RICE UNIVERSITY

The Synthesis and High Pressure Behavior of Nanoquartz

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ABSTRACT

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This work describes the first chemical method for the preparation of quartz nanocrystals. Microscopic characterization to evaluate phase purity, size distribution and extent of aggregation is performed. In addition, pressure dependent thermodynamic properties are also assessed. Submicron quartz powders are initially produced in hydrothermal reactions where soluble silica precursors reprecipitate as pure crystalline silica. To yield nanocrystalline material these particles can be purified and size selected by dialysis, filtration and centrifugation. Transmission electron microscopy and x-ray diffraction illustrate that the product is phase-pure alpha-quartz, consisting of isolated (i.e. non-aggregated) nanocrystals. Depending on the size selection method, crystallites with average sizes of 10 to 100 nanometers can be recovered. The high-pressure behavior of nanocrystalline alpha-quartz is studied by synchrotron x-ray diffraction up to 8.6 GPa. The unit cell volume change with pressure is fitted with the third order Birch-Murnaghan equation of state giving a bulk modulus, $K_0$, of $40 \pm 1.3$ GPa. The reported value of compressibility for nanoquartz is, with reasonable agreement, the same as previously published values for bulk quartz. However, quartz nanoparticles exhibit an increased pressure dependence of the bulk modulus. In addition, a size dependent lattice expansion at ambient as well as elevated pressure is observed.
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I. Introduction: Framework for size dependent investigations of nanoquartz

Investigations of the thermodynamic and mechanical properties of nanophase materials are of central importance in the further development of nanoscale structures. Since Feynman's predictions concerning nanotechnology in his famous 1959 talk, "There's Plenty of Room at the Bottom"; there have been widespread advancements in the physical sciences regarding the generation of novel nanoscale materials and devices. It is not altogether surprising that such developments have lead to an added realization that the physical properties of nanocrystals can be very different from previously observed bulk properties. Everything from the color to the compressibility of a solid can be substantially different in a nanoscale material.

Studies have shown that limited size can alter the shape, phase and mechanical properties of nanocrystals. In the case of carbon, restricted size creates completely new structures such as fullerenes or single walled tubes. Deviations from bulk behavior have been predicted and to some extent were a motivation for chemists to pursue synthetic routes to nanocrystal formation in the first place. For instance, more than 40 years ago Feynman recognized that a small cluster comprised of only a handful of atoms might be exploited for its quantum mechanical behavior. Yet, even today, the mechanisms responsible for the deviant behavior of nanoscale systems, relative to the bulk, are neither predictable nor always understood.

Additionally, the dominance of surface energy in controlling the overall stability of the nanoparticle is a central issue in understanding size-dependent properties. However, factors including the ionic or covalent character as well as the mechanical
properties of the interior can offset or enhance excess surface energy and thus mutually determine the characteristic properties of the overall nanocrystal. It is therefore evident that if nano materials are to be fully characterized and their properties are to become predictable (thereby allowing control over structure and assembly), a detailed investigation of the interdependence between surface properties and internal bulk properties is required.

In order to better understand these relationships, the work presented in this thesis evaluates the thermodynamic and mechanical properties of nanoscale quartz relative to its bulk counterpart. In general, such comparison requires both an understanding of the bulk properties of the specific crystal system to be studied, as well as knowledge of physical properties of nanosystems in general. Thus, the work reported here is prefaced by a short introduction to the origins and properties of both naturally occurring and synthetic bulk quartz. Also in the introduction, a brief review of recent developments in nanoscale materials is presented with highlights on the unique properties of nanoparticles as contrasted with extended crystal systems. The foundation for size dependent investigations of nanocrystals begins with the preparation and characterization of a specific nanophase system. Thus, chapters 1 and 2 will focus more directly on synthesis strategies relevant to the formulation of a nanoscale quartz preparation. The remaining chapters address the structure and the pressure-volume equation of state of nanoquartz.

An explanation of some terminology might be useful at this point. A number of different sources could be consulted for a definition of "nano" and each would likely give a slightly different explanation. The most common thread in most definitions seems to be a restriction in size to less than 100 nm though some sources set the maximum as high as
1000 nm. For this work, the use of the word nano refers to a size range from 1 to 100 nm referred to as the nanometer size range.¹ Nanoparticles can be any type of solid particle in the nanometer size range, whereas, nanocrystals are solid single crystallites. Nanostructured materials include one-dimensional or two-dimensional structures that have one nanoscale dimension such as thin films or thin wires.² For the sake of variety, nanophasé materials (materials with a nanometer dimension) may sometimes be referred to as limited or limited crystal systems. Likewise, bulk materials are sometimes referred to as extended crystal systems. Typically bulk materials have lengths in three dimensions far in excess of 100 nm. In such cases, the vast majority of molecular or atomic units occupy sites deep in the interior of a material.

1.1 Natural quartz

1.1.1 Descriptions and classifications of minerals in the quartz family

In its free form, alpha quartz (or low quartz) accounts for $8.6 \times 10^{18}$ tons or 12% of the natural composition of the earth’s crust.³⁴ It is the thermodynamically stable form of crystalline silicon dioxide at room temperature and pressure. It is found in rocks of almost every type from all periods of Earth’s history. Pure quartz is often referred to as quartz crystal or rock crystal. In its well-crystallized forms, quartz can look like diamond, colorless and transparent. It often appears as elongated shards with prismatic shaped bodies capped by rhombohedral, pointed ends (see Figure I.1). Above a temperature of 847 K, α-quartz undergoes a displacive reversible transition to β-quartz (or high quartz).
Figure 1.1. Monolithic quartz crystal. This image is reproduced from the website:

http://www.wikipedia.org/wiki/Quartz
1.1.2 Occurrence and uses of quartz

In the Neolithic Stone Age, long before quartz was ever written about, flint, crystal-quartz and jasper were used as tools. It is likely that these were fashioned from minerals that had been gathered and not mined. Organized mining of quartz probably first began in 3500 B.C. by the Egyptians. Ceremonial axheads were fashioned from agate by the Sumerians in 3000 to 2300 B.C. The Sumerians were also the first known to have appreciated the ornamental value of semi-precious stones. They fashioned them into beads, which was a remarkable feat for the time period considering the lack of available carving tools. By 500 B.C. agate had become an item used in bartering in Arabia. It is also suspected that commercialization of quartz occurred in India during the same time period. More than three hundred years B.C. Theophrastus is known to have written about agate in his work entitled “Stones”. It was noted in his work that agate was found only near the river Achates in Sicily, which made it highly valuable to Italians.

It was later discovered that agate as well as many other forms of quartz minerals are found all over the globe. Thereafter, agate was used throughout central Europe and Asia. One story outlines the history of a double handled wine glass with detailed carvings on the outside. It was reportedly fashioned out of agate for the emperor Nero (54-68 A.D.) and was eventually presented to the Abbey of St. Dennis where it was used during the coronations of French kings. Persians and Arabs are known to have worn rings of agate decorated with their names or particular versus and figures. Mohammed apparently wore a signet of agate from Yeman. Another famous piece fashioned of agate
is a bowl, now housed in the Kunsthistorisches Museum Vienna, measuring 58 cm in diameter that was probably made in 4th Century Constantinople and brought to Europe by the Crusaders. American Indians also used flint and chert in more recent times for bartering purposes. In addition, since the beginning of mineral collecting and fashioning, many different quartz stones have been cherished for various purported metaphysical values such as the ability to alleviate thirst or to, in the case of rock crystals, harness the good vibrations.

In 1880, Pierre and Jacques Curie discovered the piezoelectric effect in quartz, which led to its increased consideration for technological applications. Piezoelectric materials have the ability to convert volume change to electricity and electricity to volume change. Particularly useful in technology is the fact that such materials will generate electrical signals under the influence of external vibrations such as sound waves. Thus quartz was first used commercially in World War I as a piezoelectric resonator for sonar (sound navigation and ranging) systems. It was then developed as an oscillator in the 1920s, which initiated its widespread use in radio broadcasting. With the increased communication needs brought about by World War II, quartz crystals were generated in mass production for the first time. Since then the demand for them has never slowed. Today, it is second only to silicon in use by the electronic industries. It is the standard piezoelectric material for applications such as frequency sources and frequency filters and is machined for surface acoustic wave applications. It is produced in the shape of a tuning fork as a timepiece in over a billion watches per year. Due to its clarity and chemical and mechanical durability it is a widely used optical material. It also exhibits both birefringence and optical activity; properties that are used to control interference
patterns in charge coupled detectors and create $\frac{1}{4}$ and $\frac{1}{2}$ wave rotations in laser sources respectively.

1.1.3 Crystal structure of quartz

$\alpha$-Quartz belongs to the trigonal-trapezohedral crystal class of the hexagonal system. Its symmetry elements are classified into the space group P3$_2$1. It is composed of [SiO$_4$]$^{4-}$ tetrahedral units with each corner oxygen atom shared by an adjacent tetrahedron (see Figure II.3). The Si atoms are arranged in a helix on a three-fold screw axis. Quartz is for this reason either a right handed or left handed crystal, which lacks a center of inversion. The structure can be described as a series of interconnected puckered rings that assemble into open channels traversing its entirety. Consequently, it exhibits a rather low density (2.65 g/cm$^3$, contrasted with 3.970-g/cm$^3$ for $\alpha$-alumina and 5.600 g/cm$^3$ for cubic zirconia). The Si-O-Si bond angle is somewhat flexible allowing slight rotations between adjacent tetrahedra. This fact is partly responsible for the occurrence of a high temperature polymorph of quartz, high quartz or $\beta$-quartz. The Si-O bond lengths and distance between Si atoms in $\beta$-quartz differ from $\alpha$-quartz by only 0.01 Å and the distance between O atoms remains the same. The main difference between the two structures is an increase in the Si-O-Si bond angle from 144° to 153°. This results in a significant decrease in the specific gravity of the mineral from 2.65 g/cm$^3$ to 2.51 g/cm$^3$. The lattice parameters of alpha-quartz are as given in Table I.1. The lattice energy ranges from 12967 to 15043 kJ/mol.$^4$
<table>
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<tr>
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<th>$\alpha$-quartz</th>
<th>$\beta$-quartz</th>
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<td>Si-O-Si</td>
<td>144°</td>
<td>153°</td>
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</tbody>
</table>
Figure 1.3 Structural Model of α-Quartz. The top panel corresponds to the [100] direction and the bottom panel the [001] direction. These models show the channels that penetrate the structure. Silicon atoms are shown in gray and oxygen atoms in red.
Figure 1.4. Helices and Rings in $\alpha$-Quartz. The model on the left shows the arrangement of the silicon atoms in a helix about the c axis, which is the vertical direction. The model on the right shows how puckered rings interconnect the silicon helices in quartz. The starred atoms illustrate equivalent positions in the two models. The three remaining silicon atoms in the model on the left are in a plane behind the starred atoms. The analogous three silicon atoms in the model on the right are in front of the starred atoms. These models actually show two unit cells in the [001] direction and the different colored stars correspond to the different unit cells.
1.1.4 Synthesis of Quartz

Kurt Nassau gives an excellent review of quartz synthesis in “Gems Made by Man” and the following discussion is a short summary of the information available in his book. The first attempts to synthesize quartz date back to the late nineteenth century and were informed by the observation of Humphrey Davy that quartz forms in aqueous environments. However, the first apparent successful hydrothermal synthesis was documented by de Sénarmont in 1851. His work is described by Nassau. De Sénarmont precipitated microcrystalline quartz from a reaction of water, sodium bicarbonate, an alkali silicate and an unspecified mercury compound, which was sealed inside a glass tube, placed inside a gun barrel and heated.

