Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Evaluation of the formation and carbon dioxide capture of Li_4SiO_4 using in situ synchrotron powder X-ray diffraction studies

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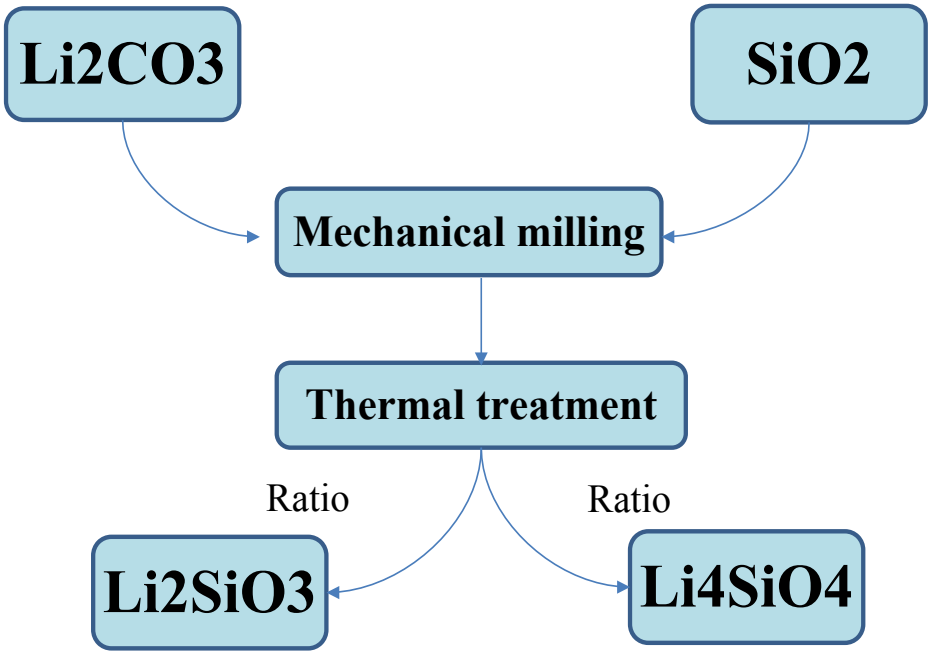

Fig. S1: Scheme of synthesis procedure of Li_2SiO_3 and Li_4SiO_4 from Li_2CO_3 and SiO_2 as starting materials.

