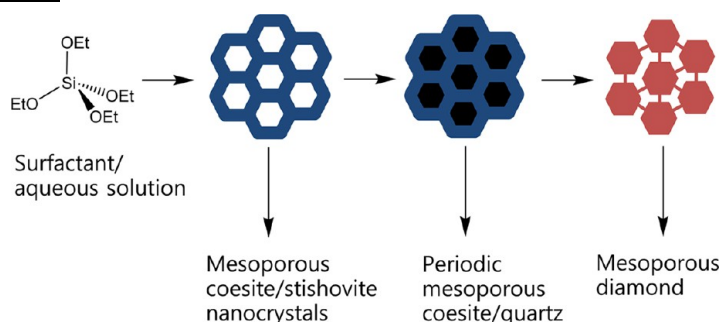# Synthetic Chemistry with Periodic Mesostructures at High Pressure

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CONSPECTUS

Over the last two decades, researchers have studied extensively the synthesis of mesostructured materials, which could be useful for drug delivery, catalytic cracking of petroleum, or reinforced plastics, among other applications. However, until very recently researchers used only temperature as a thermodynamic variable for synthesis, completely neglecting pressure. In this Account, we show how pressure can affect the synthetic chemistry of periodic mesoporous structures with desirable effects.

In its simplest application, pressure can crystallize the pore walls of periodic mesoporous silicas, which are difficult to crystallize otherwise. The motivation for the synthesis of periodic mesoporous silica materials (with pore sizes from 2 to 50 nm) 20 years ago was to replace the microporous zeolites (which have pore sizes of <2 nm) in petroleum cracking applications, because the larger pore size of mesoporous materials allows for faster transport of larger molecules. However, these mesoporous materials could not replace zeolite materials because they showed lower hydrothermal stability and lower catalytic activity. This reduced performance has been attributed to the amorphous nature of the mesoporous materials' channel walls.

To address this problem, we developed the concept of "nanocasting at high pressure". Through this approach, we produced hitherto-unavailable, periodic mesostructured silicas with crystalline pore walls. In nanocasting, we compress a periodic mesostructured composite (e.g. a periodic mesoporous silica with carbon-filled pores) and subsequently heat it to induce the selective crystallization of one of the two phases. We attain the necessary high pressure for synthesis using piston-cylinder and multianvil apparatuses.

Using periodic mesostructured silica/carbon nanocomposites as starting material, we have produced periodic mesoporous coesite and periodic mesoporous quartz. The quartz material is highly stable under harsh hydrothermal conditions (800°C in pure steam), verifying that crystallinity in the channel walls of periodic mesoporous silicas increases their hydrothermal stability. Even without including the carbon phase in the silica pores, we could obtain mesoporous coesite materials. We found similar behavior for periodic mesoporous carbons, which convert into transparent, mesoporous, nanopolycrystalline diamond at high-pressure.

We also show that periodic mesoporous materials can serve as precursors for nanocrystals of high-pressure phases. We obtained nearly monodisperse, discrete stishovite nanocrystals from periodic mesoporous silicas and coesite nanocrystals from periodic mesoporous organosilicas. The stishovite nanocrystals disperse in water and form colloidal solutions of individual stishovite nanocrystals. The stishovite nanocrystals could be useful for machining, drilling, and polishing.

Overall, the results show that periodic mesoporous materials are suitable starting materials for the synthesis of nanoporous high-pressure phases and nanocrystals of high pressure phases. The substantially enhanced hydrothermal stability seen in periodic mesoporous silicas synthesized at high pressure demonstrates that high pressure can be a useful tool to produce porous materials with improved properties. We expect that synthesis using mesostructures at high pressure can be extended to many other materials beyond silicas and carbons. Presumably, this chemistry can also be extended from mesoporous to microporous and macroporous materials.

