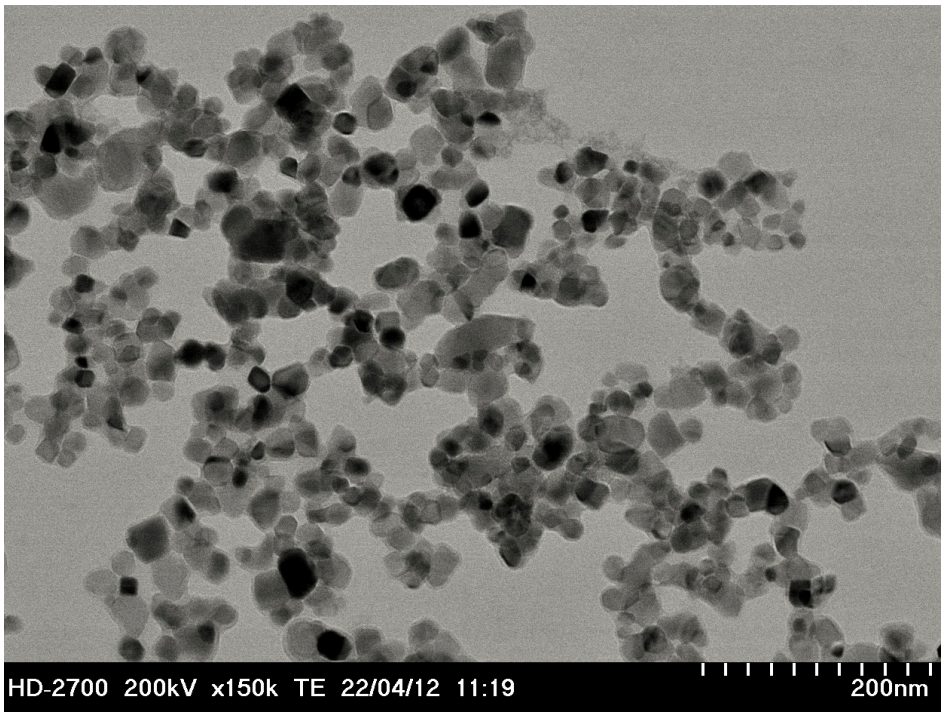

Fig. S11 TEM image of ETS-10 reaction mixture after ball milling (30 minutes 400 rpm). Only titania nanoparticles are depicted as the silica particles are too big (10-15 μm). The average size of titania particles is 20-25 nm but some particles are as small as 15 nm and as large as 40 nm.

