Elasticity through Nanoscale Distortions in Periodic Surfactant-Templated Porous Silica under High Pressure

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High-pressure infrared absorption spectroscopy is used to examine changes in local bonding upon hydrostatic compression in both ordered surfactant-templated mesoporous silica and sintered sol-gel silica with a goal of connecting atomic scale structural changes with variations in nanoscale periodicity. High-pressure IR absorption spectra are analyzed on the basis of a noncentral force model. It is found that the intertetrahedral bond angle and its distribution width in both the dense and the mesoporous silica decrease at elevated pressure up to 4 GPa. With increasing pressure above this value, decreases in the average bond angle and distribution width cease in the mesoporous silica, while they continue in the bulk material. The results suggest that in the mesoporous silica the nanometer length scale of the silica framework makes it energetically unfavorable to form high-density atomic scale structures at higher pressures (>4 GPa). Instead, further compression of the mesoporous silica takes place by distortion of the periodic pore structures on the nanometer scale (deformation of pores). Surprisingly, upon the release of pressure, structural changes on both the nanometer and atomic length scales are reversible. The results suggest that reversible nanometer scale distortions in periodic porous materials can replace the irreversible atomic scale distortions observed in bulk amorphous silica.

1. Introduction

By optimizing the secondary structure of composite materials, mechanical properties superior to the starting single-component material can be obtained. Honeycomb-structured composite materials are one such example. They have been widely used to make light but stiff materials, both in our daily life and by nature, on a variety of length scales.^{1,2} Recently we have found that surfactant-templated porous silicas with hexagonal periodicity exhibit excellent mechanical properties-stiffness and stability under hydrostatic compression (up to 12 GPa) and reversibility of changes to the nanoscale order upon the release of pressure.² Such materials, labeled MCM-41, are formed by the cooperative self-organization of surfactant molecules with soluble silicate species.³ The pore structure in the material has p6mm symmetry (a honeycomb) with pore diameters around 30 Å and wall thicknesses of the amorphous silica framework around 10 Å. In recent years, the pore size of the material has been expanded to 300 Å with varying wall thickness, and many new periodicities are also available by controlling synthetic conditions.3-6

In our previous experiments, we used high-pressure, lowangle X-ray diffraction to examine the compressibility of periodic hexagonal, surfactant-templated silicas under hydrostatic compression.² The results indicate that mesoscopic order in these materials can be retained up to 12 GPa and that pressureinduced distortions are reversible. We also found that postsynthetic treatment can greatly enhance the mechanical properties of the porous material. Bulk moduli equal to and even higher than values measured for bulk vitreous silica⁷ were obtained if both the nanometer-scale order and local atomic-scale bonding were optimized.² It should be noted, however, that when compressed under non-hydrostatic conditions in air (for example, in a steel die),^{8–10} ordered mesoporous silica structures are essentially destroyed between 0.2 and 0.6 GPa, a process which occurs mechanochemically through the hydrolysis of Si–O– Si bonds.^{9,11,12}

We also studied the molecular environment of the organic component of periodic silica/surfactant composites under elevated pressure using a rigidochromic Re complex as a molecular probe.¹³ The amphiphilic organometallic complex was incorporated into the organic component of the silica/surfactant composite during synthesis. Shifts in the luminescence peak position of the Re complex indicated changes in the rigidity or viscosity of the surrounding matrix. Again, the results confirmed conclusions from earlier experiments on the mechanical properties of silica/surfactant composites under high pressure.² While an increase in viscosity was observed with increasing pressure, the molecular environment did not become fully rigid until pressures as high as 10 GPa had been reached. This pressure is significantly higher than the solidification point of most pure organic phases and suggests that the mechanical strength of the silica framework provides a protected molecular scale environment for organic molecules situated within the silica nanopores. At the highest pressures, luminescence did indicate a rigid environment, suggestive of pore collapse on compression. Upon release of pressure, however, this collapse appeared reversible.

To understand the unique mechanical properties of the mesoporous silica under hydrostatic compression, we need to first understand what happens at the atomic scale upon application of pressure in bulk materials. We thus begin by reviewing

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the behavior of both crystalline and vitreous bulk silica under high pressure. A summary of experimental conclusions on the behavior of bulk silica under high pressure is presented briefly below.

Under high pressure, vitreous silica undergoes a variety of rearrangements. The structures of these materials, including short-range and intermediate-range order and the dependence of these quantities on pressure, are of fundamental concern. The structure of vitreous silica is usually described by a continuous random network (CRN) of tetrahedral silicon oxide (SiO₄) units interconnected by bridging oxygen atoms. The intertetrahedral bond angle that connects two tetrahedral units is one of the most important structural parameters for the CRN-type amorphous oxides as it determines, among other things, the overall density and stiffness of the solids. Experimental results from X-ray diffraction have shown that for both crystalline (quartz) and vitreous silica, the change in Si-O bond length is negligibly small under compression below 8 GPa.¹⁴⁻¹⁶ In this pressure range the deformation in silicon oxide tetrahedral units is slight and the changes are reversible. Compression occurs through bending of the Si-O-Si intertetrahedral angles. For quartz it decreases from around 144° at ambient pressure to 130° at 8 GPa.^{14,15,17} It is suggested that the compaction of vitreous silica follows a similar mechanism^{16,18}—volume compression occurs through bending of the Si-O-Si intertetrahedral angles (i.e., decreasing Si-Si separations), with little change in the individual SiO₄ tetrahedral unit.

