

Supplementary Material

The sol-gel approach as a method of synthesis of MgO·SiO₂ powder with defined physicochemical properties including crystalline structure

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Supplementary data to the chapter 3.1. *Chemical composition of powder materials*

To confirm the chemical structure of tested powders X-ray photoelectron spectroscopy (XPS) was performed.

XPS spectra were obtained using a SPECS PHOIBOS 100 hemispherical spectrometer equipped with an Mg K α source ($h\nu = 1486.6$ eV) operating at 100 W (wide-range scan) and 250 W (high resolution spectra). The spectrometer was calibrated using the following photoemission lines (with reference to the Fermi level): EB Cu 2p_{3/2}=932.8 eV, EB Ag 3d_{5/2}=368.3 eV and EB Au 4f_{7/2}=84.0 eV. The instrumental resolution, in terms of the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak, was 1.0 eV. The samples were loosely placed into a grooved molybdenum sample holder. The analysis chamber was evacuated during the experiments to better than $1 \cdot 10^{-9}$ mbar.

Data processing involved background subtraction by means of “S-type” integral profile and a curve-fitting procedure (a mixed Gaussian–Lorentzian function was employed) based on a least-squares method (CasaXPS software). Experimental errors were estimated to be ± 0.2 eV for the photoelectron peaks of carbon and nitrogen. Charging effects were corrected using the C 1s component ascribed after deconvolution to the aliphatic carbon bindings (component C₂) and taken to be 284.8 eV. The reproducibility of the peak position thus obtained was ± 0.2 eV. The surface composition of the samples was obtained

on the basis of the peak area intensities of the C 1s, O 1s, N 1s, Na 1s, S 2p, Ca 2p and Cl 2p transitions using the sensitivity factor approach and assuming homogeneous distribution of elements in the surface layer.

Analyzed samples:

- a – MgO·SiO₂ powder obtained via sol-gel method (sample MP 2.2C)
- b – commercial talc Mg₃(OH)₂Si₄O₁₀ (purchased from Riedel-de Haën)
- c – MgO·SiO₂ powder with the higher magnesium content obtained via sol-gel method
- d – mechanically mixed commercial MgO and SiO₂
- e – SiO₂ obtained via sol-gel method

Table S1 presents surface composition (% at.) of analyzed samples.

The decrease in the content of Mg is typical for talc, due to its layered structure. The mismatch of surface composition (XPS) and the volume is different for various natural talc minerals – it is the result of different thicknesses of the layers of Si-O-Si and the MgO. It also confirms the differences in Mg:Si ratio. This effect is mostly observed in the powder materials subjected to calcination in higher temperature.

Figure S1 presents the original SpecLab SPX printscreens. Presented Si 2p spectra are normed relative to the surface. When we take spectrum for sol-gel SiO₂ (yellow line) as reference, in which Si-O-Si bonds are present, together with the substitution of Mg in Si-O-Mg bridges, the decrease in energy of the bond Si 2p was observed (Fig. S1). This decrease of Si 2p bond energy is typical for Si-O-X bridges (X=Ti, Zn, Al) and is higher when more bonds is substituted (see spectrum for sample c – blue line – with the higher content of magnesium).

Table S1. Surface composition of analyzed samples.

With carbon				Without carbon			
Element	Atom %	Orbit	Reg	Element	Atom %	Orbit	Reg
C	5.20	1s	a3	O	67.19	1s	a2
O	63.70	1s	a2	Mg	5.70	2p	a6
Mg	5.40	2p	a6	Si	27.11	2p	a4
Si	25.70	2p	a4	O	65.91	1s	b2
C	4.44	1s	b3	Mg	14.32	2p	b7
O	62.98	1s	b2	Si	19.78	2p	b4
Mg	13.68	2p	b7	O	60.53	1s	c2
Si	18.90	2p	b4	Mg	25.12	2p	c6
C	11.82	1s	c3	Si	14.35	2p	c4
O	53.37	1s	c2				
Mg	22.15	2p	c6	Element	Atom %	Orbit	Reg
Si	12.66	2p	c4	O	62.10	1s	d2
				Mg	18.33	2p	d6
Element	Atom %	Orbit	Reg	Si	19.57	2p	d4
C	10.01	1s	d3	O	70.62	1s	e2
O	55.89	1s	d2	Si	29.38	2p	e4
Mg	16.49	2p	d6				
Si	17.61	2p	d4				
C	11.70	1s	e3				
O	62.35	1s	e2				
Si	25.95	2p	e4				