Introduction

While periodic microporous (pore diameter 0.3−2 nm) and macroporous frameworks (pore diameter > 50 nm) have been known for many decades and even appear in nature, for example, in the form of zeolites[1] and opals,[2] the first periodic mesoporous framework (pore diameter 2−50 nm), periodic mesoporous silica MCM-41,[3] was only discovered in 1992 at Mobil Oil. Since then, the field of periodic mesoporous frameworks has experienced explosive growth, and meanwhile a myriad of different mesostructures are known.[4−9] Periodic mesoporous materials can be obtained by the so-called "soft-templating"[10] (Scheme 1, row 1) or "nanocasting"[11,12] (Scheme 1, row 2 and 3) route. The former method has been primarily used for the synthesis of periodic mesoporous oxides, while the latter is a versatile tool

for the synthesis of many mesoporous materials that are not easily accessible by soft assembly, for example, carbides[13] and nitrides.[14] Until recently, these syntheses have only used temperature as the synthesis variable, but not pressure. In this Account, we will give an overview of the high-pressure chemistry of periodic mesostructures, a topic that has not been covered yet so far.

The Mechanical Behavior of Periodic Mesostructures at High Pressure

Initial investigations of periodic mesoporous materials at high pressure focused on their mechanical behavior, which is important because mesoporous materials must stand high pressure in many applications. For instance, in adsorption technologies the materials must be pressed to pellets, and

SCHEME 1[a]
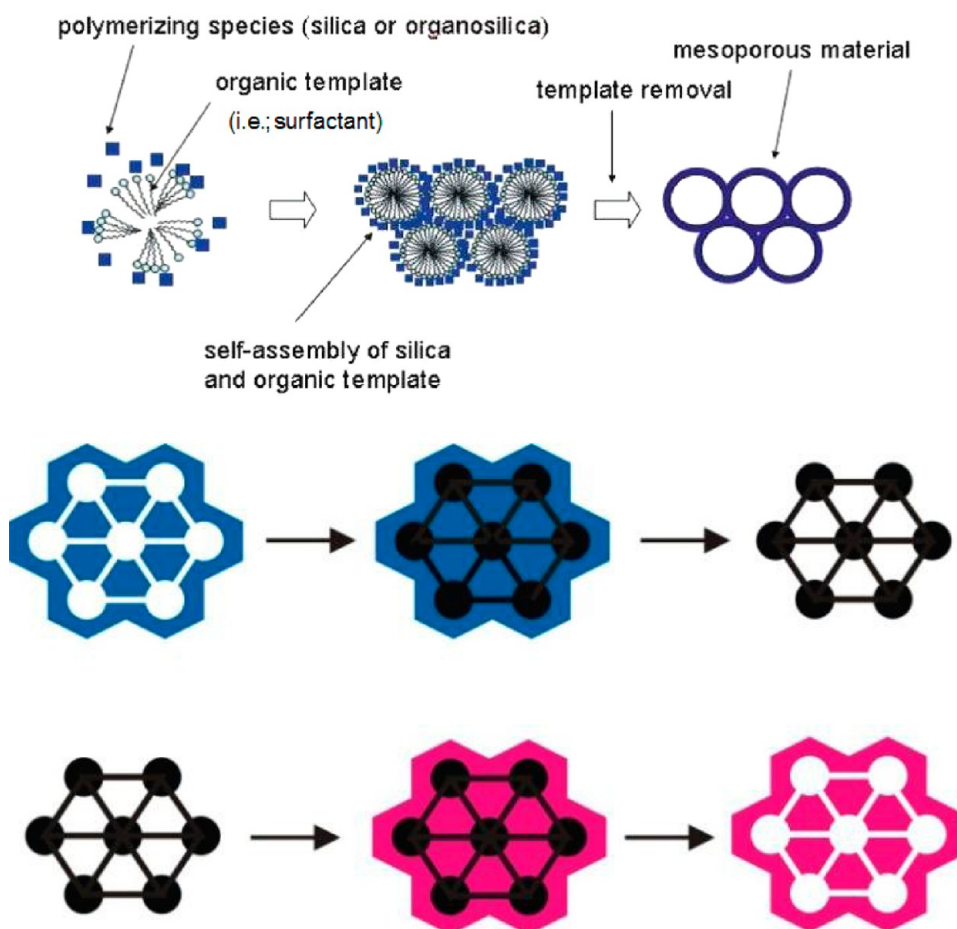
[a](Row 1) Soft-templating method. A hydrolyzed oxidic precursor (squares) co-assembles with an amphiphilic surfactant template to form a mesostructured composite. The nanocomposite can be transformed into a periodic mesoporous oxide material by template removal. (Row 2 and 3) Nanocasting strategy A periodic mesoporous material (e.g. mesoporous silica SBA-15; blue) is inverted into a negative replica (black) by nanocasting. Infiltration of sucrose into the pores of SBA-15 and carbonization of the sugar produces a carbon/silica composite (blue-black.) Selective etching of the carbon/silica nanocomposite with HF gives the mesoporous carbon (black). The so-prepared negative carbon replica can be used as hard template for the preparation of other periodic mesoporous materials (red) that have the mesostructure of the original (row 3).

therefore it is important that the materials are able to stand pressures in the megapascal range. Also the preparation of monolithic chromatographic HPLC columns requires that the materials are stable at those pressures and the pores do not collapse.