Above 8 GPa, the SiO₂ glass can be irreversibly densified by up to 20% after decompression.^{19,20} By using a uniaxial pressure-transmitting device, however, densification in SiO₂ glass at room temperature begins when subjected to pressure greater than about 2 GPa,²¹ i.e., shear stresses accelerate the irreversible densification process. This irreversible densification can be explained by a decrease in the average Si-O-Si bond angle through the formation of smaller ring structures that are meta-stable upon release of pressure.²² Upon further compression to above 20 GPa, the SiO₄ tetrahedra in vitreous silica become destabilized, and there is a gradual increase in Si coordination from 4 to 6.^{16,18} Quartz undergoes a similar increase in coordination number under high pressure and high temperature,²³ although amorphization¹⁵ is usually observed at room temperature.

The lack of irreversible densification² of the silica framework up to 12 GPa and the excellent mechanical properties in the mesoporous silica under high pressure pose interesting questions: how does the silica atomic structure (e.g., the intertetrahedral bond angle distribution) in the porous silica behave under high pressure? And how are the structural rearrangements in the material on the two different length scales (the atomic scale and the nanometer scale) related to each other? We hope that the answer to the first question concerning the changes in microstructure under high pressure will lead us to the key to the second question—the relation between microstructure and observed mechanical properties of this material.

To answer these questions we use vibrational spectroscopy tools, specifically in-situ high-pressure micro-FTIR absorption spectroscopy. IR and Raman spectroscopy have been used widely to elucidate atomic structural properties of AX_2 type amorphous oxide at ambient and elevated pressures. The general features in the IR absorption bands below 2000 cm⁻¹ at ambient pressure will be briefly summarized below. There are three main features: a high-frequency band between 1000 and 1300 cm⁻¹, an intermediate-frequency band centered around 800 cm⁻¹, and a low-frequency band at ~ 460 cm⁻¹.

It is of great interest to theoretically relate the above experimental IR absorption peaks to microstructural properties in silica, such as the intertetrahedral bond angle. Galeener has applied the Sen and Thorpe central force model for the dynamics of AX_2 networks.^{24–26} The model predicts that the highfrequency vibrational mode is due to an asymmetric Si-O stretching (AS) vibration within a fully polymerized tetrahedral silicate network. The existence of a uniform effective electric field in the glass splits this mode into transverse ($\sim 1070 \text{ cm}^{-1}$) and longitudinal ($\sim 1200 \text{ cm}^{-1}$) optical modes (TO and LO modes).^{27,28} The main reason for the existence of the effective electric field in amorphous silica is the considerable effective charge caused by the ionicity of the Si-O bond.28,29 The vibrational band at intermediate frequency (800 cm⁻¹) is mainly associated with motions of silicon atom against its tetrahedral oxygen cage, with little associated oxygen displacement30-32 and it will be labeled as the symmetric stretching (SS) band. The lowest frequency mode observed in IR is ascribed to mainly oxygen displacement in the plane bisecting Si-O-Si²⁴ and labeled as the rocking mode.

In our experiments, IR absorption spectra of MCM-41 type materials under pressure show behavior that is different from that generally observed for vitreous silica glass from the literature and from a sintered sol–gel silica sample that we have used for comparison in our experiments. Analysis of the IR spectra based on calculations using the noncentral force model in ref 33 provide us with information on changes in intertetrahedral bond angle distribution under high pressure, thus enabling us to relate modifications in atomic structures to the evolution in mesoscale order. In addition, ²⁹Si magical angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy is used to obtain intertetrahedral bond angle distributions in samples under ambient condition.^{34–36} The data are then used as input parameters for the IR analysis to examine change in bond angle distribution under high pressure.

2. Experimental Section

The details of the silica/surfactant composite synthesis and the subsequent surfactant removal are described in ref 2. Briefly, hexadecyl-trimethylammonium bromide was used to synthesize the surfactant/silica composite using tetraethyl orthosilicate (TEOS) as the silica source under basic conditions. The product was hydrothermally treated to optimize the mesoscale order and polymerization in the silica framework. The surfactant template was subsequently removed by calcination in oxygen at 500 °C. The resulting sample had a porosity of about 70 volume %. The sintered sol-gel sample, in contrast, was prepared under acidic conditions. Tetramethyl orthosilicate (TMOS), water and methanol were mixed together and homogenized in a mole ratio of 1:4:2; the pH was kept at 1.5. The sol was then sealed, aged at room temperature until a gel formed, and then further treated at 60 °C and 90 °C in air for 1 day each. The sintering process was carried out by heating the sample in air at 1000 °C for more than 30 h, followed by slow cooling to room temperature.

