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Deactivating amorphization of silicalite under pressure by insertion of CO_2/Ar. Julien Haines[a], Olivier Cambon[a], Claire Levelut[b], Mario Santoro[c], Federico Gorelli[c], Gaston Garbarino[d]. [a]*Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-Université Montpellier 2, France.* [b]*Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR 5587 CNRS-Université Montpellier 2, France* [c]*LENS, Sesto Fiorentino (Florence), Italy.* [d]*ESRF, Grenoble, France.*
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Pressure-induced amorphization (PIA) is commonly observed in open framework structures, such as zeolites, and has been linked to the effect of pressure on low-energy vibrations, such as rigid-unit modes. Silicalite is a siliceous zeolite, which presents PIA. Reverse Monte Carlo refinements of total x-ray scattering results indicate that PIA in this material corresponds to the collapse of the structure of the crystalline phase around the empty pores keeping the same structural topology, but with strong geometrical distortions [1]. Incorporation of guest species and PIA may confer useful properties in these materials for applications in the field of the absorption of mechanical shocks. High-pressure, x-ray diffraction data were obtained on the beam line ID27 at the ESRF in silicone oil, Ar and CO_2. In the case of incorporation of CO_2, the changes in orthorhombic lattice parameters **a**, **b** and **c** as compared to those obtained in silicone oil are +1.2%, +0.8% and +3.5%, respectively at 3.5 GPa. This can be linked to the lower framework and higher pore density along the **c** direction. Whereas complete amorphization is observed using silicone oil by 8 GPa, the incorporation of carbon dioxide or argon stabilizes the structure of the microporous silica polymorph silicalite up to at least 25 GPa. This is well beyond the stability range of tetrahedrally-coordinated SiO_2 and, in fact, beyond even the metastability range of low-pressure silica polymorphs such as quartz and cristobalite at room temperature. The bulk modulus of silicalite strongly increases due to the incorporation of CO_2 or Ar and is equivalent to that of quartz indicating direct compression of the framework. The insertion of these species disactivates the normal compression and pressure-induced amorphization mechanisms in this material. The presence of guest species impedes the softening of low-energy vibrations, amorphization and eventual increase in silicon coordination up to at least 25 GPa. Incorporation of guest species can be used to stabilize microporous materials with respect to PIA and such open structures can thus be retained over a very large pressure range.

[1] Haines, J., Levelut, C., Isambert, A., Hébert, P., Kohara, S., Keen, D. A., Hammouda, T., Andrault, D., *J. Am. Chem. Soc.* 2009, 131, 12333.

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