From then on, attempts to synthesize quartz have relied heavily on the presence of seed crystals of either natural or synthetic quartz inside a closed reaction vessel. Giorgio Spezia pioneered hydrothermal synthesis by regrowing the broken ends of a damaged quartz crystal in 1908. In his work, seed crystals of quartz were suspended with silver wire in a silver-lined steel pressure vessel. A mixture of aqueous sodium silicate and crushed natural quartz was used as feed material at the bottom of the closed vessel. At increased temperature the crushed quartz dissolved and then reprecipitated onto the seed crystal. His growth rates were rather slow for quartz, 15 mm in 199 days (or 8.7 Å/s), due to the fact that he kept the top of the vessel hotter than the bottom. Later, with the understanding of convection, it was realized that the inverse structure is more conducive to crystal growth.
The typical procedure for commercial quartz synthesis has not changed very much since Spezia's first experiments in the early 1900s. One difference, however, is that temperature gradients are now established in the reaction vessels such that the feed solution is hotter than the area of crystal growth. This facilitates dissolution of the feed grains while allowing a more controlled precipitation event at the top of the reactor resulting in the generation of more perfect crystals. Sealed steel vessels have become more resistant to high pressures and are now often referred to as autoclaves or bombs. Finally the composition of the feed solution has evolved to facilitate higher concentrations of dissolved SiO₂ by adding materials, such as sodium hydroxide, that increase the solubility of quartz. Despite these developments, the basic scheme is essentially the same: crushed quartz feed is dissolved in aqueous solution and reprecipitated onto a seed crystal suspended from above.

In addition to synthesis for commercial purposes, a number of reports have addressed the issue of quartz crystallization in the absence of seed material. In 1958 Carr and Fyfe published a report on the crystallization of quartz from amorphous silica in water.⁸ Campbell and Fyfe also report on the effect of hydroxyl ions on the hydrothermal crystallization of quartz from silicic acid.⁹ These works showed that quartz precipitates more easily at high pressures and that OH⁻ acts as a mineralizer to effectively catalyze the polymerization of dissolved silica. In addition fine micron sized powders have been prepared using the traditional method of hydrothermal preparation (dissolution of amorphous precursor in the presence of a mineralizer), but without suspended seed crystals.¹⁰ Similarly one report cites the formation of fibrous quartz powders and submicron crystals from granular macroporous silica gel and high surface area Aerosils.¹¹
Recently there has been one report published on the hydrothermal synthesis of nanoquartz. This paper shows the formation of polycrystalline quartz with an interesting morphology. Apparent grain sizes are on the order of 100 nm and sometimes less, however, x-ray diffraction is not reported to confirm this. In addition, the resulting material is heavily sintered. This work clearly reports a desire to pursue smaller particle sizes with better size distributions and suggest that one route is through combined increase of pH and pressure on the reaction solution. The above studies are among the only to focus on the formation of quartz powders.

The initial method to synthesize quartz reported in this work was developed before the report of W.-L. Huang showing the affect of pressure on reaction conditions. The high-pressure reaction conditions used by Huang are obviously very useful to the development of nanoquartz reaction schemes. However such high pressures require specific laboratory equipment and can be difficult and dangerous to achieve in the routine synthesis setting. Furthermore, their method generates exceedingly small amounts of product due to the 4 mm × 2mm reactor volume. The development of a lower pressure strategy like the one reported here may be an excellent complementary technique to expedite and simplify the synthesis of Huang.

1.1.5 Concluding Remarks

Quartz minerals have been an important class of materials throughout the history of human existence on Earth. In addition to its ornamental and aesthetic value, quartz has been useful for everything from rudimentary tools to laser optics. Arguably, the communications industry would have been slowed in its development without the
existence of quartz. Submarine sonar might not have been developed in time for World War I if not for the existence of a piezoelectric mineral such as quartz that had long been studied and admired and was also was widely available in natural form.

Due to the enduring importance of quartz on Earth, it is only natural that it receives continued attention in the context of scientific ventures such as nanotechnology. Perhaps with further investigation, new technologies will become evident such as nanoscale piezoelectric mechanics or electronics. Regardless, there is an evident need to understand the effects of grain size on currently studied phenomena in the phase behavior of quartz. As mentioned earlier, the discovery of unique phase behavior in size restricted crystal systems has incited questions concerning the nature of the relationship between a crystal's size and its phase. Quartz may provide a rich area of study in this regard. Both the purported amorphization at pressures above 20,000 atm, as well as the $\alpha$–$\beta$ transition at increased temperature would be interesting phenomena to study in nanoscale quartz.\textsuperscript{13,14}

The apparent need for further studies in this area requires an understanding of nanoscale science and the factors that influence a system due to its confined structure.

**1.2 The physical properties of nanoscale systems**

**1.2.1 Size dependent phase behavior in nanocrystals**

A prime example of a system that exhibits interesting phase behavior due to its confined grain size is that of carbon.\textsuperscript{15} While the phase diagram of carbon had long been accepted as established, the Nobel prize winning work of Kroto et al. showed that when the number of atoms in a carbon system is limited to sixty, the resulting carbon assembly
is that of interchanging hexagons and pentagons arranged into a sphere now commonly called a Bucky Ball. It was later discovered that carbon could also assemble into hollow tubes of helically attached hexane rings and these have received considerable attention due to their promising mechanical properties.\textsuperscript{16-20}

Other nanoscale systems exhibit preferential stabilization of one previously known phase over another in ways that counter known thermodynamic estimations of stable structures in the analogous extended crystal systems. For example, it is known that the surface energy of both metal and semiconductor nanocrystals can influence the relative stability of the solid and liquid phases resulting in reduction of melting temperatures compared to bulk values.\textsuperscript{21,22} In these reports, the modification of bulk thermodynamic models to include the presence of a surface, makes it possible to approximate the behavior of the nanoparticles within experimental error.

In addition, pressure dependent solid-solid phase behavior has been investigated in numerous nanoparticle systems. In CdS, the wurtzite to rock salt transition pressure increases from 3 GPa in the bulk to 6.5 GPa in 4.5 nm crystallites. The explanation for this behavior is slightly more complicated than that for solid liquid transitions because the higher pressure surface is not necessarily more or less relaxed with respect to the lower pressure one. In the case of CdS, the rock salt surface can be considered to have excess energy relative to the wurtzite surface. Being that the role of the surface is more important in nanocrystals, the barrier to the rock salt phase is heightened and the transition pressure is elevated.\textsuperscript{23} CdSe also exhibits a wurtzite to rock salt phase transition and the same elevated transition pressures were observed. In this work insight concerning the role of the particle shape is provided. Since a nanoparticle must convert
coherently to a new phase, the shape of the crystal changes. The resulting exposed surfaces can be of higher index than those that might occur in a bulk crystal, which can fragment into domains while converting. The existence of higher index surfaces thus forces the surface energy of a phase-transformed nanocrystal to be higher than expected in some cases.\textsuperscript{24} In the case of silicon nanocrystals, an increase in transition pressure is also observed. In this example, the recovered phase is amorphous in the nanophase while bulk systems are known to return to a different crystalline structure. This result points to an additional factor of kinetic size control in nanocrystal systems.\textsuperscript{25}

Other studies of size dependent phase transitions, many of which also include characterization of mechanical properties, have mostly shown an elevated transition pressure.\textsuperscript{26-29} One particular report demonstrates a reduced transition pressure for the conversion of maghemite to hematite. In the context of surface energy arguments, this suggests that the surface energy of hematite is lower than that of maghemite. The authors do not directly address this as a potential cause. Instead, they refer to a large volume change upon transition and speculate about the potential of high surface areas to act as efficient nucleation sites for phase transition. These arguments do not align well with previous results underlining the need for further understanding of nanophase behavior at elevated pressures.

Magnetic properties have also been shown to exhibit grain size dependence. For example, the Morin transition temperature in hematite (ferromagnetic to antiferromagnetic spin flip at 260 K) is depressed in the nanoscale system compared to the bulk.\textsuperscript{30} In the nano system studied, there is an evident size dependent lattice expansion. To understand the role of this expansion in the depression of the Morin
transition temperature, the authors estimated an effective negative pressure necessary to cause such an expansion. The volume expansion was correlated to an effective pressure of -180 kbar by extrapolating from the pressure induced spin flip transition studied in previous work (the rate of increase in the Morin transition with pressure was equal in magnitude but opposite in sign to its decrease with crystallite size). In the previous pressure dependent study of transition temperature, the spin flip had occurred at a specific temperature in the ambient bulk case but when the volume was decreased (increased pressure) the temperature required increased. Thus, the negative “equivalent pressure” of the nanoscale system is the reported cause of transition depression. Neither the implied dependence of the transition on electronic structure and orbital overlap nor the observed effect of crystallite size on the transition was fully discussed. Nonetheless, the evidence that in some cases nanocrystals exhibit size dependent lattice changes is of particular significance.

1.2.2 Lattice Distortion

While the above report on the Morin transition in hematite may have been among the first to show a size dependent lattice distortion, those results are now not among the more commonly observed behaviors regarding the direction of volume change in a nanocrystal with decreasing size. In fact, most data concerning size dependent lattice parameters have shown a decrease in unit cell volume, or a lattice contraction, with decreasing crystallite diameter. Thus the results shown in a following chapter of this work (chapter 3) are unexpected considering that they clearly show a lattice expansion with the decreased size of synthetic nanoquartz crystallites. This observed lattice expansion calls for an analysis of the underlying factors involved in the structural
stability of nanocrystals. Framing the arguments responsible for lattice contraction in nanocrystals is one valuable strategy to gain insight into the potential causes of lattice expansion. The following discussion will illustrate accepted reasoning for the behavior of lattice parameters in limited crystal systems. Both contraction and expansion will be addressed and an explanation for the observed expansion in nanoquartz will be suggested.

1.2.2.1 Lattice Contraction and Liquid Drop Surface Tension

Davisson and Germner (AT&T Bell Laboratories) first prompted speculation concerning lattice contractions in small particles in the late 1920s. In the process of understanding electron diffraction from polycrystalline nickel, an accidental explosion caused the oxidation of their nickel film. They fixed the problem by prolonged heating which had the unintended effect of ripening the grain distribution into a few larger single crystals. They thus discovered single crystal electron diffraction. Concurrently, their studies led them to report that the nickel lattice contracted near the surface by as much as 30%. Lennard-Jones and Dent were intrigued by their result and pursued a calculation based on the attractive and repulsive forces between ions at the surface and interior of a crystal. They predicted a lattice contraction due to surface effects on the order of 5% and suggested that this amount would be too small to be observed. Still, the concept of lattice contraction was pursued and during the early 1950s was reported to exist in alkali halides, bismuth, gold and silver.

Later reports on lattice contraction approached explanations for its origin from a different perspective. These formulations focused on the work required to form a theoretical new unit of surface area. Terms such as surface tension and surface stress
were used and results regarding the behavior of liquid drops were related to the behavior of small crystals. Surface tension in spherical droplets is essentially the force the surface exerts on the interior liquid. Every atom (or molecule) on the interior of a liquid droplet experiences an attractive force from the surrounding atoms. The vector sum from all the attractive forces it experiences is zero. For an atom at the surface this is not the case. Surface atoms experience a net inward force since there are no atoms beyond the surface to cancel attractions from the interior. Thus, there is a net amount of work that must be done in order to create a new unit of surface area. This can be described as the work associated with moving sufficient atoms or molecules to the surface against the inward force of attraction and is referred to as the surface tension. In liquids, surface tension acts to minimize surface area causing small amounts of free liquids to draw together and form spherical droplets. An alternative way of stating the effect of surface tension on a liquid droplet is that it exerts an isotropic radial pressure.