For the high-pressure experiments, finely ground powder samples were loaded into a Merrill-Bassett type diamond anvil cell (DAC). Argon was used as the pressure medium, which is known for its excellent hydrostatic properties.³⁷ For these experiments, changes in X-ray contrast indicate that the liquid Ar fills the channels of the mesoporous sample during cryogenic loading. After compression the pores remain filled with soft solid Ar, which serves as a compressible phase, much like the surfactant in uncalcined silica/surfactant composites. In some experimental runs, N₂ was also employed as a pressure medium



Figure 1. X-ray diffraction patterns of mesoporous silica at ambient pressure before compression and after decompression from 7.7 GPa. Good recovery of the nanoscale order is observed.

with very similar results. This indicates that the conclusions presented below are general to the mesoporous silica samples and not dependent on the details of the high-pressure experimental configuration. The pressure in the high-pressure cell was determined using the conventional ruby fluorescence technique.³⁸ X-ray diffraction spectra from the samples under high pressure were either taken at the Stanford Synchrotron Radiation Laboratory or using a Rigaku rotating anode X-ray generator; both were recorded with a Roper Scientific X-ray CCD camera. A Bruker Equinox 55 with an IR Scope I was used to collect the infrared spectra of the samples in a high-pressure cell equipped with type II diamonds with 500 μ m culets. The resolution of the spectra was set at 4 cm⁻¹. The ²⁹Si MAS NMR data were obtained using a Bruker Avance300 solid-state NMR spectrometer at a spinning rate of 4000 Hz. The length of the $\pi/2$ pulse was 6 μ s, and the recycle delay was 240 s.

Peak widths and positions were determined by fitting both low angle XRD and IR absorption with a series of Gaussian functions with appropriate baselines. The statistical error in all cases can be assumed to be smaller than the size of the actual data point. Systematic errors in the fits, however, are somewhat larger and can be approximated by the overall variations in the data across pressures.

3. Results

3.1. Ambient and High-Pressure X-ray Diffraction Patterns. The mesoporous silica samples show intense X-ray diffractions at ambient pressure. A typical X-ray diffraction pattern of the ordered mesoporous sample at ambient pressure in a diamond anvil cell (without pressure medium and before compression) is shown in Figure 1 (solid curve). The intense (10) diffraction peak and the existence of the two higher order peaks, (11) and (20) indicate the p6mm periodicity of the pore structure. For this sample the d spacing of the (10) lattice plane is about 52 Å. Also shown in Figure 1 is the X-ray diffraction pattern of the same sample after being compressed up to 7.7 GPa under hydrostatic conditions and released to ambient pressure (short dashed curve). The recovery of the (10) peak intensity after decompression is at least 72%. The peak position and peak width also retrace the ambient pressure pattern very well. This means the pore structure in the sample has been well preserved after compression, without irreversible collapse under elevated pressure. We note that a recovered intensity lower than 100% may be due to some irreversible inelastic deformation of the sample. It could, however, also result artifactually from



Figure 2. In-situ high-pressure X-ray diffraction patterns of mesoporous silica and changes in the q_{10} peak position with pressure. (a) X-ray diffraction patterns from mesoporous silica under pressure. (b) Variation in q_{10} peak position from the diffraction patterns in part (a) as a function of pressure. Here, \bullet indicates data taken upon compression, while \Box indicates data collected during decompression. Linear compressibility is observed up to about 4 GPa.

sample that is lost during the cryogenic loading of the Ar pressure medium. The relationship between silica framework bonding, sample hydration, and the reversibility of nanometer scale distortions is discussed in detail in ref 2.

Despite good recovery of low angle X-ray diffraction peak intensity and position upon release of pressure, significant changes in both peak intensity and position are observed as pressure is applied. The change in d₁₀-spacing under pressure is presented in Figure 2. This sample is prepared in a manner similar to the sample used for the experiment in Figure 1 but has a slightly smaller d₁₀-spacing. Both samples have similar properties under high pressures. As shown in Figure 2 (top), at 1 GPa the X-ray diffraction pattern still exhibits a clear higher order peak. Under a pressure of 8.2 GPa, the diffraction intensity is very low, which indicates a significant decrease in the periodicity of the sample. Since the pores in the sample are already filled with solid Ar during the cryogenic Ar loading step,³⁷ the loss of diffraction intensity at 8.2 GPa must be due to the distortion of the pore structure and a loss of coherence on the nanometer length scale, not to a decrease in electron density contrast caused by infilling the pores with Ar.

As shown in Figure 2 (bottom), the change of the d_{10} -spacing upon compression of the sample continues fairly linearly up to about 4 GPa; beyond this point, little additional change is observed. At the highest pressures, the d_{10} -spacing seems to

increase slightly. As discussed in ref 2, we ascribe this behavior to a loss of periodicity on the nanometer scale. The diminished and broadened diffraction peak at high pressures (6 GPa and up) may be assigned to a combination of diffuse small angle scattering from the pore structure of the material, and coherent Bragg scattering like that observed at ambient pressure. As the pressure is released, there is some hysteresis in the change of the d₁₀-spacing, and after complete decompression the d₁₀spacing is slightly smaller than that in the original starting material. It should be pointed out that the peak shape and the intensity of the diffraction peaks show good recovery, i.e., the decompressed sample still shows excellent p6mm periodicity and retains the ordered pore structure. The reversibility in the d spacing suggests that little or no permanent densification in the amorphous silica framework takes place in the mesoporous silica samples under elevated pressures. Similar effects have been observed to pressures as high as 12 GPa.²

On the basis of the changes in the X-ray diffraction presented above we generate the following schematic pictures of what could be happening in these ordered porous silicas at elevated pressure. As a first step in the compression process at pressures below 4 GPa, the compression occurs through the compaction of the amorphous silica walls. The reduction in diffraction intensity at moderate pressures indicates some distortion of the nanometer scale pore structure at the same time. The combined effect of compaction of the silica framework and distortion leads to smaller d spacings and weaker diffraction intensity. At higher pressures, distortion in pore structure causes accelerated loss in diffraction intensity and much broader diffraction peaks. It is known that further atomic scale compaction in bulk vitreous silica starts to introduce irreversible densification. However, the absence of irreversible densification up to 12 GPa in our experiments suggests that compaction of the ordered porous silica framework on the atomic scale does not follow the same route to densification as bulk silica at high pressures. Our experimental results in the next few sections will demonstrate the plausibility of the proposed mechanism and its microstructural origins.

