Elasticity of hybrid silica under high pressure

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A wide range of hybrid organic-inorganic silicas can be synthetized through sol-gel chemistry (figure 1). The structural organization of the material can be tuned thanks to the organic parts that exhibit diverse self-assembly properties depending on (i) the nature of the organic moieties: phenylene versus alkylene core, urea versus thiourea bridging units (ii) the synthesis conditions, notably the solvent (acidic versus NH_4F catalyst)

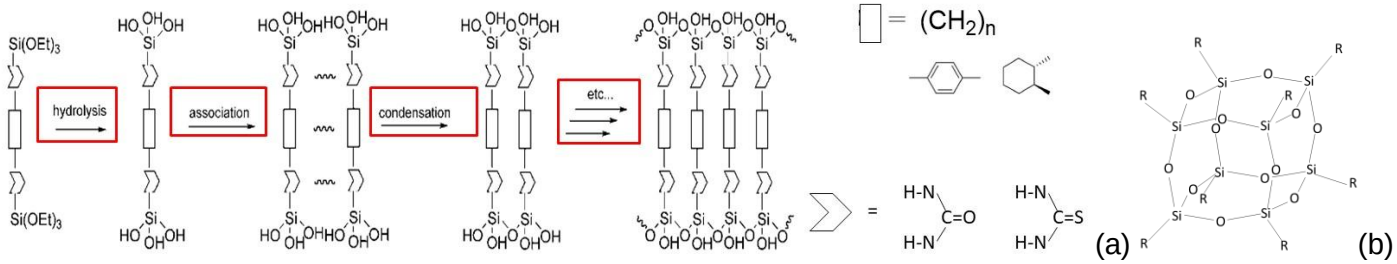

Figure 1 (a) Schematic representation of the hydrolysis–condensation process leading to self-assembling process in oranic-inorganic silicas [1], (b) Polyhedral Oligomeric Silsesquioxanes (T_n, n=8,10, 12)

Hybrids silicas are expected to combine the mechanical, thermal, and chemical stability of silica with the solution processing the flexibility and extra functionalization brought by the organic moieties. However, **their mechanical properties have been barely studied** as compared to silica glasses, which have has driven a particular interest during the two last decades, and for which high pressure experiments revealed a purely elastic regime up to 10 GPa, followed by volumetric plastic deformation above this pressure [2].

Thanks to in situ high pressure spectroscopic studies achieved in diamond anvil cells, the mechanical behavior of various organic inorganic silicas has been followed as a function of pressure. In particular, for urea or thiourea bridged silsequioxanes, **vibrational studies** coupled to ab-initio simulations show that the rigidity yielded by the inorganic polymerization is counterbalanced by the presence of the intermolecular H bond network. In a large range of pressures, these hybrid materials have a reversible behavior, and thus behave as molecular springs. We also demonstrate that the pressure behavior of these molecular springs is sensitive to the conformation of H bonds (cyclic versus linear) and to the constraints imposed by the covalent inorganic network.

References

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