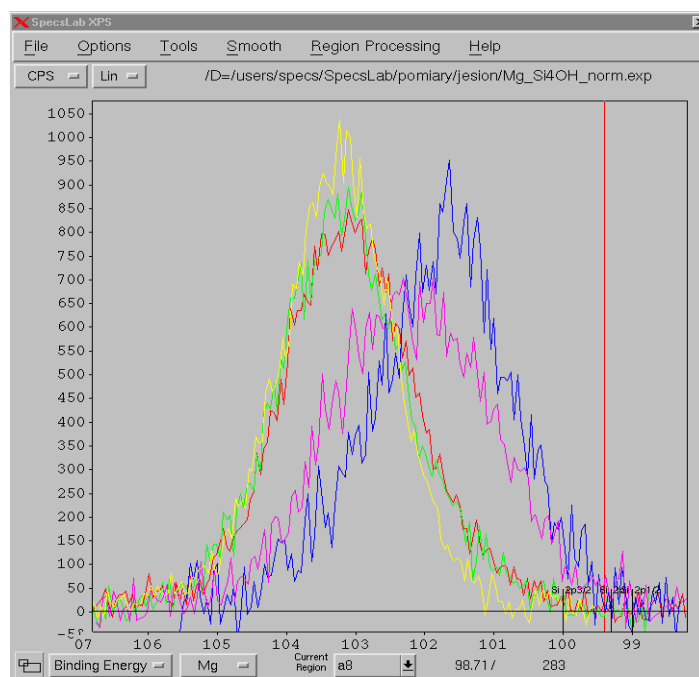


Fig. S1. XPS spectra of analyzed samples.

Moreover, using XPS analysis we were able to evaluate the % contribution of Si-O-Mg bridges in analyzed samples. As it is presented in Fig. S2, talc contains 6.6% contribution of Si-O-Mg bridges especially taking into account that those bonds are hidden under Si-O-Si bonds. In our sample MP 2.2C this contribution is 8.5%, and in the sample that contains higher amount of magnesium – 86.7%.