The very first study was performed by O'Brien et al. in 1996.[15] MCM-41 materials were compressed in piston-cylinder dyes to pressures of 86, 224, and 1200 MPa and then reinvestigated for their structural properties. It was found that the mesopores were essentially collapsed already at 224 MPa. These results were confirmed by others who reported a high-pressure stability of MCM-41 of ca. 100 MPa under uniaxial pressure.[16,17] The mechanical stability slightly improves when the silanol groups are capped with agents such as methyltriethoxysilane.[18] The mechanical stability increases significantly when transition metals are incorporated into the structures. For Co-modified MCM-41, the pore size distribution remains unchanged up to a pressure of 392 MPa; however, pore volumes and surfaces areas decrease. This phenomenon has been attributed to sectional collapse of the structure; that is, some pores remain completely intact, while others are totally destroyed. When Ti is incorporated, the mechanical stability even increases up to 518 MPa, but collapses at 814 MPa.[19]

Similar studies were performed on MCM-48.[20,21] Interestingly, no structural collapse was observed up to pressures of 400 MPa, which indicates that the three-dimensionality of the MCM-48 pore system significantly improves the mechanical stability under pressure. It was noticed that when the compression was done under air the number of silanol groups increased as seen by ^{29}Si MAS NMR spectroscopy, which leads to a broadening and intensity decrease of the small-angle X-ray diffraction peaks.[20] Apparently, the pressure promotes the hydrolysis of the Si−O−Si bridges when moisture is adsorbed to the material.

Also SBA-15 stands significantly higher pressures (at least 260 MPa) compared to MCM-41, likely because of its thicker channel walls.[22] The cubic SBA-1 material is perfectly stable under the same conditions, which is plausible because this material has both a cubic mesostructure and thick channel walls.[23]

Also periodic mesoporous organosilicas (PMOs) with hexagonal *p*6*m* symmetry templated by Brij surfactants were studied under uniaxial pressure in the megapascal range. Generally, the incorporation of the organic groups improves the stability at high pressure; however, the type of the organic groups has also a significant effect. CH_2 groups only marginally improve the mechanical stability, while rigid

groups with sp^2 hybridized carbons stand pressures of at least 268 MPa.

Studies on the high-pressure behavior of periodic mesoporous materials in the gigapascal range did not take place before the year 2000.[24] The first investigations were performed using as-synthesized MCM-41 type periodic mesostructured silicas, that is, MCM-41 with the surfactant template inside the pores at pressures up to 12 GPa by in situ small-angle X-ray diffraction in diamond anvil cells.[24−27] In contrast to the piston-cylinder experiments, a hydrostatic pressure medium (solid argon) was used. Due to the hydrostatic pressure the mesostructure does not collapse up to 8 GPa when the materials are predried in vacuum. Instead, a linear lattice contraction is observed up to a pressure of 4 GPa. Above this pressure no further contraction takes place, however, the mesostructure starts to distort. Both the contraction as well as the distortion are reversible however; that is, the original structure recovers when the pressure is released, which implies that the material behaves elastically. The distortions above 4 GPa become smaller when the materials are hydrothermally treated to reduce the number of silanol groups and increase the cross-linkage. The bulk modulus of these materials reaches that of vitreous silica.

Even calcined (template-free) MCM-41 type periodic mesoporous silicas are stable up to 8 GPa when argon as hydrostatic pressure medium is employed. This is because the argon can infiltrate the pores and thus the pressure on the pore walls from the inside and the outside of the pores is equal. An even higher bulk modulus is obtained then, which means that the argon inside the pores is actually less compressible than the silica material itself.