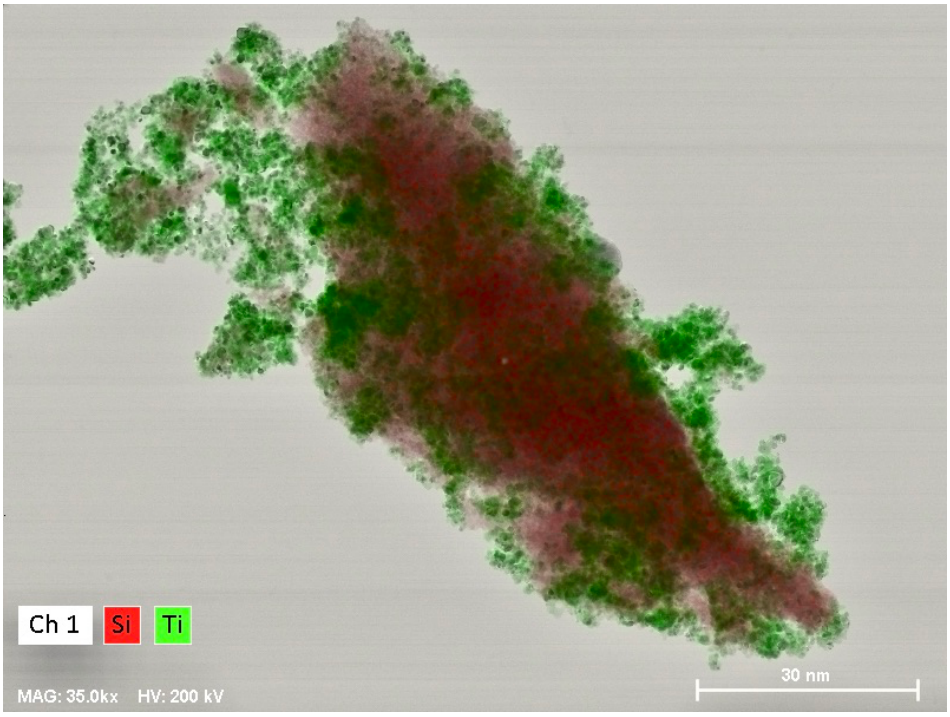

Fig. S12 TEM EDX mapping of image of ETS-10 reaction mixture after ball milling (30 minutes 400 rpm), same sample as in Fig. S11.

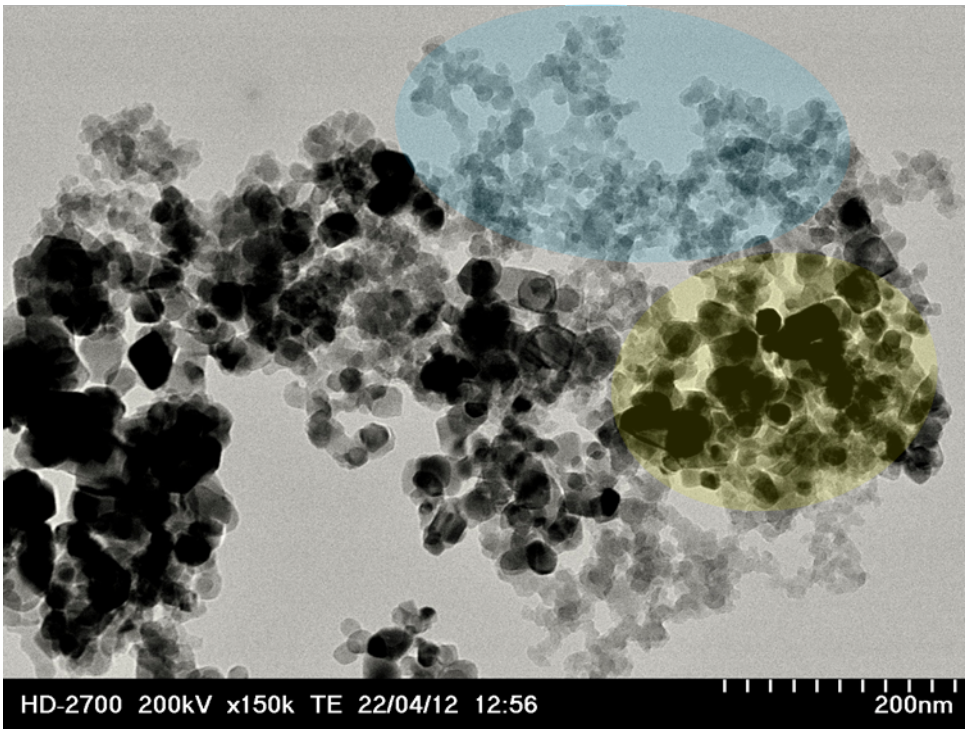

Fig. S13 TEM image of sitinakite reaction mixture after ball milling (30 minutes 400 rpm). Fumed silica particles are clearly smaller (ca. 10 nm, a rich-region highlighted in blue) than the titania nanoparticles (average size 20-25 nm but with some particles as small as 15 nm and as large as 40 nm, a rich-region highlighted in yellow).