The relationship between the size of a liquid drop and its internal pressure is given by the Laplace Law:

$$\Delta p = \frac{2\gamma}{r},$$  

[I.1]

where $\Delta p$ is the difference in pressure (force per unit area) between the inside and outside of the liquid, $\gamma$ is the surface tension (force per unit length) and $r$ is the radius of the droplet. In the case of a solid crystallite, however, surface tension depends on the specific crystallographic orientation of the surface. Several reports illustrate a method to estimate a Laplace type law for solid crystallites in an effort to use lattice distortions to
estimate surface stress in small solid particles.\textsuperscript{35,36} For isotropic particles with a cubic structure the resulting equation is

\[
\frac{\Delta a}{a} = -\frac{2}{3} \frac{gK}{r}.
\]  \hspace{1cm} [I.2]

Here, the variation \(\Delta a\), in the lattice parameter, \(a\), is expressed in terms of the crystallite radius, its compressibility, \(K\), and the stress coefficient \(g\). In equation I.2, pressure has been related to a volume change by the use of the compressibility with the assumption that for a cubic crystal \(\Delta V/V = 3\Delta a/a\). The stress coefficient is the corollary to surface tension in a liquid. It accounts for the behavior of surface tension in the solid relative to specific crystal orientation and is given by:

\[
g_{ij} = \delta_{ij} \gamma + \frac{d\gamma}{d\varepsilon_{ij}},
\]  \hspace{1cm} [I.3]

where \(\delta_{ij}\) is a Kronecker delta, \(i\) being the direction in the plane of the surface normal to which the force is applied, \(j\) is the direction of the force applied and \(\varepsilon_{ij}\) is the strain tensor. Equation I.2 is, as mentioned previously, the case for an isotropic particle with a cubic structure; the resulting stress is thus calculated as an average value and is assumed not to depend on orientation. Equation I.3 gives a rigorous definition of stress accounting for all possible variations of tension due essentially to the different bonding arrangements of specific crystal faces.

Since the formulation of crystallite surface tension in this way, a number of papers have cited this argument as an explanation for lattice contraction. Vermaak and Kuhlmann-Wilsdorf, along with formulating much of the theory, showed that gold
exhibited lattice contraction in accordance with equation I.2.\textsuperscript{36} Solliard and Flueli extend the model to their work on gold and platinum. Their particles showed lattice contractions and they used the magnitude of contraction to estimate surface stress, also according to equation I.2. In comparison with bulk values for the surface stress, their values were high, suggesting an added energy associated with the surface of a small particle (4.44 N/m for small gold clusters compared to 3.1 N/m for the bulk).\textsuperscript{35} Montano et al. have used the same equation to measure the surface stress of cold silver particles.\textsuperscript{37} Another report shows the contraction of palladium particles, contrary to previous observations of expansion, and models it with equation I.2 to estimate a surface stress. The work points to the importance of chemical and phase purity in the accurate determination of lattice parameters.\textsuperscript{38} Incorporation of C, O\textsubscript{2} and H\textsubscript{2} as well as pseudomorphism due to contact with crystalline substrates is suggested to cause false lattice expansions.\textsuperscript{39} Reports concerning the lattice contraction of semiconductor nanocrystals have been given on CdSe and CdS.\textsuperscript{40,41} In the case of CdS, the observed lattice contraction was used to measure the surface stress and a value of 2.5 N/m was reported. A number of variations to the model presented by equations I.2 and I.3 have been suggested but overall the predominant explanation for lattice contraction is one largely based on a substitution of a surface stress tensor for surface tension in the Laplace law (equation I.1).

One interesting report suggests an alternative physical explanation for the observed lattice contractions in small crystals.\textsuperscript{42} In general the particles that have been shown to exhibit lattice contractions are metallic. Apai et al. have used extended x-ray absorption fine structure (EXAFS) to analyze the interatomic distances in small copper and nickel clusters. Values of the metal binding energy for atoms incorporated into a
crystal are lower than those of isolated dimers. It is postulated that the delocalization of electron density in the metal crystal is responsible for reduced interatomic binding energy. In the extended system there is a flow of charge into the volume and the resulting renormalization of electron configuration (from $3d^{10}4s^1$ to $3d^{0.75}4s^{1.25}$) causes a reduced binding energy compared to the dimer. As particles get smaller, there are more atoms at the surface, which retain a more dimer-like electron configuration compared to those in the bulk. This results in increased binding energy at the surface yielding an overall average lattice contraction. This work has been criticized due to its use of a carbon substrate, which as previously mentioned could affect the lattice spacings of the material. Nonetheless, it gives a useful alternative perspective on the origin of contraction. In comparison of semiconductor and metal nanocrystal surface stresses, it is evident that the value of the semiconductor is lower than the metal. This supports the explanation given by Apai et al. since the covalent character of the semiconductor would presumably offset binding energy decreases upon crystallization.

1.2.2.2 Lattice expansion

A number of reports have also shown an increase in lattice parameters with smaller sized crystallites. BaTiO$_3$ is reported to exhibit a 2.5 % lattice expansion for particles 15 nm in size. In a later report this was shown to be related to the increased ionic character of the Ti-O bonds, which subsequently leads to an increased Ba-Ti bond length. The cause of the increased ionic character was not explicitly addressed. Alternatively, the same report attributes the lattice expansion of ceria nanoparticles to the mixed oxidation state of Ce. Other reports on polycrystalline nickel and barium titantate cite strain related to grain boundaries as a cause of lattice
expansion.\textsuperscript{44,45} Lattice expansion in other nanocrystalline samples has been attributed to a supersaturation of vacancies in the lattice.\textsuperscript{46} For the most part, observed lattice expansions have thus far been attributed, essentially, to defects in the crystal structures. The main report that does not cite one kind of defect or another is the early work of Schroer on hematite.\textsuperscript{30}

The report of Schroer suggested that the iron oxide lattice expands due to a "negative free surface energy" of the crystal. A helpful text on the terminology associated with surface characterization is "Solid State Surface Science".\textsuperscript{47} In this book, Linford frames what Schroer was likely to have meant as specific surface work, analogous to the surface tension of a liquid, $\gamma$, as used in equation 1.3 above.

$$\gamma = g_x - \sum \mu_i \Gamma_i .$$  \hfill \[1.4\]

$g_x$ is the specific surface Gibbs energy, $\mu_i$ is the chemical potential of the $i$th species and $\Gamma_i = n_i / A_x$ is the "surface excess" (or surface concentration) of the $i$th species. The idea of a negative free surface energy or specific surface work is neither well understood nor commonly accepted. Most nanoscale systems have exhibited lattice contractions associated with an assumed positive surface work. Contraction appears logical due to the well-known behavior of liquid droplets, as outlined above. This is essentially the explanation given to the behavior of lattice-contracted nanocrystals. But many of the systems that have been studied with respect to lattice parameters have considerable or complete ionic character. This work will later address an observed lattice expansion in alpha-quartz and for the purposes of framing those results; it is worth noting now that
there may be a significant difference between the behaviors of strongly covalent systems under size dependent confinement.

1.2.3 Concluding Remarks

The resulting lattice parameters of a small crystal have clearly been shown to differ from their bulk counterparts. Equation 1.4 gives a thermodynamic assessment of this behavior but it also provides some indication of a major factor involved in the microscopic response of a crystallite to size confinement. The response of a crystal depends on the stress-strain relationship for that particular phase and structure. While there may be thermodynamic factors involved, what determines whether a crystal will exhibit surface contraction or expansion is its stress-strain tensor.

1.3 Bibliography


1 Introduction to nanoscale oxides prepared form hydrothermal methods

Preparative techniques for nanoscale oxides of various compositions can inform strategies for the formation of quartz nanocrystals. Particularly successful at the formation of oxide nanocrystals is the technique of hydrothermal synthesis. Hydrothermal refers to conditions of high temperature and pressure in aqueous environments. Naturally occurring hydrothermal conditions, such as the veins responsible for volcanoes at the earth’s crust, are the primary locations at which quartz is found. The initial synthetic strategies for quartz were motivated by this fact.\(^1\) As will be discussed below, hydrothermal conditions have led to the formation of a number of well-crystallized nanoscale inorganic oxides.

1.1 Applications of inorganic oxide nanocrystals

Investigations of oxide nanocrystals have become more prominent in recent decades due to a number of findings concerning their size dependent properties. In general these properties, which are exploited in many materials applications, are a result of increased surface area due to smaller particle sizes. The following discussion highlights different reports that use nanoscale analogues, derived specifically from hydrothermal preparations, to achieve enhanced performance in materials applications.

For sensors and catalysts, nanocrystal size control is used to increase the reactive surface area, reduce sintering temperatures and alter grain density. For example, zinc aluminate is used in the double bond isomerization of alkenes, dehydration of saturated alcohols to olefins, preparation of polymethylbenzenes, synthesis of methanol and higher alcohols, synthesis of styrenes from acetophenones and as a support for alkane dehydrogenation catalyst. The use of the hydrothermally prepared nanocrystalline form
of this material increases its effective surface area from 50 to 340 m$^2$/g, which would presumably result in an increased catalytic activity.$^2$ Cerium oxide is used as a promoter for automotive exhaust catalysis and its sintering temperature was shown to be reduced by the use of nanoscale powders.$^3$ Selective catalytic reduction of nitric oxide with methane has been shown for scandium oxide, yttrium oxide and lanthanum oxide. The use of a nanocrystalline material for this catalysis is shown to shift methane activation to lower temperatures resulting in an improved NO to N$_2$ conversion rate.$^4$

Tin oxide is shown to have reduced electrical resistance in its nanocrystalline form which improves its sensitivity to CO and H$_2$ adsorption. This behavior is related to an increased concentration of grain boundaries present in the sintered form of the nanopowder precursor.$^5$

In ceramics processing, the crystallite size, shape and extent of monodispersity in the nanopowder precursor are parameters in pressing and sintering. Sintering is the process of compacting or fusing a powder into a solid structure typically by heating. Here the grain structure becomes a key factor in the resulting refractory properties of the material and the morphology of the precursor is shown to predetermine the resulting grain structure.$^6,7$ Nanopowders are known to sinter at lower temperatures and produce a finer grain structure resulting in better mechanical properties.$^8$ Zirconia nanopowders show an increased strength and toughness compared to traditional zirconia systems and are useful in the infiltration of intra-tow regions of fibrous materials where larger particles cannot penetrate.$^8$ This lends chemical and thermal stability to oxide ceramic composites. Boehmite particles exhibit interesting shape changes under pH change and are useful to produce high density monolithic ceramics.$^8$
Other types of oxides exhibit interesting dielectric, magnetic or electronic properties. In these systems grain boundaries can also play a key role in conductivity, magnetic properties, and optical permittivity and so nanoscale precursors are used similarly to the way they are used in ceramics. One example highlights the impact of densification in piezoelectric actuator (PZT) ceramics (ferroelectric ceramics which irreversibly transform to piezoelectric materials upon heating such as barium titanate and lead zirconate titanate) on their dielectric properties. This study showed that reduced concentrations of lead were successfully used in the hydrothermal preparation of PZTs from nanoscale materials. This resulted in higher permittivity, dissipation factors and Curie temperatures. The minimization of Pb concentration is important since it is a toxic contaminant released in the sintering of the product. Strontium titanate is another example of a material that exhibits lowered sintering temperature due to the use of a nanophase powder precursor. In this highly conductive system the denser nanofabricated system is expected to exhibit an even higher conductivity.