Synthetic Chemistry with Periodic Mesostructures at High Pressure

These early reports were restricted to the investigation of the mechanical behavior of periodic mesoporous silicas at room temperature. No actual chemical syntheses at high pressure (>1 GPa) were performed even though pressure is one of the two main thermodynamic variables in chemical synthesis next to temperature. High-pressure syntheses were restricted to hydrothermal syntheses below 0.01 GPa. While these conditions allow one to obtain mesostructured ambient pressure phases such as crystalline hierarchical zeolites,[28] no high pressure phases have been reported. Since the synthesis of periodic mesoporous materials under hydrothermal conditions has been extensively covered in numerous articles previously this topic will not be further

SCHEME 2. Nanocasting Process at High Pressure (top and bottom)[a]
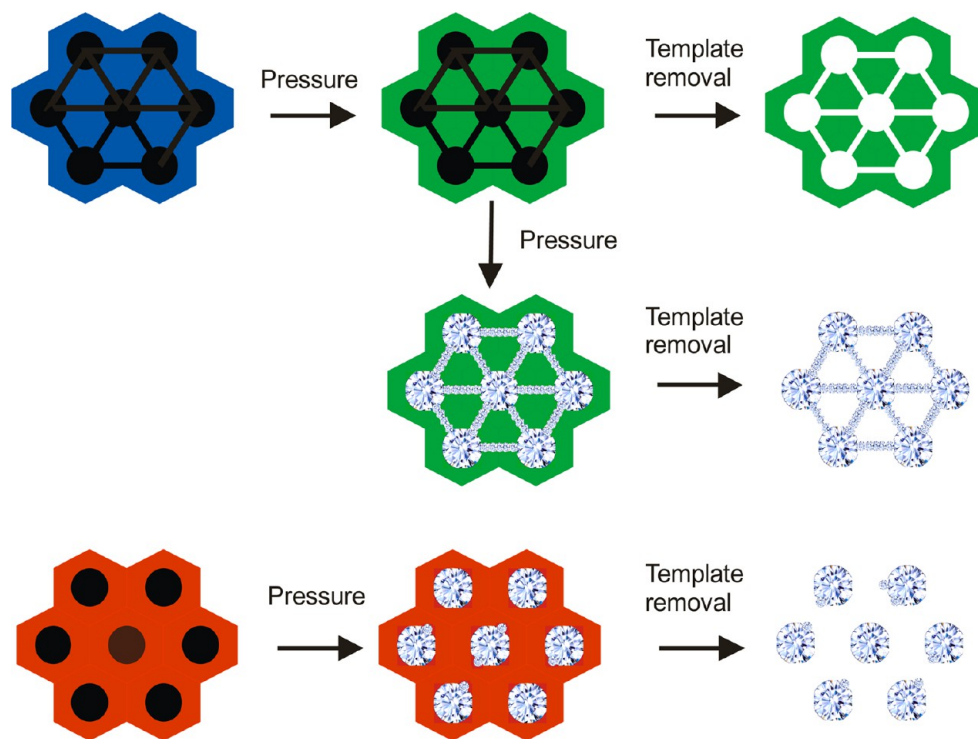
[a]Blue, red, black phases symbolize ambient pressure phases. Green and grayish phases symbolize high-pressure phases. White color indicates porosity.

discussed here. Only in 2009 the first systematic approach for the synthesis of periodic mesostructured high-pressure phases was developed, which was called "nanocasting at high pressure".[29] In this technique, pressure and temperature are applied to a periodic mesostructured composite, which induces phase transformations under the preservation of the periodic mesostructure (Scheme 2, columns 1 and 2). Depending on the pressures and temperatures chosen, either one phase (Scheme 2, row 1) or both phases (Scheme 2, row 2) can be transformed into high-pressure phases. The mesostructure does not collapse because the composite is a dense material. Upon selective removal of one phase, a periodic mesoporous high-pressure phase is obtained (Scheme 2, rows 1 and 2, column 3). When periodic mesostructures with strictly one-dimensional channels are used as starting materials, mesowires could be obtained according to Scheme 2, row 3.

