Supporting information

High performance mesoporous bioceramics mimicking bone mineralization

N_2 adsorption porosimetry and powder XRD characterization

Figure S1 shows the isotherms obtained by N_2 adsorption porosimetry and small-angle XRD patterns corresponding to mesoporous bioactive glasses (MBG) S58m and S85m. The isotherms exhibit a capillary condensation step in the adsorption branch at high relative pressure P/P_0 equal to 0.60-1.0 and 0.50-0.60 for S58m and S85m, respectively. Both isotherms show H1 hysteresis loops, which are characteristics of cylindrical pores open at both ends. The pore diameters calculated by BJH method are 9.45 and 5.73 nm, respectively. Small-angle XRD pattern corresponding to the sample S58m glass shows a unique maximum at $2\theta = 1.28°$. This pattern is consistent with a 2D-hexagonal structure with 1d pore channels oriented parallel, which was later confirmed by TEM studies. Small-angle XRD pattern of S85m sample shows one intense maximum at 2θ 1.20º, which can be indexed as 211 reflection of a cubic system. Other small peaks can be indexed as 220, 400 and 332 reflections at higher scattering angle based on Transmission Electron Microscopy (TEM) even though there are small structural deviations. The unit cell parameter calculated from 211 peak positions is 180 Å.

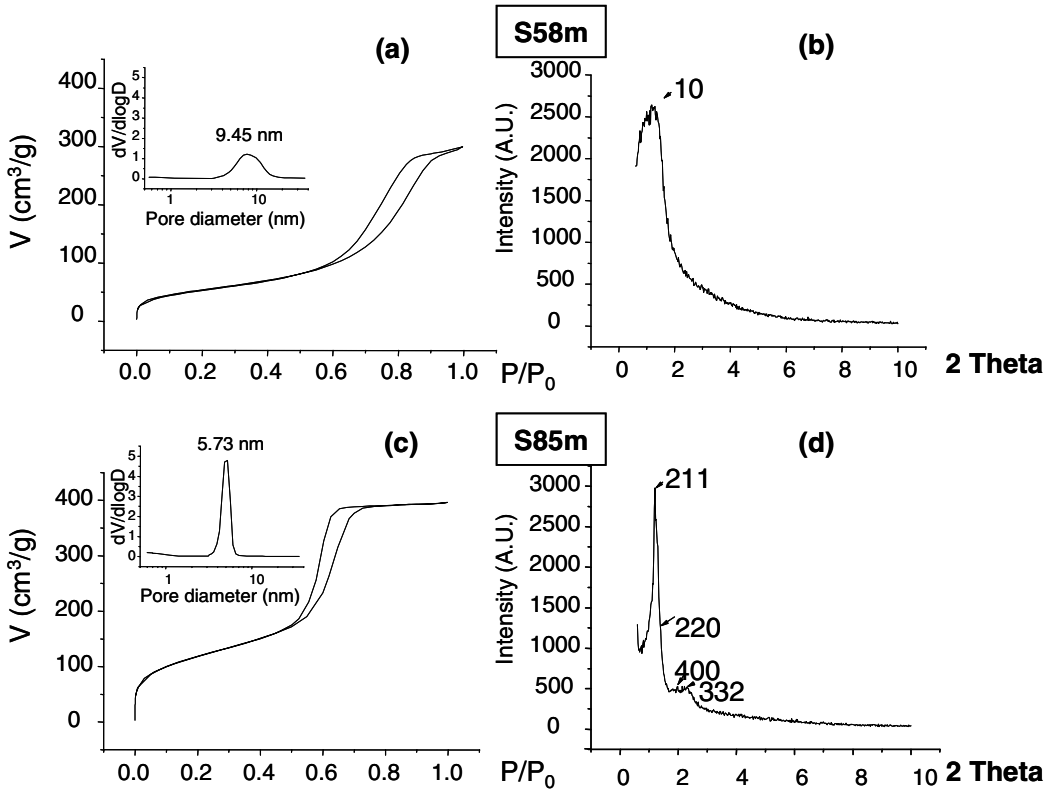

Figure S1: N_2 adsorption isotherms and pore size distribution of (a) S58m and (c) S85m. XRD patterns of (b) S58m and (d) S85m are also displayed.