The photocatalyst titanium dioxide is another very important electronic material. Its nanochemical formulation is useful in the photocatalytic oxidation of NO to NO₂ and NO₃. In the case of NO catalysis, oxidation activity is shown to drop off with increasing calcination temperatures which correspond to increased grain sizes. One of the most publicized applications of oxide materials is the Grätzel solar cell. This device makes use of titanium dioxide as a photoelectrochemical material where it acts as a charge-separating medium. The nanocrystalline character of the titanium dioxide particles serves to increase the reactive surface of this medium and thereby increase the efficiency of conversion for the cell. The use of nanoporous films of titanium dioxide nanoparticles is
important in the area of protein immobilization. Titania is an optically transparent semiconductor that is shown to act as an electrode for the electrochemistry of proteins. It shows a high affinity for the binding of certain proteins including hemoglobin and cytochrome-c and when deposited in a thin film has an increased surface area that facilitates electrochemical processes. In the immobilization of hemoglobin, titania acts as a composite electrode for the reduction of nitric oxide to nitrous oxide. Such films are useful in the quantification of nitric oxide from 1 to 15 μM.\textsuperscript{14,15}

Hydrothermal synthesis can also be important in the preparation of doped materials for electronic or magnetic applications. Here the dopants can be chemically incorporated into the nanoscale product to allow for concentration tuning. Ferrites are an example of an important electronic material in this category.\textsuperscript{16} The use of a nanoscale analogue in these systems shows how hydrothermal preparations can improve the properties of materials by offering quantitative control over dopant composition.\textsuperscript{17} These products benefit doubly from nanochemical preparations due to enhanced electronic properties associated with increased grain boundaries after calcinations.\textsuperscript{18} Another example is lead titanate and lead lanthanum titanate. In these materials reduced grain size results in a dramatic reduction of the sintering temperature and lanthanum doping systematically changes the structure, phase and phononic properties of the resulting particles.\textsuperscript{19} Ceria is an interesting example of a doped material that demonstrates ionic transport properties. Hydrothermal synthesis of nanocrystalline $\text{C}_{1-x} \text{M}_x \text{Bi}_{0.4} \text{O}_{2.6-x}$, where $\text{M} = \text{Ca, Sr or Ba}$, permits control over ionic conductivity depending on dopant concentration.\textsuperscript{20}
In the previous examples, the intrinsic properties of single nanocrystals played only a minor role in their use; however, there are a number of well known metal or semiconducting nanoparticles that exhibit size dependent properties which are found in isolated nanoparticles.\textsuperscript{21,22} Some applications are emerging which exploit these unique tunable properties in oxide systems. The hydrothermal synthesis of iron oxide nanoparticles allows nanoscale size control. Results relating to the magnetic properties of such products show size dependent superparamagnetic behavior that suggests a fundamental difference between the nanoscale product and the bulk.\textsuperscript{23,24}

Hydroxyapatite (\(\text{Ca}_3(\text{PO}_4)_2\text{OH}\)) and carbonated hydroxyapatite nanoscale oxides are receiving interest because of their potential applications as bone replacements or regrowth scaffolding. Nanocrystalline hydroxyapatite promotes osteoblast adhesion and proliferation.\textsuperscript{25,26} Because carbonated hydroxyapatite is shown to have an enhanced bone apatite formation and osteoclast resorption, it is also expected that the nanocrystalline form of carbonated hydroxyapatite will generate improved bone replacement options. Hydrothermal synthesis thus offers two important advantages for synthetic apatite formation: chemical control over grain size as well as composition. Plasma sprayed precursors subjected to hydrothermal synthesis are shown to generate these materials in their doped form with effective nano induced properties such as low tensile stress.\textsuperscript{27} The versatility of the hydrothermal method also enables the systematic study of purely synthetic routes to apatite formation. Base catalyzed reactions of mono-, di- and trialkylphosphates with \(\text{Ca}^{2+}\) ions leads to the formation of hydroxyapatite nanocrystalline particles of 1 nm grain size and roughly 150 nm average particle size. In this example the mechanism of the reaction was explored and a number of different types
of alkyl phosphates were employed for the successful production of biomimetic material.\textsuperscript{28}

Additional applications for oxide nanopowders range from ion exchangers for the treatment of nuclear waste\textsuperscript{29} to rechargeable lithium oxide batteries.\textsuperscript{30}

1.2 The hydrothermal synthesis of oxide nanocrystals

A detailed understanding of the synthetic routes involved in the production of nanocrystal products is required for the continued development of their applications and the clarification of their fundamental properties. This requires control over particle size, shape, crystallinity and size distribution. Hydrothermal synthesis, to be differentiated from post-synthesis hydrothermal treatments, offers a useful route to the formation of oxide nanocrystals. Developments in hydrothermal methodology have resulted in phase control as well as improvements in nanoparticle size distribution.\textsuperscript{31} For these reasons and others, it has become a general method for the preparation of most oxides in nanocrystal form.

1.2.1 Titanium dioxide

Early methods for the preparation of anatase TiO\textsubscript{2} focused on the treatment of aqueous mixtures of amorphous precursors at elevated temperature in hydrothermal reactors.\textsuperscript{32,33} These methods were not effective at producing well-crystallized particles of controlled size. Recent developments target homogeneous precipitation of nanocrystals from aqueous solutions, which provides more control over reaction products. For example the addition of TiCl\textsubscript{4} to ice water was shown to produce aqueous solutions whose pH, concentration and reaction temperature could be controlled to produce various products.\textsuperscript{34} Solution pH affects the size and phase of the resulting crystallites. Higher
pH generates sharp anatase x-ray diffraction patterns. Linewidths broaden with decreasing pH suggesting reduced grain size. Under extremely acidic conditions, the brookite phase is produced in conjunction with anatase. Under combined conditions of low pH and high precursor concentration, the rutile phase is favored but with elongated rod shaped grains.

Another report demonstrates the use of citric acid to suppress the hydrolysis of TiCl$_4$ at room temperature.$^{35}$ This allows increased concentrations of precursor solutions resulting in the formation of spherical rutile nanocrystals of uniform size. One reaction that favors the formation of anatase also use hydrolysis of TiCl$_4$ but in the presence of added ammonium sulfate.$^{36}$ Another strategy employs the use of titanium alkoxide as a precursor with different alcohols used as the solvent. Small amounts of water present in the alcohol initiate the hydrolysis of the alkoxide.$^{37,38}$ Finally uniform particles of anatase and rutile have been synthesized from microemulsions or mixtures of inorganic, organic and surfactant liquids. The aqueous environment in a microemulsion is concentrated inside of spheres created from surfactants that stabilize the interface with an external organic medium. This type of structure is a micelle. Alkoxide precursors can be trapped inside these micelles. Crystallization of TiO$_2$ under mild hydrothermal conditions occurs completely inside the micelle with the size of the resulting crystallite depending on the size of the micelle.$^{39}$

1.2.2 Cerium dioxide

Ceria is an important oxide due to its high refractory properties and use as a catalytic support in automotive exhaust. The methods for its direct synthesis by hydrothermal schemes strongly parallel those for titania. In general, aqueous solutions of
cerium nitrates or sulfates are exposed to high temperatures and pressures in an autoclave. One report demonstrates a near linear decrease in crystallite size with decreasing reaction temperature. From 240 to 150 °C, the average crystallite size decreases from 16 to 4 nm. The same paper also shows a size dependent concentration effect. The effect of added urea was studied as well and the results illustrate a reduction in average crystal size from 15 to approximately 10 nm.\textsuperscript{40} Reaction of aqueous cerium nitrate at 110 °C in the presence of polyethylene glycol results in the formation of nearly monodisperse crystallites. Citric acid as well as the microemulsion methods have also been used in the ceria system to effect size control.\textsuperscript{41,42}

1.2.3 Hematite and magnetite

One route for the formation of magnetite, Fe\textsubscript{3}O\textsubscript{4}, nanocrystals requires the use of a weak reducing agent, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, to generate Fe(III) and Fe(II) in a one to one ratio. The reaction solution is prepared by the slow addition of NaOH to an aqueous solution of iron sulfate and sodium thiosulfate. This produces black colloidal slurries that are then exposed to hydrothermal conditions in an autoclave. In the absence of the thiosulfate the reaction produces hematite, Fe\textsubscript{2}O\textsubscript{3}.\textsuperscript{43} A different route to the formation of magnetite cites the simple exposure of iron acetate to high temperature in an aqueous environment. The proposed mechanism suggests that molecular oxygen acts to incompletely oxidize Fe(II) to Fe(III) and corresponding iron hydroxide intermediates coalesce to form Fe\textsubscript{3}O\textsubscript{4}. In a concurrent reaction iron(II) hydroxide dehydrates to iron(II) oxide, which disproportionates to Fe and Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{44}
1.2.4 Zirconium dioxide

One method of zirconia synthesis first generates an intermediate solid zirconium sulfate by the hydrothermal treatment of zirconium sulfate solutions in the presence of urea.\textsuperscript{45} The pure zirconium dioxide is then generated by calcinations at high temperature. Another method precipitates amorphous hydrous zirconia from basic ZrCl\textsubscript{4} solutions and then subjects it to hydrothermal treatment in strong base conditions.\textsuperscript{46} Due to the basic conditions of this reaction, it is likely that the amorphous precursor is dissolved during the hydrothermal process and then reprecipitated in the crystalline phase. Consequently it is reasonable to consider this particular example a one step process. There are few other examples of direct hydrothermal synthesis of nanoscale zirconia. However, one example illustrates an apparent one step process by the use of ZrOCl\textsubscript{2}-H\textsubscript{2}O and ZrO(NO\textsubscript{3})\textsubscript{2}-H\textsubscript{2}O as starting materials.\textsuperscript{47} The precursors are dissolved in solutions of varying pH and ionic strength and treated for 2 h at 220 °C. The presence of bivalent metal ions favored the precipitation of the tetragonal (or cubic) phase over monoclinic. Monoclinic zirconia was formed in either strong base or strong acid conditions. In general the products appeared uniform and size and clearly nanocrystalline. A different report leverages solution pH and ionic strength to prevent the room temperature formation of Zr(OH)\textsubscript{4} and subjects the resulting solutions to hydrothermal treatments at 100 °C for 20 days.\textsuperscript{48} This example does not address the issue of particle size in the resulting powders.

1.3 Concluding remarks

As can be seen from the previous discussion, hydrothermal synthesis is an important technique in the formation of nanoscale oxides. In such reactions, control of temperature, pH, and concentration can generate conditions favoring the one step homogeneous
nucleation of nanocrystals from solutions. This type of chemical approach to crystal synthesis offers advantages over other routes and consistently provides uniform nanoscale products for a number of important materials applications. Thus, the extension of this general method to the silicon dioxide system is a logical step. Also apparent from the reaction strategies developed for nanoscale oxides is that no two systems require the same set of conditions. Overall, it is known that temperature, pH, and concentration affect the resulting product but to what extent depends on the specific system. However, it is clear from oxide syntheses in general that the versatility of the hydrothermal method in controlling these parameters is key in generating the desired product.

1.4 Bibliography


(25) Webster, T. J.; Ergun, C.; Doremus, R. H.; Siegel, R. W.; Bizios, R. Biomaterials 2000, 21, 1803.
(26) Webster, T. J.; Ergun, C.; Doremus, R. H.; Siegel, R. W.; Bizios, R. *Biomaterials* 2001, 22, 1327.


2 The Synthesis of Submicron and Nanoscale Quartz Particles

Two steps are required to form nanoscale quartz particles. First hydrothermal quartz precipitation is used to form polydisperse ultrafine quartz powders. Then, these powders are size selected into fractions, some of which exhibit nanoscale properties. This chapter outlines the steps involved in the first part of the method. While the initial product from the reaction reported here is not strictly nanoscale, it is among few reports on the synthesis of submicron scale quartz. The technique employed uses high surface area precursors dissolved in a strong base to establish high levels of soluble silica in the reaction solution. Evidence from X-ray diffraction data as well as electron microscopy clearly shows that the reaction proceeds by a dissolution re-precipitation mechanism. An argument will be presented which suggests the nucleation energy for quartz crystallites is unusually high. Combined with the rapid growth rate for quartz surfaces the nucleation of a monodisperse nanoscale population of crystals is not feasible.
2.1 Introduction

The study of nanometer-scale materials is a growing area of chemistry motivated by both the scientific and technological potential of these systems.\textsuperscript{1-4} Nanocrystalline solids often exhibit distinctive properties which can be exploited in new technologies,\textsuperscript{4,5} and systematic studies of how these properties evolve with the size of a nanocrystal can improve our understanding of bulk solids.\textsuperscript{6-8} The synthesis of high quality nanocrystalline materials is an important issue in this area. Of particular synthetic interest has been the generation of oxides of controlled grain sizes, which find application in areas such as sensors and ceramic processing.\textsuperscript{4,9-18} Despite this intense activity one of the most naturally abundant oxides, crystalline silica, has never been synthesized with nanometer sized domains.