3.2. Ambient and High-Pressure FTIR Absorption Spectra. Infrared absorption spectra between 700 and 1400 cm⁻¹ for both sintered sol-gel silica and MCM-41 silica under different pressures are presented in Figure 3. The usually strong IR band near 460 cm⁻¹ is not detectable due to limitations in the mid-IR detector used for the experiment. The hydrogenbonded water band at around 3400 cm⁻¹ (not shown) in the mesoporous silica is also distinctive, while in the sintered sol-gel silica it is almost nonexistent.¹²

The ambient pressure infrared spectrum of the sintered solgel silica in Figure 3 (top) is composed mainly of two bands around 800 and 1100 cm⁻¹. As described in the Introduction, the band at 800 cm⁻¹ is labeled as the symmetric stretch (SS) band, while the one at 1100 cm⁻¹ is labeled as the asymmetric stretch (AS) band. Under pressure there is a continuous linear shift to higher frequency in the SS band from 803 to 834 cm⁻¹ (diamonds, Figure 4) with a pressure derivative of 4.6 cm⁻¹ GPa⁻¹. The peak width increases with pressure as well. The AS band broadens significantly under pressure but does not shift as much as the SS band (Figure 5a). As a result, the SS and AS bands approach each other as pressure increases. According to the central force model proposed by Galeener,²⁵ this indicates that the inter-tetrahedral Si-O-Si bond angle is moving toward smaller values.

The pressure dependence of the component peaks of the AS band of the sintered silica is relatively flat (Figure 5a). The



Figure 3. IR absorption spectra of silica samples under pressure. Top, Sintered sol-gel silica; bottom, mesoporous silica. For both samples a low-pressure spectrum, a high-pressure spectrum (\sim 8 GPa), and a recovered ambient pressure spectrum are shown. Exact pressures are indicated on the figure.



Figure 4. Peak position of the symmetric stretching (SS) IR absorption band for both mesoporous silica and dense sintered sol-gel silica samples under pressure. Here $\diamond =$ sintered sol-gel silica under compression, $\bigcirc =$ mesoporous silica under compression, and $\bullet =$ mesoporous silica upon decompression. Similar shifts are observed for both materials.

component peak at lower frequency is usually ascribed to the TO mode. It can be seen that the peak position of the TO mode changes very little with pressure. Both theoretical³⁹ and experimental^{22,40} results of Raman spectra for vitreous SiO₂ under pressure indicate that the Raman peaks in this frequency range shift to slightly lower frequency under pressure. Infrared absorption experiments on SiO₂ glass under pressure also show that the position of this band is almost invariant to pressures near 10 GPa,¹⁷ as observed in our experiment. On the other



Figure 5. Shift in the component peak positions for the asymmetric stretching (AS) IR absorption band of both mesoporous silica and dense sintered sol-gel silica samples under pressure. (a) Sintered sol-gel silica; (b) mesoporous silica. Empty symbols indicate compression while filled symbols indicate data collected upon decompression. Unlike the symmetric stretch, different behavior is observed for the dense and mesoporous samples.

hand, Velde and Couty⁴¹ have utilized infrared absorption on pure silica glass pressurized up to 2.9 GPa, and reported positive shifts in the positions of the 460, 800, 1000 cm⁻¹ bands with pressure. The other major component peak of the AS band at around 1200 cm⁻¹ is associated with the LO mode. Under pressure the peak position of the LO mode increases slightly from the ambient position and eventually reaches a stable value at moderate pressures.

Unlike much of the bulk vitreous silica studied in the literature,^{22,41} changes in IR absorption of sintered silica under pressure are not completely reversible after decompression even in the pressure range below 8 GPa (Figure 3). For the sintered sol-gel silica sample, upon release of pressure from 7.4 GPa, the maximum of the SS peak seems to shift to slightly lower frequency and becomes weaker compared to the original spectrum at ambient pressure. The higher frequency edge $(\sim 1250 \text{ cm}^{-1})$ of the AS band, by contrast, moves back to near its ambient position. It also appears that there is some new intensity around 940 cm⁻¹, compared to that observed in the sample before compression. IR absorption peaks in amorphous silica in this frequency range are assigned to Si-O bond stretches involving nonbridging oxygen (NBO). These experimental observations suggest that the sintered sol-gel silica is meta-stable under high pressure, possibly due to the existence of ionic contaminants or NBOs and indicate that the atomic

structure becomes more defective after the application of a compressive force. As a result the structural changes in the sintered silica under even relatively modest pressure are irreversible.

Compared to the sintered sol-gel silica the changes in the infrared absorption spectra of the ordered mesoporous silica are more monotonic. As pressure increases, all infrared absorption bands in our observation range shift smoothly to higher frequency up to 8.0 GPa (Figure 3, bottom). The SS band behaves similarly to that observed in sintered sol-gel silica, increasing from 802 to 840 cm⁻¹ with the same pressure derivative as the bulk material (circles, Figure 4).