The first nanocasting syntheses were performed using SBA-16/carbon composites as starting materials. SBA-16 is a periodic mesoporous silica with body-centered cubic lattice of interconnected spherical mesopores with diameters of ca. 5 nm. The composite can be made by the infiltration of a carbon source into the SBA-16. Mesophase pitch is preferred because it produces a completely dense carbon

material inside the periodic mesoporous silica. At 12 GPa and 350 °C, the SBA-16 carbon composites could be converted into periodic mesostructured coesite/carbon composite materials under maintenance of the mesostructural periodicity when small amounts of mineralizing water were present. It is apparent that pressure greatly facilitates the crystallization of the silica. For comparison, silica mesostructures at ambient pressure do not crystallize even at 1000 °C. After calcination at ambient pressure in air, periodic mesoporous coesite could be produced as the first periodic mesoporous high-pressure phase. The pore sizes of the coesite material were somewhat reduced compared to SBA-16 (4.0 nm vs 5.0 nm), and also the surface area was reduced from 833 to 278 m^2 g^{-1}. This has been attributed to the greater density of coesite as well as the collapse of the micropores in the pore walls of the SBA-16.

The formation of coesite at 12 GPa and 350 °C needs an explanation because stishovite is the thermodynamically stable phase at those conditions. Possibly, the carbon phase shields some pressure from the silica phase which favors the crystallization of coesite as the product. In addition, also the Oswald step rule likely plays an important role. This rule states that a system tends to crystallize as a metastable phase first before it converts into the thermodynamically

stable phase. The formation of the stable phase may be prevented when the activation barrier between the metastable and the stable phase is too high. This is likely the case for the coesite to stishovite phase transition that requires a change in the coordination number of Si and O.

Periodic mesoporous coesite was not only the first periodic mesoporous high-pressure phase, but also the first periodic mesoporous silica with crystalline channel walls. Periodic mesoporous silicas with crystalline channel walls have been long sought after as catalysts for petroleum cracking applications. At 12 GPa synthesis pressure, large scale applications of materials are prohibited because of the insufficient scalability of the synthesis, and thus, it has been investigated if crystallization of silica in a mesostructured silica/carbon composite can also be achieved at lower pressures. For this reason, additional syntheses at 4, 2, and 1 GPa were performed using a carbon-filled large pore FDU-12 silica as starting material.[30] At 4 and 2 GPa, a large-pore periodic mesoporous quartz was successfully synthesized this way. The material synthesized at 2 GPa showed a somewhat lower degree of periodic order, likely because a piston-cylinder assembly was used instead of a multi-anvil assembly, which has a more isostatic pressure. At 1 GPa, no crystallization was observed anymore, indicating that the lower pressure limit for the crystallization of silica is in between 1 and 2 GPa. This pressure range is industrially easily achievable, however it needs to be seen if an industrially viable route for periodic mesoporous silicas with crystalline channel walls for catalytic applications can evolve from that, as the traditional zeolite synthesis under mild hydrothermal conditions is extremely inexpensive. At this stage, a high-pressure route to synthesis of crystalline mesoporous materials may not be economical compared with traditional zeolites. However, the wider pore sizes of the mesoporous materials in combination with a higher stability due to the presence of the dense crystalline channel walls might make a higher cost acceptable. Nonetheless, it may be possible that the pressure–temperature conditions can be further lowered, further improving the economics of the synthesis.

It has also been attempted to produce periodic mesoporous diamond from SBA-16/carbon composites at 10 GPa and temperatures $\geq$ 1000 °C.[31] However, under those conditions, the mesostructure disintegrated. Between 1000 and 1300 °C, stishovite was observed as the silica phase and graphite remains as the carbon phase. Above 1400 °C, coesite and diamond were obtained as the thermodynamically stable phases. The loss of mesostructure may explain

the formation of stishovite between 1000 and 1300 °C. Due to the phase separation, pressure shielding effects are disabled and consequently stishovite is obtained as the silica mesophase. Additionally, within this temperature range, the activation barrier for the coesite to stishovite transition is overcome and kinetic effects are eliminated. It is currently an open question why the mesostructure disintegrates at very high temperature. One possible explanation is that the forces at the silica/carbon interphase are repulsive. This may be because the silica is a much more polar material in comparison to carbon. The results demonstrate that pressure has a dramatic effect on the stability of mesostructures. While a periodic mesostructured silica/carbon composite is quite stable at 1000 °C at ambient pressure, it is unstable at 10 GPa.

In addition to the nanocasting synthesis at high-pressure, also the phase-transformation behavior of periodic mesoporous silica materials without support at high pressure and elevated temperature was investigated. One would suspect that the periodic mesoporous silica would simply undergo pore collapse. However, the contrary was found.

