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Deactivation of Pressure-Induced Amorphization in Silicalite SiO_2 by Insertion of Guest Species

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Pressure-induced amorphization (PIA) is commonly observed for framework structures such as zeolites.[1] Inelastic X-ray scattering has shown that low-energy, nondispersed phonon modes of librational origin are responsible for destabilizing the crystalline forms of these materials.[2] Silicalite is a microporous SiO_2 polymorph that exhibits PIA.[3] Silicalite has an MFI (Mobil-Five)-type structure (orthorhombic with space group *Pnma* and monoclinic with space group $P2_1/n$ at high and low temperature, respectively) and is characterized by a framework built of four-, five-, six-, and ten-membered rings of SiO_4 tetrahedra with 5.5 Å diameter pores that are linear in the **b** direction and sinusoidal in the *xz* plane.[4,5] Reverse Monte Carlo refinements of total X-ray scattering data indicate that PIA corresponds to the collapse of the structure around the empty pores while keeping the same structural topology but with strong geometrical distortions.[3] No recrystallization of this dense, nonporous amorphous form is observed. There has been considerable interest in the incorporation of guest species in microporous materials for catalysis, separation and adsorbent applications,[6] and many high-pressure studies have focused on pore filling, the effect of these species on the compressibility of the crystalline phase,[7,8] and reversible PIA[9] at moderate pressures. Incorporation of guest species[10] and PIA[11] may confer useful properties on these materials for applications in the field of the absorption of mechanical shocks. Here we show that the incorporation of CO_2 or Ar in silicalite deactivates the PIA process and that silicalite is stabilized to higher pressures than the common, nonporous, tetrahedral, low-pressure forms of SiO_2, such as cristobalite and quartz.

Silicalite-1-OH powder and single-crystal silicalite-1-F were obtained from SOMEZ (France). The refined cell constants of monoclinic silicalite-1-OH are $a = 19.8946(4)$ Å, $b = 20.1252(4)$ Å, $c = 13.3786(3)$ Å, and $\beta = 90.629(2)°$, in very close agreement with previous results for silicalite-1-F.[3] The high-pressure experiments were performed with membrane diamond anvil cells (DACs). The samples were loaded into stainless steel or rhenium gaskets. The pressure was determined from the shift of the ruby R_1 fluorescence line.[12] Silicone oil was used as a pressure-transmitting medium (PTM) in one run. Ar and CO_2 were loaded cryogenically in the liquid phase. X-ray diffraction data ($\lambda = 0.3738$ Å) were obtained on the beamline ID27 at the ESRF with a Bruker SMART CCD 6500 detector and analyzed using the program FIT2D.[13] There was no evidence of beam damage (line broadening, etc.). Raman measurements were performed in single- and triple-monochomator configurations with the 647.1 nm line from a Kr ion laser.

In silicalite-1-OH using silicone oil, a phase transition occurs at close to 1 GPa, corresponding to the disappearance of the splitting of certain reflections and giving rise to sharp reflections of the more symmetric orthorhombic structure [$a = 19.728(1)$ Å, $b = 19.583(3)$ Å, $c = 13.174(1)$ Å at 1.1 GPa]. The negative $P-T$ slope for this transition indicates that the orthorhombic form has a higher entropy or heat capacity. Progressive amorphization is observed, becoming complete just above 8 GPa (Figure 1).

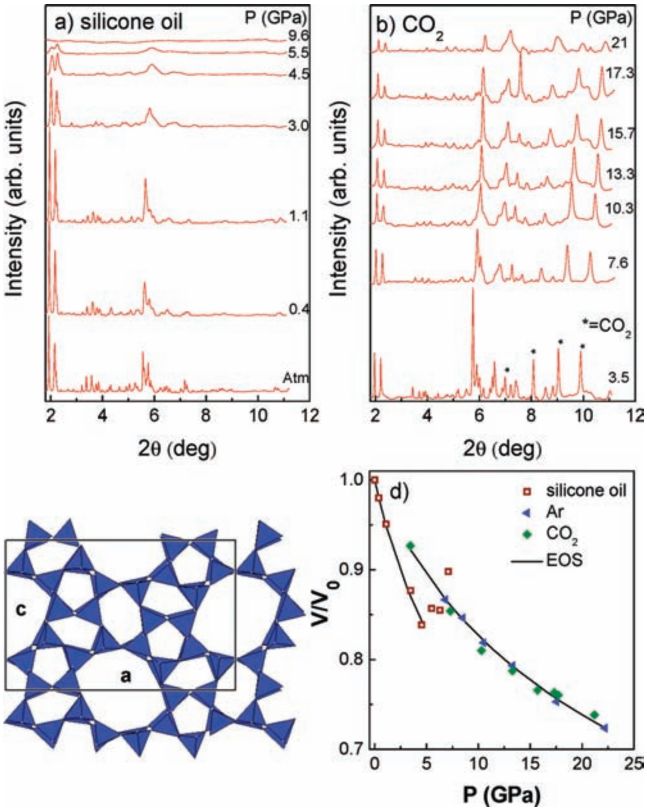

Figure 1. (a, b) X-ray diffraction patterns of silicalite-1-OH as a function of pressure with (a) silicone oil and (b) CO_2. (c) Crystal structure of silicalite. (d) Relative volume of silicalite-1-OH as a function of pressure; solid lines are fits to the Birch−Murnaghan EOS.