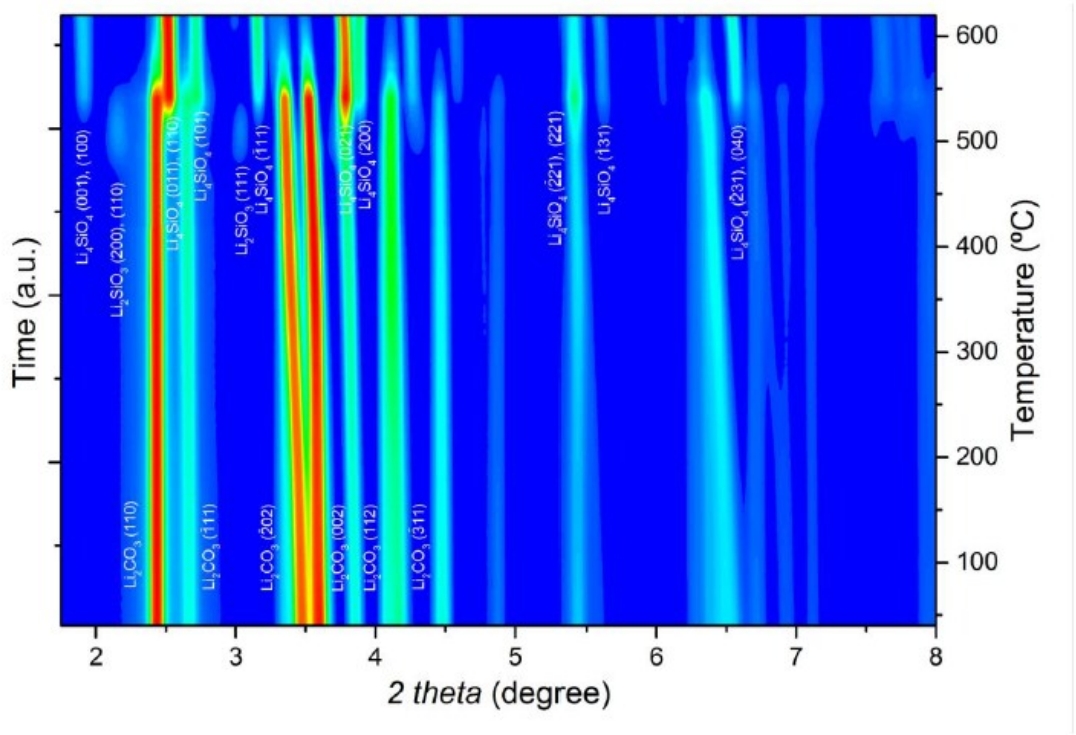

Fig. S2: Contour plot of the acquired in situ SR-XRPD data during the synthesis of Li_4SiO_4 under synthetic air as a function of time and temperature (heating rate 5 ºC/min up to 620 ºC). The most intense XRPD reflections of each phase are indicated.

Starting phases: Li_2CO_3, monoclinic C2/c (reference code 01-087-0728) and SiO_2 (amorphous phase). The intermediate phase Li_2SiO_3, orthorhombic Cmc21 (reference code 01-070-0330) appears in the temperature range from 490ºC to 550ºC. The formation of crystalline Li_4SiO_4 starts at 525ºC.

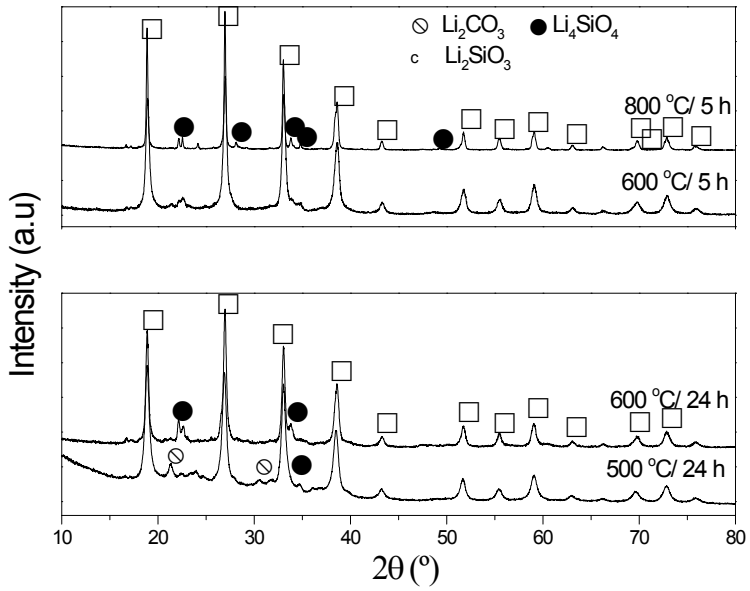

Fig. S3: Ex-situ XRPD patterns of Li_2SiO_3 formation from the as-milled Li_2CO_3-SiO_2 mixture: A) 800 and 600 °C, 5 h; B) 600 and 500 °C, 24 h.