SBA-16 heated to 300 °C at 12 GPa yielded mesoporous single crystals of coesite with mesopores of ca. 2−50 nm (Figure 1).[32] The porosity of the material is very high (ca. 49%), and the pore size distribution is centered at 4 nm. The formation of a highly porous material at an extreme pressure of 12 GPa is surprising because pressure has a strong tendency to eliminate porosity rather than create porosity. So why does a crystalline porous material form at high pressure and what is the mechanism of formation? To clarify this question, an additional experiment at 200 °C and 12 GPa was performed, which yielded a nonporous amorphous glass. This suggests that the porosity of the coesite was not a residual porosity stemming from the SBA-16 starting material. Instead, it seemed that the pores formed from a nonporous glassy intermediate upon crystallization of the coesite. Why would the pores reform upon crystallization? A possible answer to this question leads back to the investigations, which have shown that the mesopores of MCM-41 can elastically and reversibly deform at high pressure and ambient temperature.[24,26] Because pore collapse is the ultimate state of pore deformation, it is likely that elastic strain existed in the collapsed pore structure of the intermediate glass formed from SBA-16 at 12 GPa. Upon crystallization, the bulk modulus of the material increased and simultaneously induced a volume shrinkage which leads to reformation of the pores. After the crystallization is complete, the porous coesite remained metastable at the short reaction times (5 min). The mechanism is schematically graphed in Scheme 3.
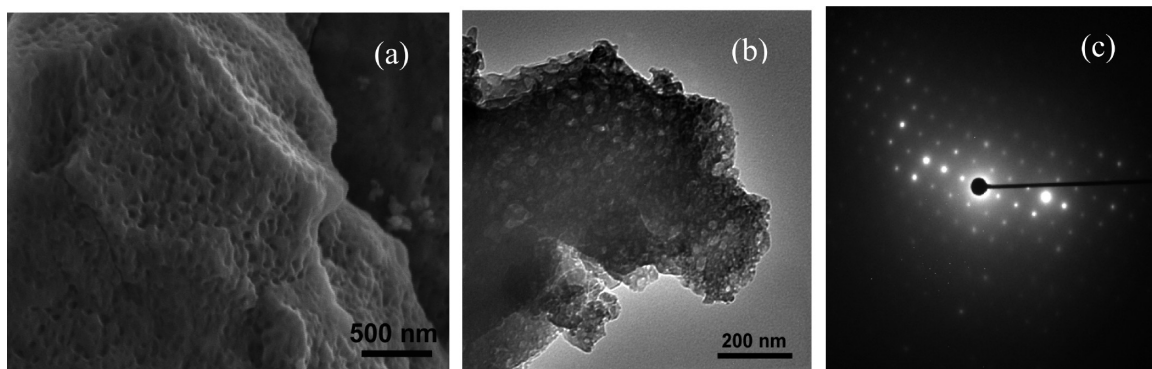
FIGURE 1. SEM (a), TEM (b), and SAED (c) of mesoporous coesite. Reprinted with permission from ref 32. Copyright 2010 Wiley.
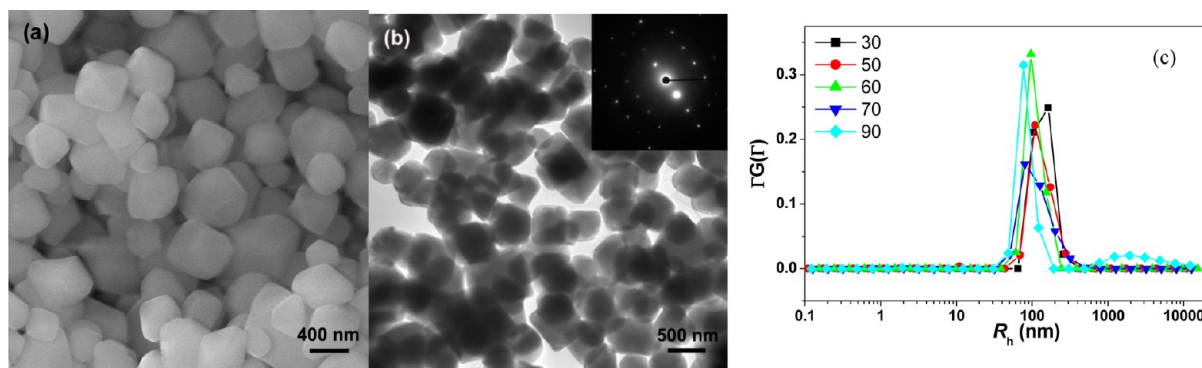

FIGURE 2. SEM (a), TEM (b), and dynamic light scattering (c) at different angles of stishovite nanocrystals. Inset is selected area electron diffraction pattern of the region shown in TEM. Reprinted with permission from ref 34. Copyright 2009 American Chemical Society.