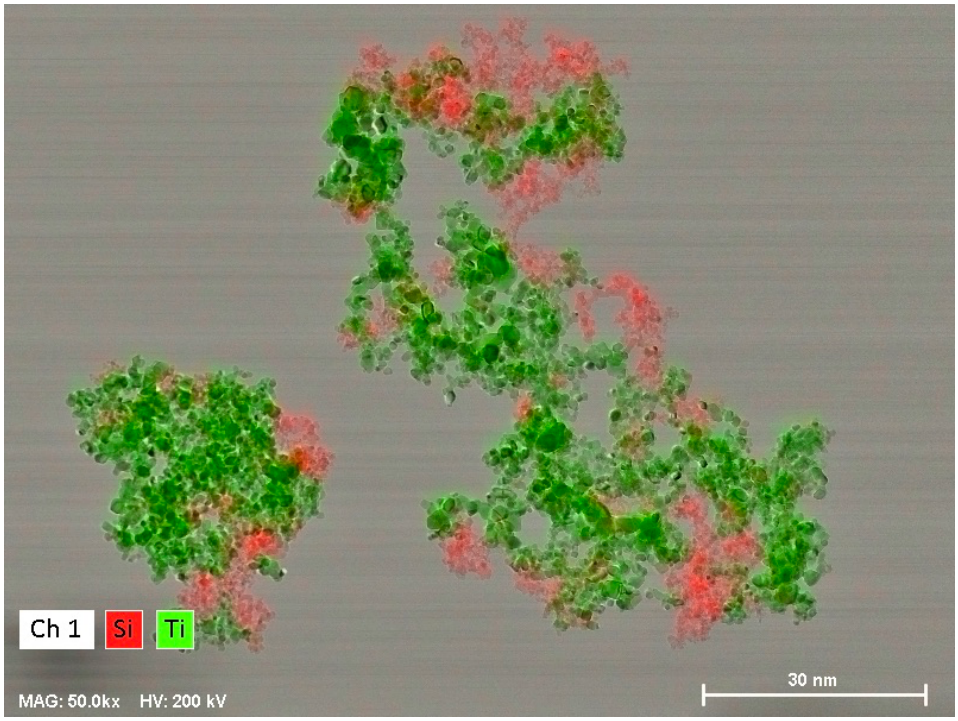

Fig. S14 TEM EDX mapping of image of sitinakite reaction mixture after ball milling (30 minutes 400 rpm), same sample as in Fig. S13.

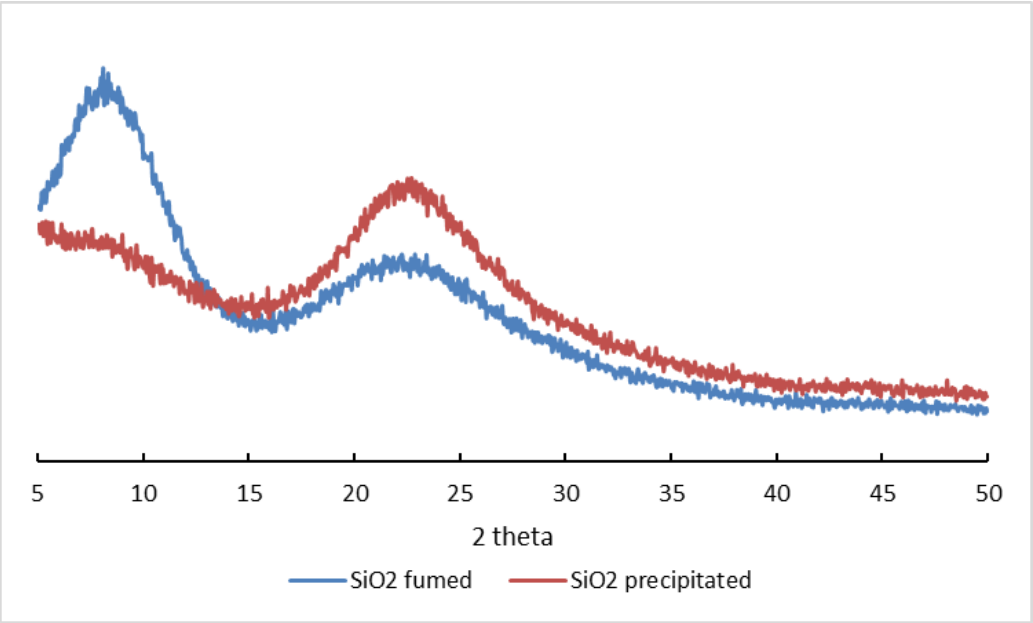

Fig. S15 Powder XRD pattern of parent fumed and precipitated silica used.