The mesoporous silica has a much more pronounced shoulder than the sintered silica. This shoulder, which is located near 1200 cm⁻¹ (LO mode) on the high frequency side of the AS band, is due to the extremely high surface area of the sample.⁴² Because electromagnetic waves are transverse, IR radiation normal to a surface can be absorbed by the TO phonons but not by the LO phonons in an infinite (thick) solid. By contrast, the p polarized component of radiation obliquely incident on a surface will have electric field components both parallel and perpendicular to the surface, thus interacting with both TO and LO modes, respectively. As a result, the existence of large amounts of randomly oriented internal pore surface in mesoporous silica makes it possible to have a significant amount of IR radiation incident at an oblique angle to the surface, thus allowing for strong LO mode absorption. For example, it has been found that the ratio of the LO mode to TO mode absorption in hybrid silica-titania sol-gel films clearly decreases as the porosity in the film decreases with heat treatment.⁴³

At the same time the high surface area in mesoporous silica leads to a relatively large amount of nonbridging oxygen atoms in the form of unsaturated Si–OH groups on the surface. According to ²⁹Si MAS NMR most of the silicon oxide species in the sample exist in the form of fully polymerized tetrahedral clusters (Q⁴ species) or with one unsubstituted Si–O bond (Q³ species). The Q³ species consists of both surface silanol groups and NBOs within the silica framework. The unsaturated Si–O bonds in the Q³ species show up as a small IR absorption peak at 940–950 cm⁻¹ in bulk samples. In the diamond anvil cell this peak is overlapped by the strong AS band and not resolved, although a corresponding peak around this frequency is requisite in the fitting of the AS band under pressure.

To fit the AS band for the mesoporous silica well, three component peaks have to be used (Figure 5b). At ambient pressure, as in sintered silica, the lower frequency peak around 1070 cm⁻¹ is ascribed to the TO mode. The LO mode consists of the two higher frequency components. The peak around 1200 cm⁻¹ is the LO mode as observed in the sintered silica sample. The highest frequency peak around 1242 cm⁻¹ is completely absent in the sintered silica and may be due to an AS LO type mode with significant surface (O^3) character. The pressure derivative for the TO mode is 3.3 cm⁻¹ GPa⁻¹. For the LO mode at 1200 cm⁻¹ it is 1.6 cm⁻¹ GPa⁻¹, and 3.2 cm⁻¹ GPa⁻¹ for the mode at 1242 cm⁻¹. These shifts in the AS band under pressure contrast with the relatively invariant peak positions in sintered sol-gel silica (Figure 5a). The broadening in the overall AS band under pressure is also much smaller than that observed in the sintered sol-gel silica. This suggests that in mesoporous silica there are smaller changes in the 4-fold silicon environments (e.g., distorted tetrahedral) at high pressure than in the sintered sol-gel silica. Upon decompression, all of the observed peaks (SS and AS) return to the original peak positions observed before compression. This correlates directly with the excellent reversibility of *p6mm* periodicity on the nanometer scale observed in the X-ray diffraction measurements.

3.3. ²⁹Si MAS NMR and Inter-tetrahedral Bond Angle Distribution under Ambient Conditions. Following the experimental technique and theoretical analysis detailed in ref 36, we obtain the inter-tetrahedral bond angle distribution for the four coordinated SiO₂ species in both sintered sol-gel silica and mesoporous silica. It is found that in the sintered silica the most probable bond angle is 142° with a distribution width at half-maximum around 24°. In the mesoporous material, the angle distribution is deconvoluted from the component of the NMR signal due to the unsaturated O^3 species. The angle distribution of the Q⁴ species peaks at 141° with a distribution width close to 20°. It should be pointed out that the NMR analysis only applies to the fully polymerized Q⁴ SiO₂ speciesmeaningful information about the large fraction of surface silica species with one or more unsaturated Si-O bonds is not obtainable by the above analysis. Because Q³ species must be excluded, the calculations described above probably underestimate the real width of the distribution of Si-O-Si bond angles in mesoporous silica. The bond angle and its distribution will be used as the input parameters and comparison for the IR analysis in the next section.

4. Discussion

4.1. Changes in Si-O-Si Bond Angle Distribution for Silicas under Pressure. There is a considerable amount of theoretical research aimed at relating the experimentally observed vibrational spectra to the microscopic properties of vitreous silica.44-46 Analytical expressions for the vibrational spectra of silica have been proposed on the basis of a variety of force field models and other calculation methods.^{24,25,33,47} Generally these expressions relate the vibrational frequency to various force constants and the inter-tetrahedral bond angle in bulk silica. The calculations by Lehmann et al.³³ are particularly interesting. In their calculations, the Born potential⁴⁸ is used to model the short-range interactions in SiO₂. Both a central force constant for Si–O stretching (α) and a noncentral force constant for perpendicular displacement of the O atom in the Si-O-Si bridge (β) are used. In addition to the short-range potential, they also introduce an effective electric field acting on the ions in silica in order to calculate the LO-TO splittings. The analytical relation for the TO mode ω_{TO}^{AS} (~ 1100 cm⁻¹) of the asymmetric stretching (AS) band as a function of atomic parameters is listed below in eq 1:

$$\omega_{\rm TO}^{\rm AS} = \left[\frac{2}{M_{\rm O}} \left(\alpha \sin^2 \frac{\theta}{2} + \beta \cos^2 \frac{\theta}{2}\right)\right]^{1/2} \tag{1}$$