SCHEME 3. Schematic Presentation of Direct Formation of Mesoporous Coesite from Periodic Mesoporous Silica
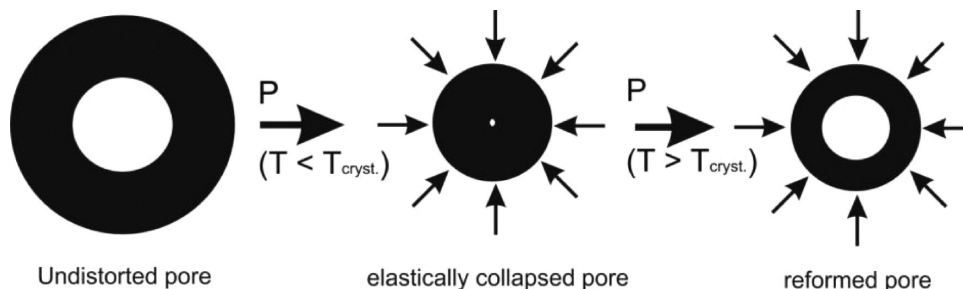
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When the temperature was increased to 400 °C, SBA-16 (without carbon support) formed quite well-defined stishovite nanocrystals at 12 GPa (Figure 2). The nanocrystals have nearly monodisperse diameters between 200 and 400 nm and were single crystalline. Despite the high-pressure conditions the nanocrystals were not agglomerated or sintered and could be easily dispersed in water. Dynamic light scattering of such dispersions showed that the stishovite nanocrystals exist as individual particles in solution as the hydrodynamic radius determined by CONTIN[33] analysis matches that seen in SEM. Also KIT-6, a cubic periodic mesoporous silica with gyroid structure, gave stishovite nanocrystals, however with somewhat large sizes (ca. 400−800 nm). SBA-15 gave coesite as the product. In this case, no specific morphology was observed. The formation of coesite in the stability field of stishovite can be explained by assuming that the hexagonal mesostructure induced a different kinetic crystallization pathway that led to a coesite intermediate which cannot further convert because of the high activation barrier for the coesite-stishovite phase transformation.[34]

High pressure chemistry with periodic mesostructures has meanwhile been further extended to periodic mesoporous

organosilicas (PMOs). In PMOs, about 25% of the bridging O atoms are replaced by bridging organic groups. It was of interest how these organic groups would influence the high pressure behavior of the mesostructure. Would they change the crystallization temperature at high pressure and would the organic groups remain in the framework during the crystallization? When periodic mesoporous organosilicas (PMOs) with ethylene ($-CH_2-CH_2-$) bridging groups were subjected to 12 GPa and 300 °C, coesite nanocrystals with diameters of ca. 200 nm were obtained.[35] Increasing the temperature to 450 °C led to a rapid growth, and crystals in the micrometer range yielded. At 200 °C, no crystallization was observed. The organic groups were eliminated from the materials when the crystallization temperature (300 °C) was reached. The cleavage of the Si−C bonds at high pressures occurs at lower temperature compared to ambient pressure (ca. 450 °C), which is plausible because pressure kinetically activates bonds.

The investigation of the phase transition behavior of periodic mesoporous materials has been further expanded to periodic mesoporous carbons.[36] When CMK-8, which is the carbon replica of KIT-6, was subjected to 21 GPa and 1300 °C, the first examples of mesoporous diamond materials were produced. The materials were obtained as transparent monoliths with a brown color, which is most likely due to defects in the material. The transparency can be attributed to the nanopolycrystallinity of the diamond. The overall structure consists of small, ca. 5−20 nm sized grains that are interconnected to form a mesoporous structure. The formation of mesoporous diamond from mesoporous carbon is an interesting analogy to the formation of mesoporous coesite from mesoporous silica, possibly by a similar formation mechanism. When the temperature was increased to 1600 °C nearly colorless, transparent diamond is obtained. Even at this extremely high temperature, the mesostructure can still be detected. The formation of the diamond at low temperatures can be attributed to the porosity in the starting materials. For comparison, graphite as the starting material gives nanopolycrystalline diamond only at temperature of ca. 2000 °C.[37] The porosity of the CMK-8 material clearly lowers the transformation temperature. At the lower temperature, the diamond nanocrystallites cannot quickly sinter together which leads to a porous nanopolycrystalline material. By contrast, graphite yields a dense nanopolycrystalline diamond because the required high synthesis temperature allows for quick sintering of the nanocrystals. When the pressure is lowered to 14 GPa, a transformation into diamond is still observed at