Silicalite-1-F is highly compressible, with a bulk modulus (B_0) of 13.6 GPa.[3] The present data on silicalite-1-OH can be fitted to a Birch−Murnaghan equation of state (EOS)[14] with B_0 value of 18.8(5) GPa and a first derivative (B_0') of 4. Expanding the EOS to third-order gives very similar results: $B_0 = 20.5(22)$ GPa, $B_0' = 3(1)$. The

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difference between the compressibility of the two materials and the points from 5.5−7.1 GPa may be due to nonequilibrium effects, as the material was in the process of undergoing amorphization, which can give rise to local depressurization.[1,3,11]

Very different behavior is observed in the presence of CO_2. The relative intensities of the diffraction lines are very different, with those at low angles being weaker, as a result of changes in structure factor in the presence of CO_2. Similar differences have previously been observed in neutron diffraction patterns of silicalites containing 10−30 molecules of adsorbed gas per unit cell at low temperature.[15] The structure is orthorhombic at the first high-pressure point after loading of the DAC [a = 19.4558(7) Å, b = 19.381(1) Å, c = 13.1541(5) Å, compared with a = 19.224(2) Å, b = 19.224(2) Å, c = 12.700(3) Å in silicone oil at 3.5 GPa]. The incorporation of guest species preferentially increases the c lattice parameter. This can be linked to the lower framework and higher pore density along the **c** direction. Silicalite-1-OH was found to be significantly less compressible in CO_2 or argon because of the penetration of these species into the pores of the structure. The compressibilities in the two cases are very similar, indicating that pore filling is comparable for the two species. A fit to the combined data yielded a B_0 = 35.9(4) GPa and B_0' = 4.7(5). The bulk modulus is almost identical to that of α-quartz,[16] indicating direct compression of the framework. The compressibility in the *ab* plane and along **c** is close to isotropic with or without guest species because of the three-dimensional nature of the pore network, giving rise respectively to isotropic collapse of the pores or direct isotropic compression of the framework. In contrast to the experiment in silicone oil, there is no evidence of PIA. There is no increase in the width of the diffraction lines between 7.6 and 21 GPa. Similar results were also obtained using Ar, again with no evidence of PIA up to 22 GPa. The changes in structure factors, the increase in bulk modulus, the isotropic compression, and the absence of PIA are consistent with complete filling of the pores by the PTM (i.e., CO_2 or Ar), which is in equilibrium with the PTM outside the pores. No increase in compressibility is observed at higher pressure, in contrast with other microporous systems[7,8] compressed in alcohols and/or H_2O. In silicalite, the interactions between the SiO_2 framework and Ar or CO_2 are much weaker, leading to a much greater mobility[8] of the guests, and an increase in compressibility is not observed up to at least 22 GPa.

Raman spectra were obtained for a silicalite-1-F single crystal in argon up to nearly 25 GPa (Figure 2). The many overlapping peaks arise from the 432 Raman modes predicted by group theory. There is no evidence of the amorphous phase obtained without a PTM, which gives rise to a spectrum characterized by broad bands, as observed previously.[3] Softening of certain low-frequency modes from their ambient-pressure values in the monoclinic phase to those observed for the first high-pressure point in argon at 1.5 GPa is observed. This softening can be linked to the monoclinic−orthorhombic phase transition. All of the modes harden in the pressure range from 1.5 to 25 GPa, that is, from above this transition to the highest pressure reached. The spectrum of the recovered sample is identical to that of the starting material. These results confirm the stability of the orthorhombic form of silicalite in the presence of guest species and the absence of PIA.

The usual compression mechanism in silicalite, which involves collapse of the structure around the empty pores, is hindered by the presence of the guest species. This modifies the energy of low-frequency vibrations, which destabilize the crystalline phase. This leads to the deactivation of the PIA mechanism in this material rather than the reversible amorphization found in the presence of a limited amount of exchangeable cations and/or guest molecules.[9] In the present study, the PTM represents a reservoir of mobile guest molecules in equilibrium with silicalite. The present results indicate that upon insertion of guest species, silicalite is retained to pressures of at least 25 GPa. This pressure is higher than that observed for low-pressure, tetrahedrally coordinated polymorphs of silica,[17,18] such as α-cristobalite and α-quartz, which undergo phase transitions below this pressure at ambient temperature. No increase in silicon coordination to six is observed in silicalite, in contrast to quartz.[18] Guest species modify the energy of low-frequency vibrations and the compression and amorphization mechanisms in open structures and can thus be used to stabilize microporous materials, including metal−organic frameworks[19] and certain metal cyanides,[20] with respect to PIA; such open structures can be retained over a very large pressure range. Partial pore filling may be used to tune the physical properties (including PIA) of these materials.

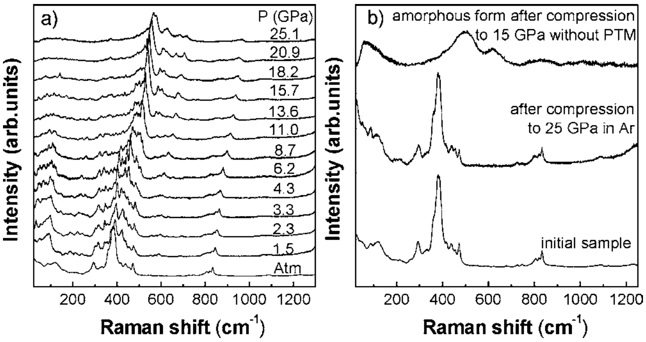

Figure 2. Raman spectra of silicalite-1-F (a) as a function of pressure and (b) after decompression.

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