Our interest in quartz is specifically motivated by its interesting phase behavior and relevance to a wide range of geological processes. Over 25% of the earth’s crust is made of silicon, predominantly in the form of quartz; geologists have studied the phase behavior of bulk quartz under high temperature and pressure for decades.\textsuperscript{19-22} A quartz material of controlled domain size offers the potential for evaluating how the phase diagram of this important mineral depends on crystallite size. In other nanocrystalline systems, studies of size-dependent phase properties have offered unique insights into the interplay between kinetic and thermodynamic control of crystal structure.\textsuperscript{23-25} Also because of the abundance of quartz in nature, its surface chemistry is central in rock erosion processes and soil chemistry.\textsuperscript{26,27} A high surface area nanomaterial could facilitate systematic and quantitative measurements of the behavior of the quartz surface.
Given the absence of any report on the control of quartz grain size, a primary goal of this work is to devise a strategy for the synthesis of sub-micron or nanometer-scale quartz. Hydrothermal methods have been successful at producing other nanocrystalline oxides such as TiO$_2$ and BaTiO$_2$\textsuperscript{14,25,28,29} and recent reports have highlighted hydrothermal synthesis of micron-scale quartz powders\textsuperscript{30,31} General schemes for producing small monodisperse crystallites attempt to create rapid nucleation events from supersaturated solutions followed by slow growth.\textsuperscript{32} Sodium hydroxide has been reported to accelerate nucleation rates in quartz.\textsuperscript{33-38} In addition, rapid dissolution rates of high surface area precursors are reported to generate finer powders in zeolite syntheses.\textsuperscript{39,40} In light of these factors, we aim to tailor existing hydrothermal synthesis strategies to the production of nanoscale quartz through the use of high surface area precursors under strong base conditions.

2.2 Experimental

2.2.1 Synthesis

Quartz powders were prepared by the use of amorphous silica at elevated temperature and pressure as outlined in Scheme 2.1. Except for the use of amorphous silica spheres (referred to as Stober silica), most of the reactions used fumed silica as the starting material (99.8%, 390 m$^2$/g, Sigma). When used, 500 nm silica spheres were prepared by the Stober method\textsuperscript{41} with 0.29 M tetraethoxy orthosilicate (99%, Alfa), 1.19 M NH$_4$OH (reagent grade, 29.4% Fisher), and 7 M ultra-pure water (Milli Q UVPlus, Millipore) in ethanol (200 proof USP grade, Pharma). In either case, 3.5 g of the dry precursor was added to 100 mL 0.1 M NaOH and ramped at 6°C/min to 200-300°C (the pressure at 300°C was 84 bar) in a Parr 4550 minireactor.
Solid precursors are measured into a separate container and the sodium hydroxide solution is carefully poured over the powder. (Care is taken to avoid creating plumes of the solid silica since it is very light and easily airborne. High surface area silica is known to become deposited in the lungs and can cause inflammation.) The resulting slurry is added to the vessel body (shown in Figure 2.1). The reactor is assembled and the heater is placed over the vessel body. The reaction temperature is then ramped, using a Parr 4843 programmable temperature controller providing ± 2°C accuracy, to the set point in 50 minutes. The sample is constantly stirred (Diagram 2.1A) throughout the reaction. A magnetic stir drive assembly that attaches at the top of the reactor rotates the stir rotor.

Scheme 2.1 The reaction conditions for hydrothermal synthesis of quartz. The reaction begins with fumed amorphous silica as seen in the scanning electron micrograph shown on the left.
Aliquots may be removed from the vessel using the sampling port (Diagram 2.1 C). When this is done, a beaker of ice water is placed around the sampling outlet ‘U’ (Diagram 2.1 F) so that the escaping sample condenses into the collection vial. When samples are collected in this fashion, the volume remaining in the reactor is changed and this is determined to have an effect on the remaining reactants. For this reason, a maximum of two 5-10 mL aliquots are taken from a single reaction. When 5-10 mL condense in the collecting vial, nearly twice that amount has escaped the vessel due to evaporation.

All reactions are kept at elevated temperature for 2 hours unless otherwise noted. To quench the reaction the temperature was reduced to less than 70°C in roughly 10-15 minutes by water circulation through the internal reactor cooling-loop (Diagram 2.1 E). The water quenching was automated using the temperature controller, which actuates a solenoid valve in the cooling line. This is programmed to happen after 2 hours at the soak temperature of 300 °C. In addition, a ‘wait-for’ step is programmed into the temperature profile. This allows for the specification that the two-hour soak period does not begin until the temperature inside the vessel reaches the specified 300 °C. Not shown in the diagram but essential to the performance of the reactor is a secondary cooling loop that protects a pair of o-rings in the neck of the magnetic stir drive assembly. It is important to keep the cooling water circulating through this loop whenever the reactor is running.
Figure 2.1. Parr minireactor. The head of the reactor is resting on a stand. The pipes below it include the sampling probe, stirrer, internal cooling loop and thermocouple as detailed in Diagram 1. Also visible on the left toward the back is the heater. Resting on the base of the stand is the vessel body which stands roughly 5 inches tall.
Diagram 2.1. Schematic of the Parr minireactor. This diagram shows A) the stirrer B) the magnetic stir drive assembly, C) the sampling pipe, D) the thermal probe, E) the internal cooling loop, F) the collection piping for the sampling port and G) the water inlet and outlet for the cooling loop. F is hollow copper piping bent into an ‘S’ shape so that the ‘U’ portion can be immersed in a beaker of ice water to allow condensation of sampled aliquots. The thermal probe is attached to a thermocouple that operates in a feedback loop for the precise specification of internal temperature.
2.2.2 Purification

Products were dialyzed in 3500-Dalton dialysis tubing (Spectra/Por 3, Spectrum Laboratories) in a 4 L beaker of ultra-pure water to remove unreacted soluble silica and excess base. The dialysis bath was changed 2-3 times daily. Initially, due to sample/bath pH equilibration, the pH of the bath increased from 5.8 (pH of ultra-pure water which is acidified by the activated carbon filter) to 10.5. The initial pH of the sample was 12. Consecutive bath changes resulted in lower values of the final pH. Once the bath pH fell below 8 (after 3-4 bath changes), baths and samples were titrated to pH 8 following bath changes. Samples were dialyzed until, upon reaction of molybdic acid with a sample of the bath water, no color change was observed.\textsuperscript{42,43} This required 8-10 bath changes. Baths were stirred constantly throughout the dialysis process.

The performance of different types of dialysis membranes was evaluated to better understand the relationship between their reported molecular weight cutoff (MWCO) values and their ability to filter a given size nanoscale particle. In addition this procedure evaluated a rough rate of dialysis in an effort to improve the efficiency of the procedure. In general, dialysis membranes are categorized according to the size of a biomolecule that will escape from them. The size of the pore is then "measured" as the molecular weight of the corresponding molecule that can escape. There is no direct correlation between MWCO and the size of a nanoparticle that will be passed. Figure 2.2 shows that higher MWCO membranes result in a slightly faster dialysis as expected. M1, M4 and M7 correspond to membranes with 6-8k, 12-14k and 3.5k cutoffs, respectively. The bath water from each of these different systems was evaluated by transmission electron microscopy to determine whether any small quartz particles had escaped. It was
determined that very few particles escape in the cases of M1 and M4 but no particles escaped for M7. Because of the relatively small increase in dialysis rate for the larger pore sizes, as shown in Figure 2.2, a 3500 Dalton MWCO membrane was always used. The particular type of membrane used was SpectraPor3 (Fisher Scientific). SpectraPor7 also comes in a 3500 Dalton membrane but it is pre-treated for the removal of heavy metals and this extra treatment is assumed to be unnecessary in the case of nanoquartz. SpectraPor3 is a dry membrane that should be washed thoroughly before use. Typically membranes were soaked for at least 30 minutes prior to use.

One set of experiments was done to investigate the effect of heating on the dialysis process. Mild heating shows a very favorable effect on the rate at which the silica concentration increases in the bath. However, due to the increased solubility of quartz at increased temperatures and the suspicion that this effect might be enhanced for smaller particles the method of heating was abandoned.

2.2.3 Methods

**Molybdic Acid Test.** Soluble silica concentrations were determined by reaction with molybdic acid, which is known to form a yellow complex with Si(OH)_4 monomer.\(^{42,43}\) 5 mL samples of either reaction product or dialysis bath water were acidified with 0.1 mL 6M HCl and combined with 0.2 mL molybdic acid. Color changes were evaluated either by eye (to evaluate the progress of dialysis) or by UV/Visible absorbance. Absorbance was measured at 410 nm (Ocean Optics ST2000) and standardized against curves generated from the absorbance of sodium silicate solutions prepared to specified concentrations. For the case of reaction products that were cloudy with dispersed solids, samples were centrifuged at 900 G for 10 minutes prior to testing.
Figure 2.2. Silica concentration in the dialysis bath with time. The product from the hydrothermal reaction was dialyzed using three different types of dialysis membrane, M1, M4 and M7; all made by Spectra Por (Fisher Scientific). Dialysis procedures require the repeated change of bath solutions. Concentrations were monitored for the initial (B1) and second baths (B2).
Pre-filtration. After dialysis the samples were first filtered over coarse filter paper (Whatman 541) and then over a glass-fiber pre-filter (Millipore AP15). The use of ceramic filters was evaluated and abandoned due to an apparent reaction of the filter with the strong base of the product. Subsequently it was determined that it was more effective to dialyze prior to filtration due to gelation of soluble silica during filtration. This eliminated the issue of filter dissolution because dialysis effectively reduces pH. However, because dialysis can bring the pH of the system down to that of water, and such low pH values can cause flocculation of silica\textsuperscript{43}, the pH was adjusted to 8 before filtration. Filter cakes were washed with ultra-pure water, which increased the sample volume roughly 50%. Up to 6 different samples were combined and concentrated 8× by rotary evaporation.

X-Ray Diffraction. Powder diffraction patterns were obtained on a Bruker AXS General Area Detection Diffraction System (GADDS, CuK\textsubscript{a}, 50 kV and 40 mA) at a sample-to-detector distance of 12.3 cm. The detector distance and 2θ spacing was calibrated (GADDS system software) using the d\textsubscript{111}, d\textsubscript{220} and d\textsubscript{311} reflections from silicon powder (325 mesh, Aldrich).

Microscopy. Transmission electron microscopy was performed on a JEOL JEM 2010 operating at 200kV. Samples were prepared by placing a drop of dilute water dispersion on a 300 mesh copper grid that was coated with approximately 8 nm of amorphous carbon (Electron Microscopy Sciences). The droplet was allowed to completely dry on the grid. Scanning electron microscopy was performed on a JEOL JSM 6500F. Samples were dried onto silicon wafers and sputter-coated for 15 seconds with Au.
Figure 2.3. Scanning electron microscopy of morphological change in two different types of silica precursor. Panels A and C correspond to the use of fumed silica in 0.1 M NaOH. Panel A shows the precursor prior to reaction and panel C shows the same sample after heating to 300 °C for approximately 60 minutes. Panels B and D are silica particles prepared by the Stober method. Panel B is the precursor prior to hydrothermal treatment and panel D is the same sample after approximately 60 minutes.
2.3 Results

The scanning electron micrograph shown in Figure 2.3 reveals a morphological change in the amorphous precursors after one hour under hydrothermal conditions. Panel A and C illustrate the dissolution and reformation of fumed silica upon hydrothermal treatment. The particles in panel C are likely to have formed upon cooling the reactor. Panels B and D exemplify the same effect for amorphous Stober particle precursors. Initially the precursor is comprised of compact, uniform and isolated spheres (C), which during temperature elevation under basic conditions, transform to web-like aggregates of distorted shape (D).