High Resolution Transmission Electron microscopy of the mesoporous glasses

In order to make a nano-structure study of the pore wall constituting mesoporous arrangement, high resolution transmission electron microscopy was performed. Figure S2 shows such characterization on the pore wall corresponding to S58m and S85m samples. HRTEM images show that pore walls are constituted by an amorphous phase in both cases. Fourier patterns confirmed this point, showing the characteristic halo of amorphous materials. EDX experiment carried out over different areas indicated the homogeneous chemical distribution within the pore walls. For S58m sample, the composition is silicon 60.2±0.5, phosphorous 5.4±0.7 and calcium 34.4±0.2 (% in atoms) and in the case S85m sample, the composition is silicon 85.1±0.3, phosphorous 4.3±0.3 and calcium 10.6±0.5 (% in atoms). No

crystalline nuclei of calcium phosphates of silicates were observed neither within the hexagonal (S58m) nor the cubic phase (S85m).

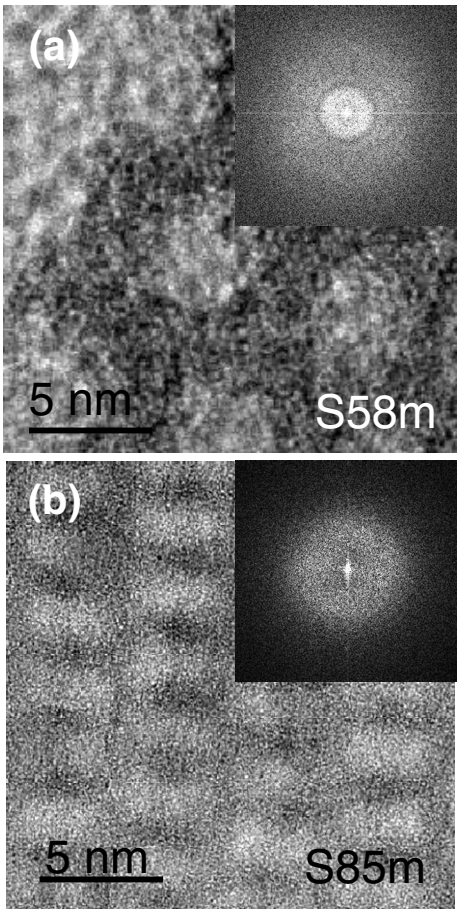

Figure S2: HRTEM images together with their corresponding Fourier diffractograms of pore wall of S58m and S85m, respectively.

Electron crystallography: 3D reconstruction of bicontinuous mesoporous glass S85m.

Electron Crystallography (EC) is very powerful tool that provides direct information on the detailed structured inside of the mesoporous crystal such as diameter, shape, and connectivity of the pores. Since all these parameters will play a fundamental role on the biological fluids diffusion when implanted, a deep comprehension of their structure must be acquired before their clinical application.

Crystal structure factors obtained by electron crystallography of S85m sample

hkl	**$h^2+k^2+l^2$**	**d[nm]**	**F (hkl)**
211	6	73.48	-100
220	8	63.64	-45.75
321	14	48.11	5.80
400	16	45.00	10.27
420	20	40.25	-5.02
332	22	38.38	-3.21
431	26	35.30	-0.13
440	32	31.82	-0.78
532	38	29.20	-0.66
611	38	29.20	-0.67
620	40	28.46	-0.29
541	42	27.77	-0.63
444	48	25.98	0.88
640	52	24.96	0.58
552	54	24.49	0.64
633	54	24.49	0.18
642	56	24.05	0.19
820	68	21.83	-0.24