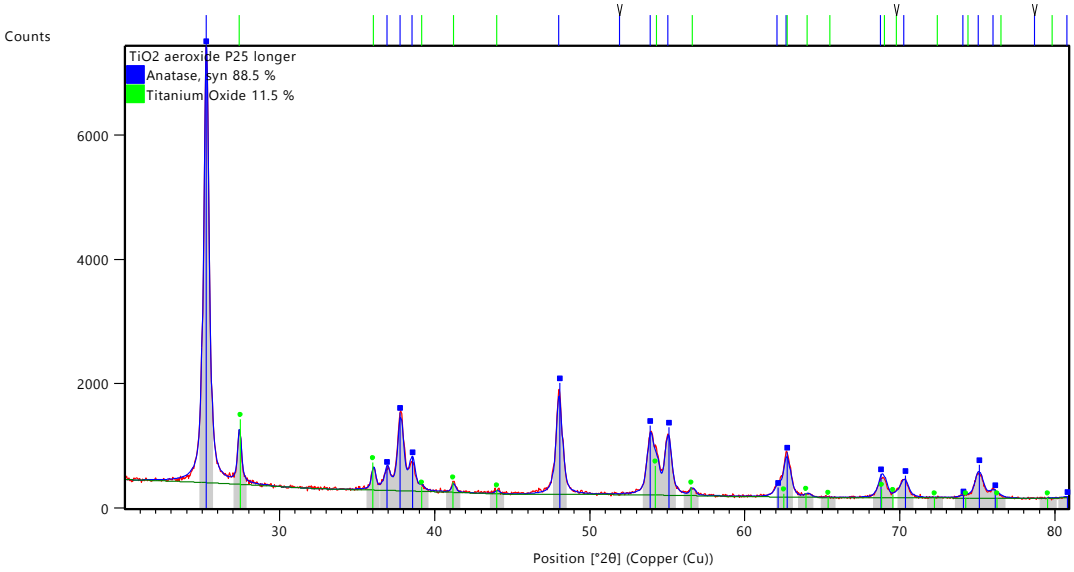

Fig. S16 Powder XRD pattern of parent P25 titania used, revealing the presence of mainly anatase and some rutile. Some amorphous titania is also likely to be present.