Concurrent with the morphological change of the solid precursor, the soluble silica concentration increases. This is demonstrated in Figure 2.4. Measurements of soluble silica were taken every ten minutes during the reaction of fumed silica with 0.1 M NaOH as the temperature was ramped to 300 °C. The concentration of dissolved silica was determined from the molybadic acid complexation technique as described in the previous section. The concentration apparently increases at a rate of approximately 0.1 mg/mL/min as the temperature is increasing. The peak Si(OH)₄ monomer concentration occurs at roughly 10 mg/mL after 70 minutes of reaction time. At this point the concentration suddenly drops. This is shown in Figure 2.4 with the vertical dashed line corresponding to a reduction in the amount of dissolved silica present in the reaction at 80 minutes. Figure 2.5 shows the concentration of dissolved silica over an extended time period. The reaction concentration drops off slowly until after approximately five hours the concentration is less than it was prior to heating. This corresponds to reaction completion at which point the yield is measured at nearly 95% quartz product.
Figure 2.4. Concentration of dissolved silica during the reaction of fumed silica. Concentration was determined from the absorbance of monomeric Si(OH)$_4$ complexed with molybdic acid. The error is 10% of [Si(OH)$_4$] as indicated by the bar on the last data point. A series of reactions using fumed silica as the precursor were subjected to 0.1 M NaOH and ramped to 300 °C. Aliquots were taken from the reactor every ten minutes and the dissolved silica content was measured.
Figure 2.5 Solubilized silica after initial induction period. Measurements were performed on three different aliquots from a sample of fumed silica subjected to 0.1 M NaOH. The time of zero on this graph corresponds to the point when quartz formation was apparent in the reaction. Error bars are estimated from the standard deviation of the three different samples.
The X-ray powder patterns of Figure 2.6 demonstrate the formation of \(\alpha\)-Quartz as the reaction evolves. These patterns are from reactions that begin normally and are stopped at the times indicated to their right in the figure. The products are dried directly and without further purification (dialysis or filtration). Samples are pipetted onto silicon wafers and then dried in a vacuum oven overnight. The powders are then collected and mounted for x-ray analysis using Collodion glue (Electron Microscopy Sciences). Evidence for quartz precipitation appears as a small peak, at 26.56 \(^{\circ}\)2\(\theta\), in the pattern taken after 75 minutes. Although the peak height is small for this reflection, the peak width can be measured and from it an average grain size is calculated as 31 nm using the Scherrer equation.\(^{44}\) The background, due to scattering from the glue, is subtracted before measuring the peak width. An additional 10 minutes of reaction produces powders that generate strong quartz patterns. At this point the diffraction peaks are narrowed to the instrumental resolution limit.
Figure 2.6. Reaction Evolution. SiO\textsubscript{2} phase evolution by x-ray diffraction (XRD) of samples quenched at different reaction times. The time of sampling is listed in minutes at the right of each pattern. Reflections marked by diamonds can all be indexed to \(\alpha\)-quartz. No \(\alpha\)-quartz reflections are absent. Reaction was performed using amorphous fumed silica in 0.1 M NaOH at 300 °C.
Figure 2.7 shows the evolution of pH throughout the reaction. The initial pH of the sample is approximately 10.3. After quartz precipitates the pH increases due to the reduction of silicic acid concentration in solution. This has a weak effect on pH due to the relatively weak dissociation constant of silicic acid. At times of 200 to 300 minutes, the pH is approximately 10.7, which is close to what is expected in 0.1 M NaOH.

In Figure 2.8, which shows reactions prepared from Stober particles, soluble silica concentrations do not drop until after 90 minutes of reaction time. The increased time associated with the Stober silica reaction is assumed to be due to the increased density and lower surface area of the Stober particles.
Figure 2.7. pH evolution with time during reaction of fumed silica. The pH was measured using an Accumet pH meter.
Figure 2.8. The evolution of soluble silica for reaction of Stober particles. Concentration was determined from the absorbance of monomeric Si(OH)$_4$ complexed with molybdic acid. A series of reactions using amorphous Stober particles as the precursor were subjected to 0.1 M NaOH and ramped to 300 °C. Aliquots were taken from the reactor at roughly ten minute intervals and the dissolved silica content was immediately measured.
Table 1 presents data for different reaction conditions and the resulting phase produced. The phases of the products were measured by x-ray powder diffraction. Reactants are introduced into the reactor and ramped to the specified temperature. With one exception, the time periods specified correspond to the initial point at which an identifiable crystalline phase is present. The exception is the last reaction listed where no crystalline product is observed after 12 hours. Both fumed silica and amorphous Stöber particles can be used as precursors in the formation of quartz. Quartz precipitation occurs after time periods of five hours or less when the reaction temperature is above 250 °C and the concentration of NaOH is 0.1 M.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>M NaOH</th>
<th>T (°C)</th>
<th>Time</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.1</td>
<td>300</td>
<td>1 hr 20’</td>
<td>s\textsuperscript{b}Q\textsuperscript{c}</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
<td>250</td>
<td>5 hr</td>
<td>w\textsuperscript{d}Q</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
<td>200</td>
<td>40 hr</td>
<td>C\textsuperscript{e}, wQ</td>
</tr>
<tr>
<td>S\textsuperscript{f}</td>
<td>0.1</td>
<td>300</td>
<td>1 hr 30’</td>
<td>sQ</td>
</tr>
<tr>
<td>F-ethanol</td>
<td>-</td>
<td>200</td>
<td>12 hr</td>
<td>amorph.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} fumed silica, \textsuperscript{b} strong, \textsuperscript{c} quartz, \textsuperscript{d} weak, \textsuperscript{e} cristobalite, \textsuperscript{f} Stöber silica
Figure 2.9. Scanning electron micrograph (SEM) of quartz product. The reaction conditions are 3.5 g fumed silica for 2hr at 300° C in 100 mL 0.1M NaOH. Panels (A) and (B) are different regions of the same sample.
The morphology of the reaction product, after 2 hours at 300 °C, is illustrated in Figure 2.6. Both panels are scanning electron micrographs of the same sample that are taken at different magnifications and in different locations. Panel A illustrates the broad size distribution and the general morphology in a sample that has already been filtered over coarse filter paper. The faceted shape of the mid-sized crystallites and the presence of many small particles are apparent in panel B. In Figure 2.7A, a transmission electron micrograph supports the observation of a broad size distribution and the presence of nanometer scale solid particles. Selected Area Electron Diffraction (SAED) (2.7B) shows spots from single crystal diffraction as well as faint rings from powder diffraction that can be indexed to the expected reflections for quartz (as indicated in the figure). The SAED pattern in 2.7B was taken from a similar but more heavily loaded area compared to the region shown in 2.7A.

Figure 2.8 is an example of early work in the production of nanoscale quartz. The image shown is from a small region of a sample that actually exhibited a larger size distribution. The image clearly shows isolated small particles of quartz product. This data served as proof that in principle, nanoquartz size selection should be possible. The particular sample shown was subjected to filtration over a 0.1 μm filter.
Figure 2.10. Transmission electron microscopy of hydrothermal quartz. (A) TEM of the unfiltered product. (B) Selected area electron diffraction (SAED) pattern for the same type of sample. The rings indicated match to known quartz reflections. The reaction conditions are 3.5 g fumed silica for 2hr at 300 °C in 100 mL 0.1M NaOH.
Figure 2.11. TEM of a fraction of small particles from a sample prepared identically to Figure 6A after it had also been filtered through a 0.025 μm cellulose filter and further concentrated.
2.4 Discussion

2.4.1 Quartz Formation Proceeds by a Dissolution/Reprecipitation Mechanism.

Mechanistic data suggests that this reaction proceeds by the dissolution of the amorphous precursor followed by the reprecipitation of silica in its crystalline quartz form. Figures 2.3 through 2.8 clearly illustrate this process. Figure 2.3 shows a morphological change in the reactant during the initial time period of 0-75 min. This is evidence that the precursor is in fact being dissolved. Figures 2.4 through 2.6 support this argument showing a concurrent increase in the concentration of dissolved silica during the same period of reaction time. Also evident in Figures 2.4 and 2.8 are drops in the concentration of dissolved silica after 80-100 minutes of reaction time. This reduction corresponds to the same time at which quartz appears in the x-ray diffraction data (Figure 2.6). Thus the reduction in dissolved silica can be attributed to the precipitation of quartz. The proposed mechanism for reaction is thus:

\[
\begin{align*}
\text{SiO}_2\text{(precursor)} + \text{H}_2\text{O} & \rightarrow \text{Si(OH)}_4 + \text{SiO}_x\text{H}_y \\
\text{Si(OH)}_4 + \text{SiO}_x\text{H}_y & \rightarrow \text{Si}_x\text{O}_y\text{H}_z + \text{H}_2\text{O} \\
\text{Si}_x\text{O}_y\text{H}_z + \text{H}_2\text{O} & \rightarrow \text{SiO}_2\text{(quartz)} + \text{H}_2\text{O}
\end{align*}
\]

[2.1]

There is an apparent difference in reaction evolution between the fumed silica precursor and Stober silica precursor. When the evolution of soluble silica in the fumed silica reaction (Figure 2.4) is compared to the evolution in the Stober silica reaction (Figure 2.8), it is clear that the peak SiO_2(aq) concentration and consequently the precipitation event are both shifted to longer times. This is explained by the difference in precursor morphology. The lower surface area and higher density of Stober particles
compared to fumed silica makes Stober particles more resistant to dissolution. This results in an incomplete dissolution after one hour for Stober while the fumed silica has clearly dissolved completely and then reprecipitated as solid spheres upon quenching (Figure 2.3). Additionally the different dissolution rate produces a delay in the reduction of silica concentration.

If a different mechanism were involved wherein the precursor did not dissolve and reprecipitate the silica concentration would not change. Moreover, there would be no explanation for a change in silica concentration to accompany the appearance of quartz reflections in the x-ray patterns. The difference between the Stober and fumed silica precursor behavior further supports the argument for a dissolution/reprecipitation mechanism. Since both amorphous precursors exhibit a random network of silica tetrahedral, there would be no conformational barrier different between them that would encourage one to behave differently from the other in any type of solid-solid transformation process. Finally the pH increase that occurs at the same time quartz precipitates also supports the idea of a dissolution/precipitation mechanism.

2.4.2 The Nucleation and Growth of Quartz

Among other hydrothermally prepared nano-oxides, nanoquartz synthesis is unique. A number of other nanoscale oxides have been made via hydrothermal routes under similar conditions to these. Contrasting quartz to these systems underlines important factors that direct the formation of nuclei in the quartz system. These factors include the high surface energy, low density and fast growth rate of quartz as well as multi-phase stability in the silica system. Together such factors ultimately result in a higher barrier to nucleation, broader size distribution and constrained control of reaction
parameters in quartz synthesis. What follows is an analysis of how these issues impact the problem of nucleating quartz.