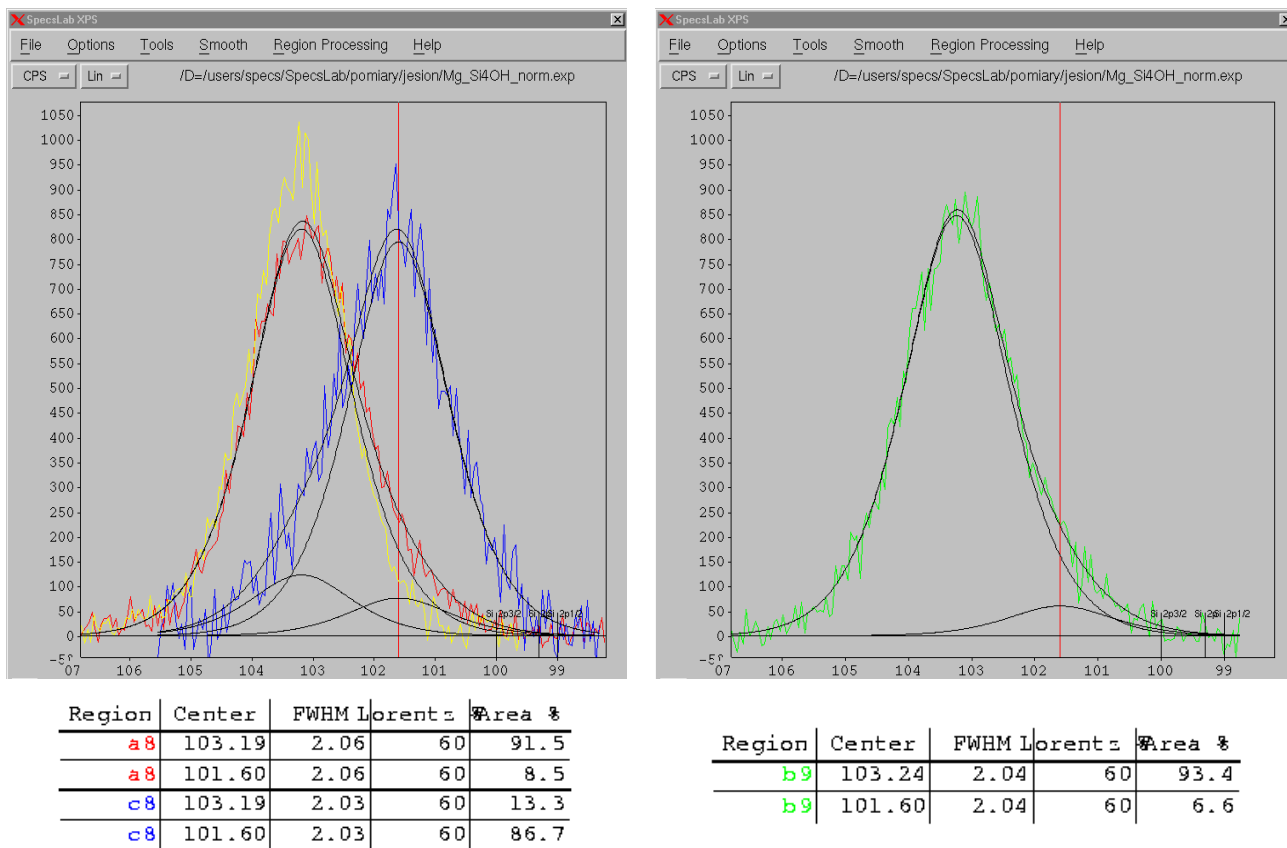


Fig. S2. Contribution of Si-O-Mg bonds in the structure of MgO·SiO₂ powder.

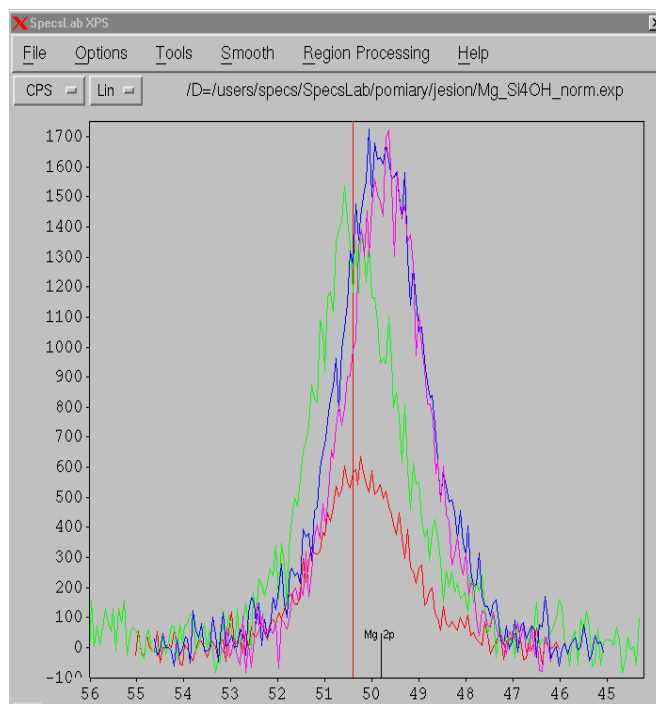


Fig. S3. Energies of Mg 2p bonds.

In the opposition to the energy of Si 2p bonds are energies of Mg 2p bonds which increase with the amount of Si. Fig. S3 shows that in the talc sample whole magnesium is related to the Si-O-Mg. In turn, maximum of the peak in sample d (mechanically mixed commercial MgO and SiO₂), basically corresponds to Mg 2p bond in MgO. In our sample MP 2.2C (red line) you can observe that maximum is closer to talc.

Supplementary material to the chapter 3.2. *Crystalline structure*

Additionally scans of WAXS images together with the identification lines of material obtained as well as the individual reference samples to which it was compared to, are presented (Fig. S4). As it is presented (Fig. S4a), in the structure of obtained compound (sample 2.2C) there is only a forsterite phase identified and not a mixture of individual oxides that form the material. This is confirmed also by the FTIR spectra of the uncalcined and calcined sample, which clearly confirm the presence of bands for individual bonds characteristic for MgO·SiO₂ powder.