1300 °C, however, the diamond loses its transparency, and white diamond consisting of platelet-shaped particles is obtained. The transparency is lost because the particles grow significantly larger and reach a size regime that leads to light scattering effects.

Conclusions and Future Prospects

Synthesis with mesostructured materials at high-pressure offers opportunities to synthesize new materials that would have been otherwise impossible to realize. Up to date, a mesoporous high-pressure coesite phase, an ambient pressure quartz phase, and mesoporous diamond was obtained. Besides, stishovite and coesite were synthesized as well-defined nanocrystals. The stishovite nanocrystals have potential to be used as materials for polishing, drilling, and machining because stishovite is the hardest oxide. Mesoporous diamond could possibly be used as a biocompatible drug-delivery material. The periodic mesoporous silicas with crystalline walls could find applications in catalysis such as crude oil-cracking. To produce catalytically active materials heteroatoms like aluminum and other metal atoms could be introduced into the silicas prior to the high-pressure synthesis. After the crystallization at high pressure, these metal atoms could become highly acidic sites. At high-pressure conditions, one would expect that the channel walls will remain nonporous which could have substantial stability advantages over hierarchical zeolites. To produce these materials more economically, the method of hydrothermal hot-pressing could be applied.

So far, we have investigated only mesostructured silica and carbons; however, many other mesostructured materials with different compositions, tunable pore sizes as well as pore systems are available and could be used as starting materials for syntheses at high pressure, for example, boron nitride or titania. Besides the synthesis of nanocrystals of high-pressure phases and porous high-pressure phases, also the synthesis of mesowires of high-pressure phases is conceivable when nanocasting with hard templates having non-interconnected cylindrical mesopores are being used. After the template removal these mesowires could be obtained in nonagglomerated form, which means that they can likely be dispersed in other materials such as polymers. This could lead to interesting new composite materials with improved properties. For instance, dispersion of diamond mesowires in organic polymers could produce mechanically reinforced transparent plastics. The concept of nanocasting at high pressure could also be extended to microporous and macroporous materials giving this chemistry an even wider

scope. Many microporous (such as zeolites, covalent-organic frameworks, metal−organic frameworks) and macroporous (such as silica opals) materials are available and could be used as precursor material for studying such high-pressure synthesis. In a further extension of the concept of "nanocasting at high pressure", a mesoporous material could also be filled with small inorganic or organic molecules such as hydrogen, carbon dioxide, or benzene. The behavior of these small molecules in the confined environment of a mesopore may be different from the behavior in the bulk which could result in a difference with regard to phase transformation pressures and temperatures.

BIOGRAPHICAL INFORMATION

Manik Mandal received his B.Sc. and M.Sc. in chemistry from University of Calcutta, India, in 2001 and 2003, respectively. He obtained his Ph.D. in chemistry from City University of New York in 2010 working with the research group of Michal Kruk on the synthesis and characterization of large-pore periodic mesoporous organosilica materials and hollow nanoparticles. Following brief postdoctoral work at the College of Staten Island, he joined the materials research group of Kai Landskron at Lehigh University as a postdoctoral research associate, where he is working on various aspects of mesostructured materials under extreme conditions.

Kai Landskron received his diploma in Chemistry from University of Bayreuth, Germany in 1998. He received his Ph.D. in Chemistry from University of Munich (LMU), Germany working with Wolfgang Schnick on the synthesis of phosphorus(V)-nitrides. Following postdoctoral work in the research group of Geoffrey Ozin at University of Toronto, he joined the faculty of Lehigh University in 2006 where he is currently an associate professor. His current research interests are focused on high-pressure chemistry with mesostructures as well as new materials and methods for gas adsorption and separation.

FOOTNOTES

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