Nucleation of quartz is costly due to its high molecular volume and high surface energy. According to the cluster approach to nucleation theory, nucleation energy is essentially the amount of PV work associated with the density fluctuation that irreversibly generates a stable nucleus. It can be shown that this value is proportional to both the molecular volume and surface energy of the nucleating species. The free energy of a system after a nucleation event is defined as the energy of the system before, plus the amount of work required in forming the stable nucleus, \( G_2(n^*) = G_1 + W^* \) (\( n^* \) is the number of molecules involved in the irreversible formation of a stable nucleus). The nucleation work (assuming homogeneous nucleation and spherical nuclei) can be described by

\[
W^* = -n^* \Delta \mu + G_{ex}(n^*)
\]

where \( \Delta \mu \) is the change in chemical potential required for the transformation (in this case liquid to solid) and \( G_{ex}(n^*) \) is the nucleus excess energy. In the case of phase equilibrium, the chemical potentials of the old and new phases are defined as equal. The case where the chemical potential of the new phase exceeds that of the old, \( \Delta \mu > 0 \), is referred to as supersaturation. Supersaturation can be related (in sufficiently dilute solutions) to concentrations in excess of the equilibrium solubility by the following:

\[
\Delta \mu = kT \ln \left( \frac{c}{c_{eq}} \right).
\]

Here, \( c \) is the concentration at which nucleation occurs while \( c_{eq} \) is the equilibrium concentration or solubility. Thus, the excess solubility of silica in our reactions is a
measure of excess chemical potential, or supersaturation, which in turn is an indication of the level of excess Gibbs energy associated with nucleation. $G_{\text{ex}}(n^*)$ (for condensed phases) can be approximated as

$$G_{\alpha}(n^*) = c\sigma_n V_n^{2/3},$$

where $c$ is a factor associated with the shape of the nucleus, $\sigma_n$ is the specific surface free energy of the nucleus/liquid interface, and $V_n$ is the molecular volume.\(^{45}\) One reason for high $G_{\text{ex}}$ immediately becomes clear: quartz has quite a low density—high molecular volume—in contrast with other materials, particularly those oxides that have been prepared by nanoscale synthesis strategies. While the density of $\alpha$-quartz is 2.635-2.660 g/cm\(^3\), the densities of anatase and rutile titania, cubic zirconia, cubic ceria, hexagonal barium titanate, and $\alpha$-alumina are 3.840-, 4.260-, 5.600-, 7.132-, 5.806-, and 3.970-g/cm\(^3\) respectively. In addition, the surface energy of quartz is high. While measurements of this value disagree (335-385 mJ/m\(^2\), 57 mJ/m\(^2\)),\(^{46,47}\) some of the discrepancy could be due to measurement techniques. However, in comparison to rutile- and anatase-TiO\(_2\), the quartz surface is of considerably higher energy (1.91 mJ m\(^{-2}\) for rutile and 1.32 mJ m\(^{-2}\) for anatase\(^{25}\)). Hence, low molecular volume and high surface energy is a reasonable explanation for the origin of energetically expensive nucleation.

Further evidence for the high nucleation energy of quartz is the excess solubility of silica as shown in Figure 2. This is because, for dilute solutions, excess concentration is proportional to the difference in chemical potential (supersaturation) between the solid and liquid phases, which acts to offset the work required for nucleation. While the equilibrium solubility of quartz at 300 °C is roughly 1-mg/mL\(^{43}\), these data show that
monomeric silica concentrations reach a value of 10-mg/mL before quartz forms. This excess saturation illustrates that considerable chemical potential is required to offset the energy consumed by work.

In addition to having high nucleation energy, quartz exhibits a faster growth rate than other oxides. It is not clear what the mechanism for growth is or why the growth rate for quartz is high. Regardless, reports have shown its value to be large even at equilibrium solubility. One report cites the growth rate for a large single crystal of quartz (in approximately 1.3 mg/mL aqueous silica, 263 °C) as 0.74 mm/day or 500 nm/min.\textsuperscript{48} This value is comparable to the initial growth seen in the method we report where individual particles grow to sizes of 500 nm in roughly five minutes. In contrast, growth rates for hydrothermally synthesized, monodisperse TiO\textsubscript{2} particles are approximately 1 Å/hr.\textsuperscript{49} It is important to note that growth rates for single crystals can be quite different from the rates for powders due to the absence of additional nuclei that compete for feed material. In any case, the growth rate observed in this method generates crystallites of relatively large sizes within minutes of nucleation. Figure 3 illustrates the problem. The diffraction pattern of the product after 75 minutes shows the early formation of quartz particles. While the peak is slightly broadened, it also rides on the background of a large amorphous silica component. The nanocrystal yield at this point would be exceedingly low. Five minutes later, the pattern is more crystalline but the grain size has increased considerably. In fact, the peaks are narrowed to the instrumental resolution limit of the diffractometer. There is no discernible difference in the pattern taken after 85 minutes compared to the one after 2 hours.
In this system, there is further evidence to show that the properties of quartz make control over the reaction problematic. For example, it can be argued that size control is sacrificed for phase purity. This is because there are many accessible forms of silica and silicates within a small energy window and the energy of the amorphous phase of silica is very close to that of quartz. In the case of TiO₂ and ZrO₂, size control is achieved by the manipulation of parameters such as temperature and concentration. In our case, when conditions are varied to acquire size control, phase purity is lost. For example, a study on the effect of temperature in the formation of TiO₂ revealed a clear crystallite size dependence. If temperature is used to attempt size control with quartz, a number of other phases can be formed. The data of table 1 show that certain reaction conditions favor quartz formation. 300 °C, corresponding to a pressure of 84 bar, appears to be the best temperature. Lower temperatures require more time before nucleation and generate considerable amorphous product. Still lower temperatures will enable the formation of cristobalite.

Another study reports size control (at 200 °C in several hours) by the manipulation of precursor concentration. While the control of SiO₂ concentration is not systematically assessed here, preliminary reactions were run to consider its effect. Results at low concentration, ~0.1-1.0% SiO₂, showed the presence of unidentifiable phases (perhaps silicates), presumably due to high Na⁺:SiO₂ ratios since sodium is known to facilitate silicate formation. Higher concentrations, 5-7%, generated larger particles and cristobalite/quartz/amorphous silica mixtures. The effect of pH was only minimally considered by the reduction in NaOH concentration. Amorphous products were obtained in these conditions, which is reasonably explained as insufficient supersaturation. In the
end, we adopt reaction conditions that lead to phase purity while simultaneously minimizing growth. The sacrifice is monodispersity.

2.5 Conclusions

The results of this work demonstrate that hydrothermal synthesis is a useful route for the production of ultrafine quartz powder containing crystallites from one to hundreds of nanometers in size. Amorphous fumed silica as well as Stoer silica is shown to dissolve under hydrothermal conditions in the presence of a strong base. At the appropriate level of supersaturation, quartz particles precipitate. The reaction yield is roughly 95% when the reaction is run to completion (~ 5 hr). X-ray diffraction clearly assigns the phase of the product to alpha-quartz illustrating that the material is phase-pure. Elemental analysis shows only trace amounts of metal contamination in the product. Quartz nucleation occurs at reaction times sufficient to allow the concentration of dissolving precursor to reach 10 mg/mL. This occurs after 80 minutes when the reaction conditions are 300 ºC, 84 bar, 3.5 wt-% fumed silica precursor, and 0.1 M NaOH. The same conditions simultaneously favor rapid growth resulting in sub-micron sized particles five minutes after nucleation.

This is apparently the first work to produce ultrafine α-quartz powder containing a nanoscale component less than 80 nm in size.52 It is useful to acknowledge that, though the goal of this investigation was production of nanoscale samples, this synthesis is one of few to report on quartz powders in the sub-micron length scale.30,31

2.6 Bibliography


(34) Fyfe, W. S.; McKay, D. S. Amer. Miner. 1962, 47, 83.


(41) Stoiber, W.; Fink, A.; Bohn, E. J. Colloid and Int. Sci. 1968, 26, 62.


3 Size selection and characterization of nanoquartz

This chapter details the techniques and important parameters involved in the size selection of four different size regimes of quartz crystallites. Due to the high nucleation energy associated with the formation of quartz nuclei as well as their rapid growth rates, the formation of a population of monodisperse nanoparticles is not achieved by direct manipulation of synthesis parameters. Instead, the method employed relies on product filtration and centrifugation to generate four different sized fractions of nanocrystals with three out of the four showing significant nanometer scale character.

Also addressed in this chapter will be the evident lattice expansion of quartz nanocrystals relative to their bulk analogues. Synchrotron x-ray diffraction was performed on all but the smallest size selected fractions. Two of the studied fractions show clear size dependent lattice expansions. The amount of lattice expansion is roughly 2.5% of the bulk value for particles with an average diameter of 37 nm.
3.1 Introduction

Due to the amount of useful information that can be obtained from size dependent studies of nanocrystals (see the introduction to Chapter I), we subject our quartz product to size selective post-synthesis processing. The method of hydrothermal treatment of amorphous silica, as detailed in the previous chapter, generates quartz crystallites that range in size from one to several hundreds of nanometers within minutes of nucleation. Such products are not ideal for the study of limited-size properties since they bridge the behavior of both bulk and nano systems. However, in the case of ultrafine quartz powder from hydrothermal synthesis, the product is amenable to size selection techniques once purified by dialysis. As discussed in Chapter 2, dialysis removes the solubilized silica from the reaction product mixture, which is essential to prevent agglomeration during size selective treatments. Once dialysis has been performed we then resort to size selection of the nanoscale component.

In an attempt to select out different size regimes with improved size distributions, we employ a combined strategy of vacuum filtration and centrifugation. Filtration includes several steps using different sized porosity filter papers as well as careful control over solution pH. Centrifugation can then be used to successfully reduce the size and size distribution of the resulting product. Four different fractions with sizes of 440-, 87-, 37- and 18 nm have been prepared. In addition, size distributions improve as particle sizes decrease, reaching 28% in the smallest fraction.

X-ray diffraction and line broadening analysis of the resulting products shows an unexpected size dependent lattice expansion. Electron microscopy of the product after dialysis and size selection clearly shows isolated crystallites in the nanometer size
regime. When these samples are studied by x-ray diffraction, the resulting unit cell volume is increased. In the case of the smallest sized fraction this expansion is roughly 2.5%. Background information concerning lattice expansion in small particles is discussed in detail in Chapter 1.2.2. However, many of the known mechanisms for lattice expansion are not clearly relevant to the case of nanoquartz. A thermodynamic argument based on the competition between surface tension and surface stress is a more likely explanation.

3.2 Experimental

Final size selection. Samples were filtered over a smaller pore size (1.2 or 0.2 \( \mu \m\)) nylon filter (Osmonics). Size selection of the smallest fractions reported was achieved by centrifugation (Marathon 22k, Fisher). Centrifuge times varied for different samples and are noted in the text and figure captions. The smallest sized fractions (fraction 3 in Figure 9 as well as others) were always taken from the supernatant of a centrifuged dispersion.

X-ray diffraction. The powder diffraction patterns in Figure 3 were obtained on a Bruker-AXS General Area Detection Diffraction System (GADDS, CuK\(_\alpha\), 50 kV and 40 mA) at a sample-to-detector distance of 12.3 cm. The detector distance and 2\( \theta \) spacing was calibrated (GADDS system software) using the \( d_{111} \), \( d_{220} \) and \( d_{311} \) reflections from silicon powder (325 mesh, Aldrich). Broadening of the quartz \( d_{101} \) peak-width was calibrated against the width of the silicon \( d_{111} \) reflection. Reflections shown in Figure 10 were obtained using 14-keV synchrotron radiation at the Advanced Light Source (Beamline 7.3.3, Lawrence Berkeley Laboratories, Berkeley CA). An X-ray CCD detector was used. Spatial distortion and sample-to-detector distance was calibrated
(FIT2D two-dimensional data analysis program\textsuperscript{1-3}) using the $d_{012}$, $d_{104}$, $d_{110}$, $d_{113}$, $d_{024}$, and $d_{113}$ reflections from an alumina standard (NIST SRM-676). Instrumental line broadening was calibrated using the $d_{100}$ reflection from LaB$_6$ (Sigma, $<10\mu$m). Peak widths were measured by least squares refinement of Voigt fits (Peak Fit v4, Jandel Scientific Software). Grain sizing was done by the Scherrer method\textsuperscript{4} according to:

\begin{equation}
 t = \frac{0.9\lambda}{B \cos \theta_n} .
\end{equation}

$t$ is the crystallite size in angstroms, $\lambda$ is the x-ray wavelength, $B$ is the Full Width at Half Maximum (FWHM) and $\theta_n$ is the peak position. For Debye-Sherrer powder diffraction, $B$ can be taken as the difference of the observed peak width and the peak width of a standard whose average grain size is well beyond 1000 Å (LaB$_6$, above$^4$).