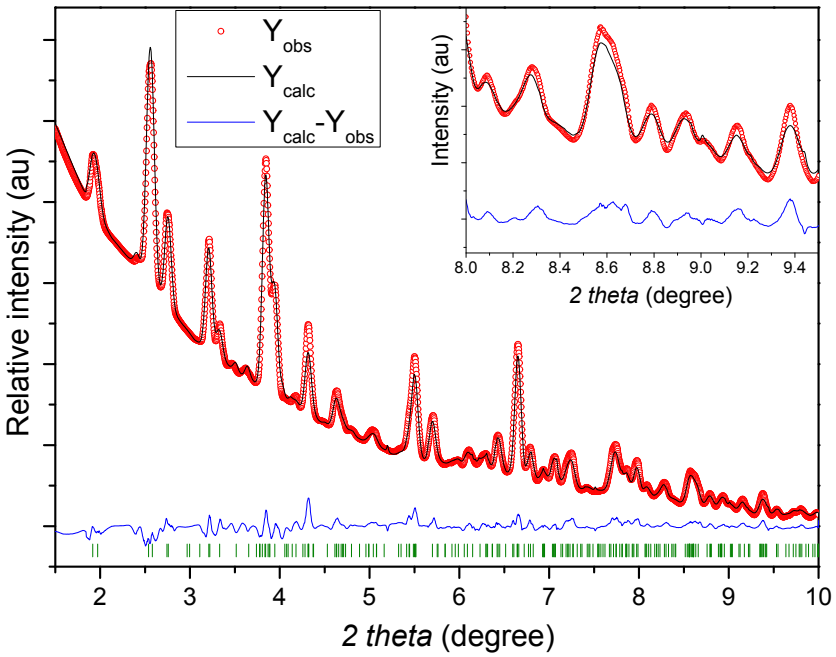

Fig. S4: Rietveld refinement of SR-XRPD data of the synthesized Li_4SiO_4 at room temperature. Red circles correspond to experimental data, the black line corresponds to the data calculated from the Rietveld analysis and the blue line is the difference between experimental data and fitted data. Inset plot shows a detail of the refinement in the high angle area.

In Figure S4 is presented the Rietveld refinement of the starting phase Li_4SiO_4, monoclinic (P21/m), reference code 00-034-1416 (*a*=11.5460, *b*=6.0900, *c*=16.6450, α=γ=90, β=99.5). Li_2CO_3 (monoclinic C2/c, reference code 01-087-0728, *a*=8.3588, *b*=4.9738, *c*=6.1938, α=γ=90, β=114.7890) is present as impurity, probably because of the incomplete reaction.

	a	*b*	*c*	Wt.%
Li_4SiO_4	11.55072	6.095727	16.72408	94.01
Li_2CO_3	8.826215	4.929495	6.07494	5.99

Table S1: Lattice parameters and phase percentage of the synthesized Li_4SiO_4calculated from the Rietveld analysis.

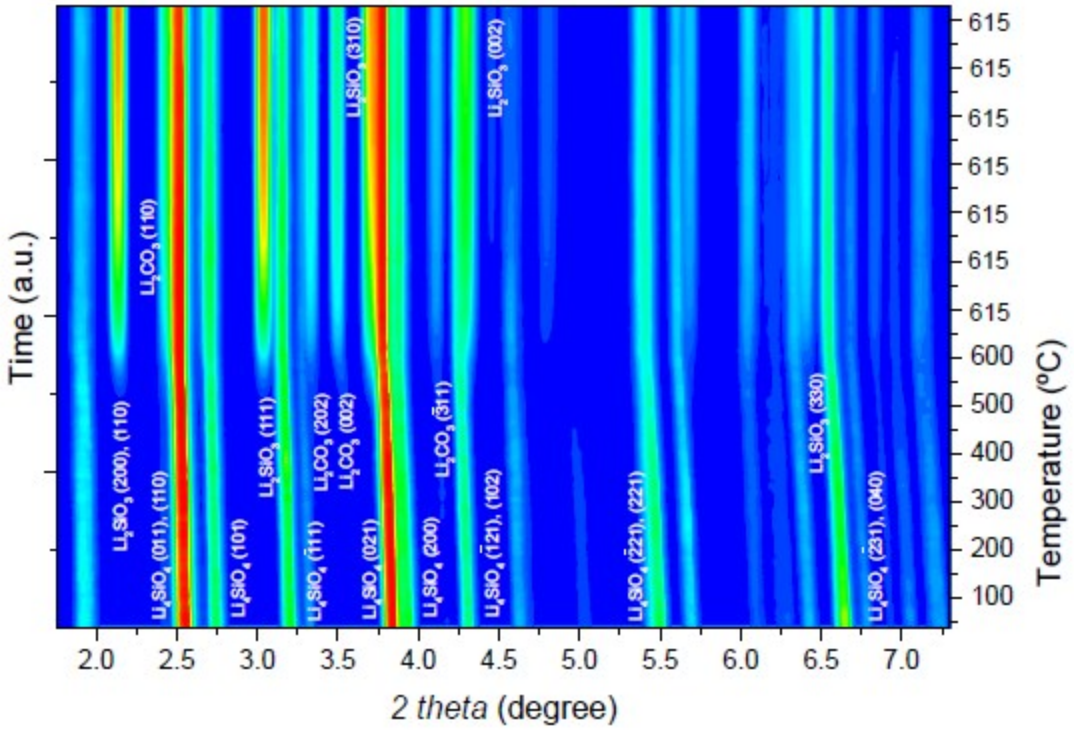

Fig. S5: Contour plot of the acquired in-situ SR-XRPD data during the carbonation as a function of time and temperature (heating rate 5ºC.min-1, up to 615 ºC). The most intense XRPD reflections of each phase are indicated.