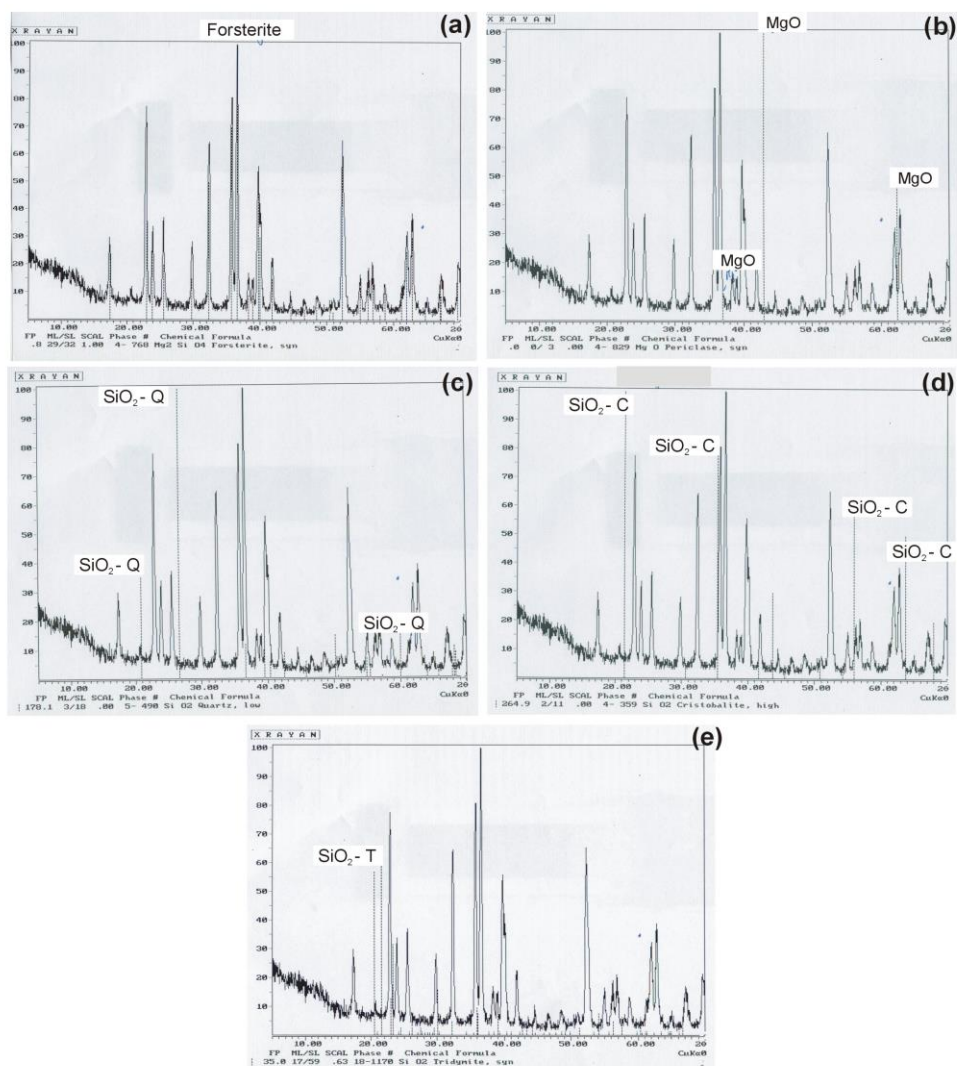


Fig. S4. (a) XRD of sample MP 2.2C (crystalline structure of forsterite) with marked crystalline structures of (b) MgO – periclase, (c) SiO₂-Q – quartz, (d) SiO₂-C – cristobalite and (e) SiO₂-T – tridymite.

Supplementary material to the chapter 3.3. FT-IR analysis

To unambiguously confirm that the indicated bonds are related to a specific chemical compound, in Figure S5 the FTIR spectrum of talc ($Mg_3(OH)_2Si_4$)₁₀) is presented, which also contains marked characteristic absorption bands that overlap with the bands observed in the case of MgO·SiO₂ samples synthesized utilizing proposed sol-gel method.

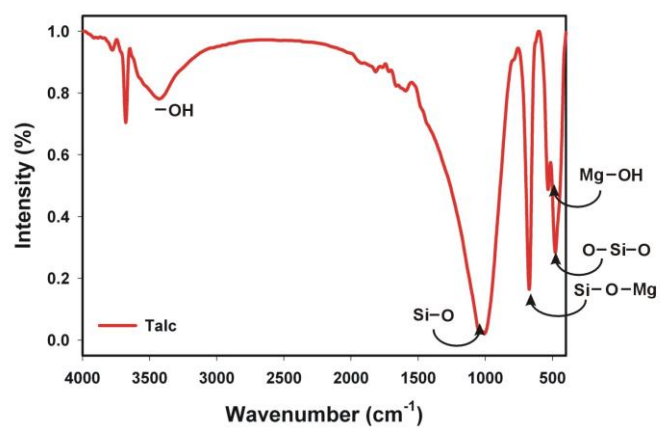


Fig. S5. FT-IR spectrum of talc.