Here, α and β are the central and noncentral force constants, θ is the Si–O–Si bridging bond angle between adjacent SiO₄ tetrahedra, and $M_{\rm O}$ is the mass of the oxygen atoms. The use of both central and noncentral force models in the literature is abundant and fruitful.^{49–51}

Usually in the analysis of experimental infrared absorption spectra, force constants α and β are chosen to reproduce the measured TO frequencies. For example values of $\alpha = 600$ N m⁻¹ and $\beta = 100$ N m⁻¹ have been used to describe the entire IR spectrum of relaxed amorphous SiO₂.³³ In these analyses the ratio between the force constants α and β is often considered to be constant. It is found that the relation between measured IR asymmetric stretching TO mode frequency and the bridging bond angle, which ranges from ~120° to ~180° in various crystalline and amorphous silica polymorphs, can be described with a single α/β ratio using eq 1.⁵² This demonstrates the validity of the noncentral force model calculations in eq 1. Also the fact that a single constant α/β ratio describes SiO₂ with many different bridging angles under ambient condition suggests it should be reasonable to assume that this ratio is fairly invariant under pressure (<8 GPa) as well. This is supported by the fact that the major modification of the silica structure under low pressure is the reduction in the bridging angle with little accompanying change in bond lengths. We note that the absolute values of the force constants will increase at elevated pressures as a result of increased atomic interactions.

To calculate the mean bridging Si–O–Si bond angle in silica, an additional relation between IR absorption frequency and atomic parameters is required. The frequency of the TO mode of the SS band, ω_{TO}^{SS} (~800 cm⁻¹), is given by an approximate relation (eq 2) from ref 33.

$$\omega_{\rm TO}^{\rm SS} \approx \left[\frac{4}{3M_{\rm Si}}(\alpha + 2\beta)\right]^{1/2} \tag{2}$$

Here, M_{Si} is the mass of a silicon atom, and α and β are defined as in eq 1. The atomic motion of this mode involves mostly motion of silicon atoms,^{30,31} and so the lack of a specific Si–O–Si bond angle dependence may be reasonable. We can use eq 2 and the peak positions from the SS band (Figure 4) to calculate the force constants assuming a fixed force constant ratio as a function of pressure. The validity of the approximate relation in eq 2 and the assumption of a fixed ratio of force constants will be discussed in more detail later.

By using the most probable Si–O–Si bridging angle obtained from NMR data, the frequency of the TO mode of the AS band from ambient pressure IR absorption spectra, and eqs 1 and 2, the force constant ratio can be calculated. A value of 4.98 is found for both mesoporous silica and the sintered sol–gel silica. Using this value (4.98), combined again with eq 2, the central force constant, α , is found to increase from 572 N m⁻¹ at ambient pressure to 617 N m⁻¹ at 7.4 GPa in sintered silica. For mesoporous silica the force constant changes from 570 N m⁻¹ at ambient pressure to 626 N m⁻¹ at 8.0 GPa.

Once the force constants under different pressures are known, eq 1 and the frequency of the AS TO mode can be used to calculate the inter-tetrahedral Si-O-Si bond angle. The results for both sintered and mesoporous silicas are shown in Figure 6a, circles and squares, respectively. In the sintered sol-gelsilica (empty circles) under pressure there is a continuous decrease in the bridging angle from 142° at ambient pressure to around 114° at 7.4 GPa, a reduction of 28°. In crystalline silica polymorph such as quartz the reduction in bond angle at 8 GPa is about 13° from an ambient pressure value of 143°.^{14,15,17} Compared to the experimental results in the quartz, the decrease in the Si-O-Si bond angle in the sintered silica is quite high, which may be due to different sample conditions, but more likely, is due to the approximations made in our calculations.

There have also been many experiments utilizing a wide range of experimental techniques to probe the change in the Si-O-Si bridging angle in densified amorphous silica. The reduction in the average Si-O-Si angle after a densification between 16% and 25% is found to be around 5° .⁵³⁻⁵⁵ However, these measurements on the densified silica were taken after the pressure was released, a situation unlike our current experiment. Theoretical studies of in-situ densification show larger changes with a decrease from 147.4° for normal density to 133.7° for a 20% densified sample under pressure.³⁹ Thus, both theoretical and experimental data suggest that the model we use predicts



Figure 6. Inter-tetrahedral Si-O-Si bond angle calculated for both mesoporous silica and dense sintered silica samples under pressure calculated from the data shown in Figures 4 and 5. (a) Bond angle changes calculated assuming an invariant force constant ratio; (b) Bond angle changes calculated assuming an invariant rocking mode frequency as a function of pressure. See text for details. Qualitatively similar results are obtained with either assumption. For both graphs, O = sintered sol-gel silica under compression, $\Box =$ mesoporous silica under compression, and \blacksquare = mesoporous silica released from 8.0 GPa. In both cases, marked differences are observed between the dense and mesoporous silica samples.

an exaggerated angle change and that therefore we should look for qualitative rather than quantitative trends.