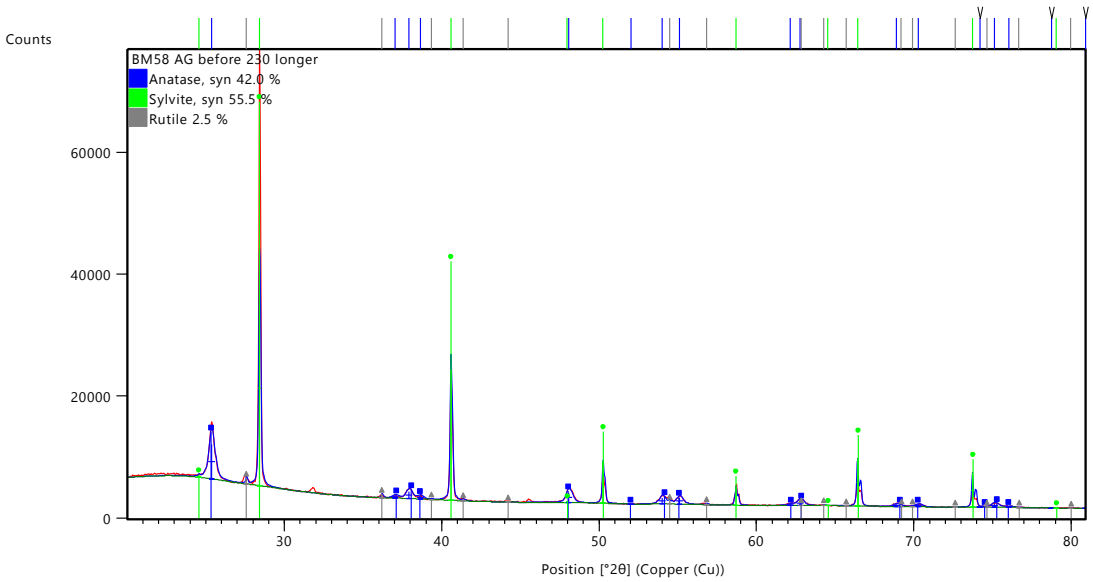

Fig. S17 Powder XRD pattern of ETS-10 reaction mixture after ball milling (30 minutes 400 rpm). Anatase, some rutile and KCl (sylvite) are observed. Amorphous material is also likely to be present.

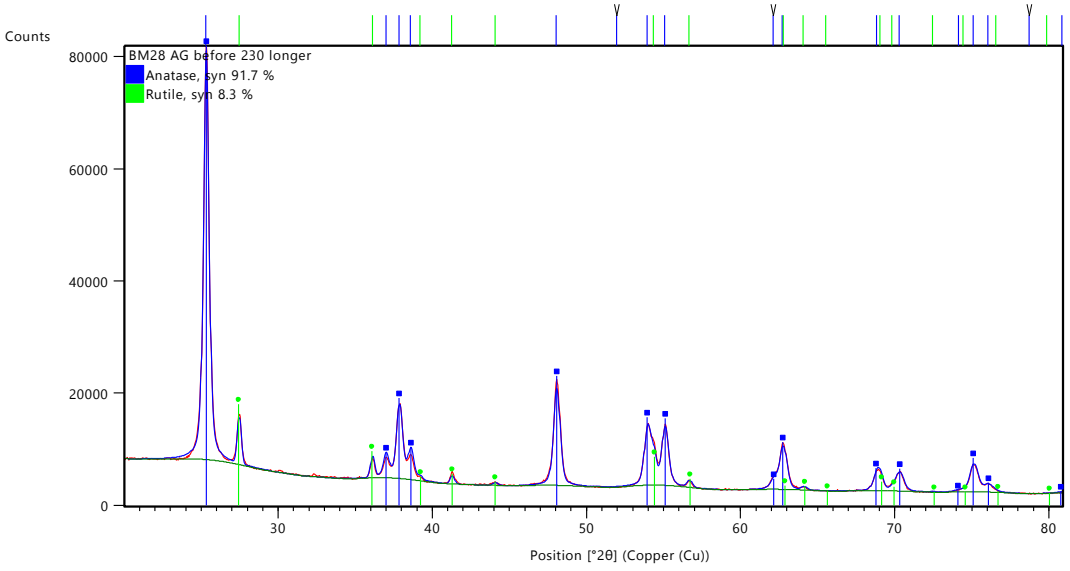

Fig. S18 Powder XRD pattern of sitinakite reaction mixture after ball milling (30 minutes 400 rpm). Anatase and some rutile are observed. Amorphous material is also likely to be present.