In Fig.S5 is shown the contour plot of the phase evolution during carbonation of Li_4SiO_4. The temperature was increased from 40 ºC to 615ºC with a heating rate of 5ºC/min and then it was kept constant at this temperature during 1 h. In the Figure the most prominent reflexions of the main phases are indicated (Li_4SiO_4, Li_2CO_3 y Li_2SiO_3).The shifts to the left of the peaks belonging to the starting phase (Li_4SiO_4) are due to the lattice expansion because of the temperature increase.

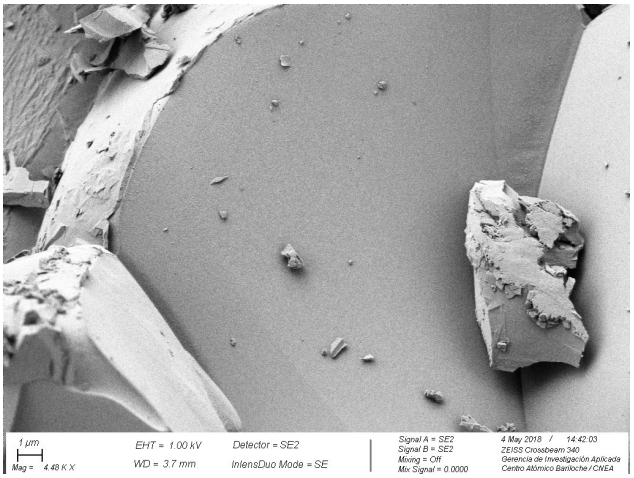

Fig. S6: SEM micrograph of the surface of an agglomerate of as-synthesized Li_4SiO_4.

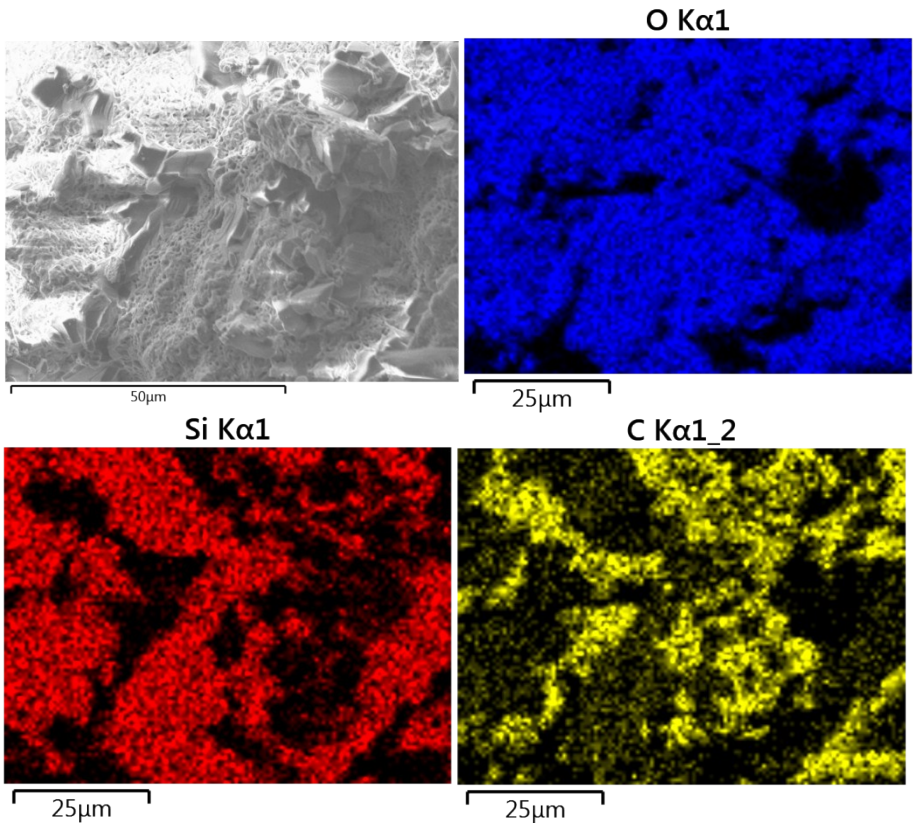

Fig. S7: SEM micrograph and chemical mapping of the Li_4SiO_4 after CO_2 capture (point 2, Figure 9).