In the mesoporous silica, the change in the inter-tetrahedral bond angle (Figure 6a, squares) follows a different trend from that seen in the sintered sol-gel glass. The reduction in the bond angle occurs at a slower rate up to 4 GPa, decreasing from 141° to about 126°. After that, the change in the bridging angle flattens, instead of decreasing continuously as in sintered silica. Near 8 GPa, the Si-O-Si bond angle is only about 123°. This turning point at 4 GPa agrees well with the turning point for the change in periodic repeat distance (q_{10}) in the mesoporous silica (Figure 2b), as determined by X-ray diffraction.

On the basis of the calculated change in Si-O-Si bond angles, it appears that the main feature of the micro-structural evolution below 4 GPa is the gradual reduction in the intertetrahedral bond angles and rearrangement of tetrahedral units to produce a denser silica framework. At the same time these atomic scale rearrangements lead to a gradual decrease in the quality of the nanoscale periodicity, i.e., distortion in the pore structure. The rearrangements in the silica framework are similar in magnitude to what happens in bulk amorphous silica in a comparable pressure range, and so this might be described as the normal elastic range. As pressure is increased above 4 GPa, the change in *d* spacing slows and even turns slightly to higher values, as discussed in Section 3.1. At the same time the reduction in the bridging bond angle stops, suggesting that deformation of the hexagonally periodic pore structure begins to take the central role. This also explains the significant degradation in the diffraction patterns at higher pressures. The invariance of the inter-tetrahedral bond angle in mesoporous silica above 4 GPa appears also to be related to the atomic scale memory effect, which leads to surprisingly good reversibility upon decompression. This will be discussed further later.

It should be noted that there are two significant approximations in the above analysis: constant α/β ratio and the use of the approximate relation in eq 2. An alternative set of approximations can be made if the behavior of the low-frequency IR rocking mode at high pressure is known and eq 3 is applied.

$$\omega_{\rm TO}^{\rm OR} = \left(\frac{2}{M_{\rm O}}\beta\right)^{1/2} \tag{3}$$

Here $M_{\rm O}$ is the mass of an oxygen atom. TO and OR refer to the TO mode of the rocking mode that involves solely the motion of oxygen atoms.³¹ It is known from the literature that the frequency of the rocking mode (ω_{TO}^{OR}) is relatively constant at elevated pressures.¹⁷ Since β can be calculated directly from $\omega_{\rm TO}^{\rm OR}$ using eq 3, this result suggests that a reasonable alternative approximation is to assume that the force constant β is invariant as a function of pressure. By keeping β constant and combining eqs 1 and 2, the variation in bridging angles at high pressure can again be calculated. The results are shown in Figure 6b. Although different in absolute values from the data calculated using a fixed α/β ratio, the qualitative trend in bridging bond angle variation is exactly the same as in Figure 6a with a decrease in slope near 4 GPa. This suggests that despite quantitative difference, the qualitative results presented here are robust across calculations.

We note that for both models, the bond angle decrease is smaller for the mesoporous silica than for the sintered sol-gel silica, even below 4 GPa. This may correlate with the higher bulk modulus measure for the nanoscale material in this low-pressure regime (47 \pm 6 GPa) compared to the bulk value of \sim 32 GPa obtained over the same pressure range.^{2,7,56} This higher compressive modulus may be the direct result of reduced atomic scale distortions.

Besides the average bridging bond angle, the width of the distribution of the bond angles is a good indication of the intermediate range order in silica. The bond angle distribution width is directly related to the TO mode of the AS band by differentiation of eq 1.

$$\Delta \theta = \frac{2\omega_{\rm TO}^{\rm AS} M_{\rm O}}{(\alpha - \beta) \sin \theta} \Delta \omega_{\rm TO}^{\rm AS} \tag{4}$$

Here, $\Delta \omega_{TO}^{AS}$ is the peak width at half-maximum of the measured IR absorption band. From an analysis of IR absorption spectra for the silicas under ambient conditions using KBr pellets, the width of the bond angle distribution in sintered sol–gel silica is 50° while that in mesoporous silica is 32°. These calculated distribution widths are wider than those obtained by ²⁹Si MAS NMR. This may be due to the approximations made in the above calculations. Because there is some broadening of the IR absorption spectra obtained on samples contained in the



Figure 7. Relative distribution width for the inter-tetrahedral Si-O-Si bond angle for both mesoporous silica and dense sintered silica samples under pressure calculated using the data presented in Figures 4 and 5. Top, relative peak width at half-maximum of the TO mode for the AS band of both dense and mesoporous silicas under high pressure; bottom, calculated relative distribution width for the inter-tetrahedral bond angle for both samples under pressure. For both graphs, O = sintered sol-gel silica under compression, $\Box =$ mesoporous silica under compression, and $\blacksquare =$ mesoporous silica released from 8.0 GPa. Again, a marked difference is observed between the dense and mesoporous silica samples.

diamond anvil cell (even those at ambient pressure), the measured distribution widths appear even greater for these samples. To compare changes in the bond angle distribution width under high pressure, it is thus more reasonable to look at the relative change with respect to the distribution at ambient pressure in the DAC.

The change in Si-O-Si bond angle distribution is shown in Figure 7 (bottom). Also shown in Figure 7 (top) is the relative peak width of the TO mode versus pressure. Again we see a similar trend as in Figure 6. The reduction in the bond angle distribution in sintered sol-gel silica is almost continuous, while the distribution width turns to a stable value around 4 GPa in the mesoporous silica. The decrease in the bond angle distribution in vitreous silica at high pressure has been proposed on the basis of the narrowing of Raman bands with increasing pressure.²² This again demonstrates that the major changes in the microstructure of mesoporous silica below 4 GPa are similar to those in bulk amorphous silica-a decrease in the bridging bond angle and narrowing in its distribution. At higher pressures, however, atomic scale changes in the silica framework become more energetically costly and are replaced by distortion of the nanoscale pore structure.