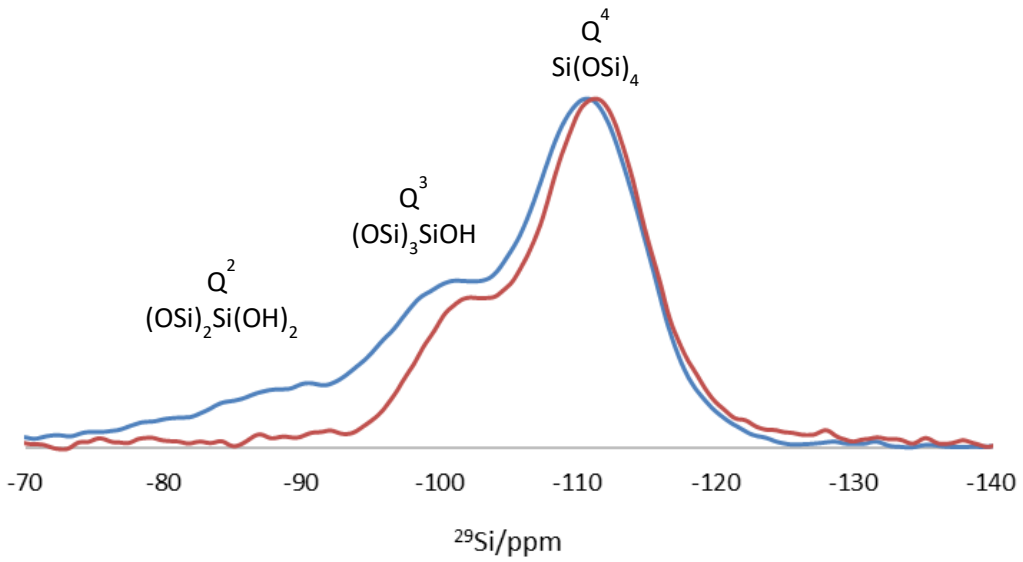

Fig. S19 ^{29}Si MAS NMR spectra of parent precipitated silica (red) and of ETS-10 reaction mixture after ball milling for 30 minutes at 400 rpm (blue). The latter is richer in Q^3 and Q2 bearing silanol environments.

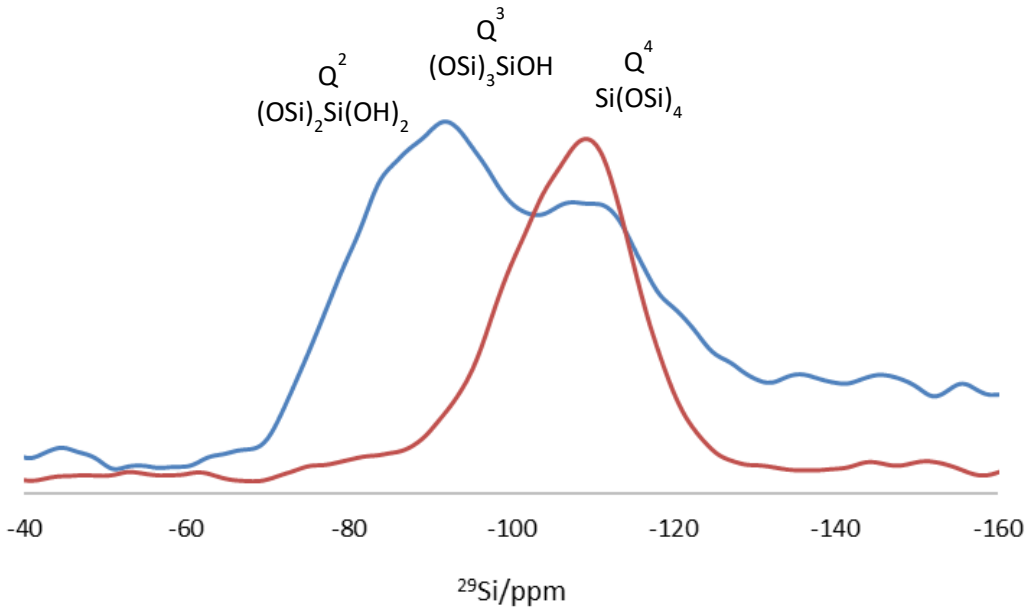

Fig. S20 ^{29}Si MAS NMR spectra of parent fumed silica (red) and of sitinakite reaction mixture after ball milling for 30 minutes at 400 rpm (blue). The latter is richer in Q^3 and Q2 bearing silanol environments.

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