4.2. Nanoscale Confinement and Structural Transformations in Mesoporous Silica. The different behavior of the microstructures in mesoporous silica and bulk amorphous silica may shed light on the extraordinary mechanical properties of mesoporous silica under hydrostatic compression. The compaction of vitreous silica in the elastic region happens by the cooperative rotation of the SiO₄ tetrahedra.¹⁸ At high pressure the corner-linked SiO₄ tetrahedra are forced to rotate toward each other, resulting in smaller bridging angles. In bulk vitreous silica, this leads to high-density/high-energy structures, such as three- and four-membered rings of tetrahedral SiO₄ in samples above 8 GPa.^{22,31,57,58} As pointed out in recent molecular dynamics simulations,^{59,60} there are localized mechanical instabilities in silica glass. As pressure increases, the barriers between the localized energy minima disappear and the silica structure transforms to a higher density phase. Upon release of pressure, these transformations are not reversible, and so dense meta-stable silica is recovered.^{59–61}

However, in the silica framework of mesoporous silica the formation of dense silica may be limited, perhaps by the finite wall thickness (<10 Å). For example, structures with higher density could be unable to form within the silica framework without disrupting the continuous random network of SiO₄ tetrahedra in the silica framework, which would be a very energy-costly route. As a result, at higher pressures (>4 GPa), nanometer scale distortion or buckling of the hexagonal periodic pore structures in mesoporous silica further accommodates the compression applied on the material. Even if formation of highdensity silica is not a higher energy process in mesoporous silica, nanometer scale distortions might still become energetically more favorable, compared to atomic scale changes, at pressures above 4 GPa. The data presented in Figure 6 is strong evidence for this type of mechanism-if densification of the silica framework continued at pressures above 4 GPa, a continued decrease in Si-O-Si bond angles would be observed.

When the pressure is released, the rotated SiO₄ tetrahedra in the silica framework can decompress and restore the ambient inter-tetrahedral bond angle distribution. This can occur because even at high pressure, atomically, the silica never samples metastable dense configurations⁵⁹⁻⁶¹ and mesoscopically, the pore structure is mostly intact. This is shown in Figures 6 and 7 (filled square) by the complete restoration, within experimental error, of the bond angle and bond angle distribution back to ambient pressure values. It is likely that this atomic recovery process is coupled to the recovery of the diminished nanometer-scale order. As the lowest energy atomic scale configurations are regained, the pore structure is restored as well, resulting in excellent mechanical stability and reversibility. Data on surfactant containing composites show that this effect continues up to 12 GPa,² well beyond the point where irreversible changes are observed in bulk silica.19,20

Beyond any nanoscale confinement effect in the silica framework of these mesoporous materials, the hexagonal pore structure must also be of vital importance for withstanding compression under pressure. Sol-gel silica with porosity, pore diameter, and silica wall thicknesses similar to our mesoporous silica can be readily made, but this family of porous material is characterized by weak mechanical strength under pressure and low bulk moduli.62,63 As discussed above, for mesoporous silica at pressures greater than 4 GPa, the densification of the silica framework through atomic scale structural rearrangements stops as nanoscale deformations become energetically favorable. Compression above 4 GPa thus appears to be mediated by distortion of the ordered pore structure. In sol-gel silica lacking an ordered pore structure, distortion on the nanoscale is likely to be favorable, compared to atomic scale distortions, at all pressures and so a compressive force results in collapse of the porous silica framework.

5. Conclusions

Porous silica with nanometer-scale p6mm periodicity has been shown to have excellent mechanical stability and reversibility under hydrostatic pressure (up to 8 GPa). High-pressure infrared absorption spectra of both sintered sol-gel silica and the ordered mesoporous silica were used in combination with a noncentral force model to calculate changes in the Si-O-Si intertetrahedral bond angle with pressure. As with bulk amorphous silica, at pressures below 4 GPa compaction in the mesoporous silica occurs through rotation of the SiO₄ tetrahedra, resulting in a reduction of the inter-tetrahedral Si-O-Si bond angles and a decrease in the angular distribution. At higher pressures, however, distortion of the atomic scale structure becomes energetically unfavorable compared to distortions of the nanometer scale architecture. This results in retarded changes in both the average bridging bond angle and its distribution. These nanoscale distortions appear to prevent the formation of metastable atomic configurations to pressures as high as 12 GPa.²

Under pressure, the structural changes on these two different length scales (atomic and nanometer) may thus be inherently correlated, establishing a structural memory effect for the ambient pressure structures. As a result, during decompression, changes to the localized atomic scale structure of the silica framework and to the mesoscopic periodicity of the pore structure are both reversible, avoiding the irreversible densification observed in bulk amorphous silica in a similar pressure range. This work suggests that atomic scale rearrangements in nano-periodic amorphous oxide materials under high pressure may be fundamentally different from those observed in bulk materials. As a result, properties such as elasticity can potentially be optimized, combining lightweight, stiffness, and structural reversibility through appropriate nanoengineering.

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