**Energy dispersive x-ray analysis (EDX).** EDX was performed on a Philips XL30 Environmental Scanning Electron Microscope equipped with an EDAX ES3030 detector. Samples were embedded in Eponate-12 resin (Ted Pella) and polished using a Leica UCT Ultramicrotome. They were then mounted onto aluminum holders (Electron Microscopy Sciences) and sputter-coated for 15 seconds with Au.

### 3.3 Results

#### 3.3.1 Size selection

Figures 3.1 and 3.2 exemplify the change in sample polydispersity due to size selection. Both of the transmission electron micrographs in Figure 3.1 are of a sample that has been dialyzed, pre-filtered, concentrated and filtered over a 0.2-μm Nylon
membrane. The difference in the two micrographs is that 3.1B is the pellet while 3.1A is the supernatant from an 8-minute centrifugation at 3313 G. The morphology of the particles imaged in 3.1A, is identical to that of the small particles present in 3.1B; however in 3.1A, most of the large particles (>50 nm) and all of the aggregates are absent. Figure 3.2 shows additional TEM data for a sample treated similarly to the one in Figure 3.1. It is the supernatant after 20 minutes of centrifugation at 3313 G.

Particle sizing by transmission electron microscopy (TEM) illustrates that size selection methods provide four different fractions of submicron to nanoscale α-quartz. Histograms of these fractions are included in Figure 3.3. The average particle size of each fraction was generated from measurements of the long axis of over 150 particles. The resulting sizes are, fraction 1 - 440 nm, fraction 2 – 84 nm, fraction 3 – 37 nm, and fraction 4 - 18 nm, with size distributions of 52-, 110-, 120-, and 28-% respectively.

Samples were dried for synchrotron powder XRD and the resulting reflections exhibit line broadening. The linewdths for the (100) and (101) reflections of quartz are broadened considerably (Figure 5) in the smaller samples, to 0.18 and 0.20 degrees respectively, as compared to the larger fractions in which peaks are narrowed to the instrumental resolution limit of 0.08 degrees measured using LaB₆ (NIST standard). Scherrer analysis of the d₁₀₀ peaks finds a grain size of 28 nm for fraction 3. The reasonably good agreement between this grain size, and the statistical particle size (37 nm) determined by TEM shown in figure 3.3, is evidence that these small particles are nanoscale quartz crystallites. Additionally, the agreement between the TEM and XRD grain size determinations suggests that particle particle defects and grain boundaries are not extensive in these materials. X-ray diffraction was not obtained on Fraction 4
because it was not available at the time synchrotron diffraction was obtained from the other samples and it is of insufficient yield to diffract on the available conventional X-ray systems. Fraction 3, and presumably Fraction 4, exhibits elemental impurities of 0.1 at.-% Ti, 0.08 at.-% Fe, 0.36 at.-% Ni and 0.13 at.-% Cu as determined by energy dispersive x-ray analysis.
Figure 3.1. Size selection of quartz crystallites. (A) Fraction 4—the supernatant from a sample after it was dialyzed, pre-filtered, concentrated, filtered over a 0.2-μm Nylon membrane and centrifuged for 8 minutes at 3313 G. (B) Transmission electron micrograph (TEM) of the re-dispersed pellet from the sample in panel A. Reaction conditions are fumed silica in 0.1 M NaOH for 2 hours at 300 °C.
Figure 3.2. Transmission electron microscopy of nanoquartz.
Figure 3.3. Sizing by TEM. Measurements were taken on the longest axis of at least 150 isolated particles. (A) Fraction 1 (retained from glass fiber pre-filter) has an average size of 440 ± 228 nm. (B) Fraction 2 (filtered through 1.2 μm Nylon paper, pellet after 20 minutes at 3313 G) has an average size of 84 nm and a size distribution from 1 to 175 nm. (C) Fraction 3 (filtered through 1.2 μm Nylon paper, supernatant after 2 minutes at 3313 G) has an average size of 37 nm and a distribution from 1 to 83 nm. (D) Fraction 4 (the same sample as figure 3B; filtered through 0.2 μm Nylon paper, supernatant after 8 minutes at 3313 G) has an average size of 18 nm ± 5 nm. Reaction conditions were identical to Figure 3.1. All samples were dialyzed, concentrated and coarse paper filtered. Fractions 2-4 were also filtered over a glass fiber pre-filter prior to further filtration as above.
Figure 3.4. Sizing by XRD. (A) $d_{101}$ peaks of the first three fractions shown in Figure 9. (B) $d_{100}$ peaks of the same fractions. $\bigcirc$ – fraction 1, $\bigtriangleup$ – fraction 2, $\blacklozenge$ – fraction 3. Both $d_{101}$ and $d_{100}$ for fractions 1 and 2 are limited in peak width by the instrumental resolution. Scherrer analysis of fraction 3, $d_{100}$ peak width gives a grain size of 28 nm while the $d_{101}$ peak gives a grain size of 25 nm.⁵
3.3.2 Characterization

In order to verify small particles imaged in TEM were indeed α-quartz we performed small area electron diffraction (SAED). The SAED of these materials provide rings, rather than spots, as expected for nanocrystalline samples; additionally, four quartz reflections were matched in the data (Figure 3C). High resolution TEM images of nanocrystals can be found Figure 3.6; they were less informative than the SAED in confirming the presence of quartz. Quartz has poor contrast in TEM due to its low electron density. Additionally, it is very sensitive to beam damage in electron microscopes, forming silicon quite readily.\textsuperscript{6-8} We found that the spacing of the lattice fringes in high resolution images matched equally well to silicon as they did to quartz. We also found a weak reflection in the SAED that indexed to the Si 100 planes, but no evidence of silicon in x-ray diffraction data.
Figure 3.5 Selected Area Electron Diffraction (SAED) of nanoquartz. The indicated reflections match to those of alpha-quartz. The sample was prepared in reaction conditions identical to those of Figure 3.1.
Figure 3.6. High resolution transmission electron microscopy of nanoquartz. These images are from a nanoquartz sample prepared identically to fraction 4.
Synchrotron x-ray diffraction reveals a change in the lattice parameter of nanoquartz. The increase in unit cell volume for quartz nanocrystals with an average size of 37 nm is roughly 2.5% of the bulk value. Figure 3.7 shows unit cell volume at a given pressure, relative to the volume of the bulk sample (fraction 1--440 nm) at that same pressure. These data were obtained while performing high-pressure experiments and so multiple data points for the same sample are shown at different pressures. For this figure, the data for fraction 3 is always experimental. Some of the data points of fractions 1 and 2 are interpolated using the corresponding Birch-Murnaghan fit (this fit will be discussed in detail in Chapter 4) because data is not available at the exact same pressures as it is for fraction 3. However points are chosen so as to maximize the total number of shown experimental data.
Figure 3.7. Unit cell volume expansion in nanoquartz. This figure shows the size dependence of the unit cell volume in percent expansion calculated relative to the bulk volume at the same pressure. 37 nm quartz particles exhibit roughly a 2.5 % lattice expansion at ambient as well as elevated pressures (pressure experiments will be addressed in the next chapter).
3.4 Discussion

3.4.1 Key parameters during dialysis and filtration

Before the actual size selection step, it is important to dialyze the product. This is for two reasons. First, dried or drying silicic acid forms gels that clog filter papers and obscure sample characterization. In samples that are not dialyzed, microscopy reveals regions with characteristic sol-gel morphology as well as areas of quartz crystals enclosed within uniform amorphous solid (not shown). Second, the room temperature solubility of amorphous and crystalline silica increases with pH and the surface area of the dissolving species. If the pH of the sample is not lowered, then removal of excess amorphous silica is ineffective. More will form by dissolution. This could potentially result in consumption of the crystalline nanoscale fraction. Dialysis is the preferred method for reducing sample pH because neutralization with acid increases ionic strength, which increases silica dissolution, as well as coagulation.\(^9\)

During this dialysis procedure, as well as during filtration, it is important to maintain a slightly basic pH. This is because coagulation is observed when the sample becomes too acidic, pH < 6. According to the literature, the amorphous silica surface bears insufficient negative charge at values less than pH 6 to allow the stable dispersion of small silica colloids.\(^10\) If the crystalline surface behaves similarly to the amorphous one—an arguably good approximation—this is likely to be the reason for our observations on the aggregation of quartz colloids. Although the stability of silica sols is reported to increase from pH 6 up to pH 10.5, increased solubility due to alkalinity turns on around pH 8.\(^9\)
To achieve better size distributions in the smallest fractions, centrifugation as well as filtration should be performed. Filtration alone is insufficient to produce reasonable size distributions because filter membranes do not provide strict cut-offs in size. Our results show that particles larger than the given physical pore-sizes permeate the filter as well (Figure 6B). Furthermore, filters with very small pore-sizes (0.025 μm, Millipore) tend to become clogged during filtration, which makes cake re-dispersal ineffective. Centrifugation alone is prohibitive because the largest particles create vortexes, which trap and carry down the smallest particles, as they sediment. Although the yield from this method is low, 0.1-1.0%, the result is a dramatically improved size distribution.

Yield and size distribution could be improved by modifications to the synthesis or size selection method. We suggest that the given yield is a lower bound, due to the presence small particles in the larger-sized fractions as seen in Figure 6A. This yield is likely to improved if the samples could be surface stabilized to aggregation prior to filtration. There are a number of other possibilities that could lead to further improvement on the selectivity of this method. Colloidal silica has been shown to exhibit solute dependent coagulation. If this behavior could be reproduced in quartz, our system would become amenable to size selective precipitation schemes used in other nanoscale systems. Furthermore, literature on the formation of zeolite colloids suggests that the OH'/SiO₂ ratio is a key factor in ZSM-5 colloid size control. The argument is that the presence of excess OH' enhances redissolution and impairs larger grain growth. Further addition of base could be useful in our method but concern remains over formation of silicate phases due to high Na⁺ content (assuming the OH- source comes from NaOH—perhaps a different, less silica-stabilizing, base would work).
3.4.2 Lattice distortion in nanocrystals

Characterization of the size selected nanoscale product reveals an unexpected expansion or decrease in density relative to the bulk quartz phase. The unit cell volume in nanoquartz is approximately 2.5% greater than the bulk value. This is a significant amount considering other nanocrystals that exhibit lattice expansions do so to comparable extents at much smaller sizes (see section 1.2.2). Pressure extrapolation of the bulk data to a unit cell volume of 115.5 Å³ (the ambient value for fraction 3), estimates an effective pressure of -0.7 GPa. It is useful to consider why a reduction in particle size might cause such a dramatic change in unit cell volume.

A number of examples of nanocrystals and nanocrystalline materials have been reported to show volume expansion but for reasons which are probably not pertinent to the case of nanoquartz. BaTiO₃ is reported to exhibit a 2.5 % lattice expansion for particles 15 nm in size.¹³ In a later report this was shown to be related to the increased ionic character of the Ti-O bonds, which subsequently leads to an increased Ba-Ti bond length.¹³ Increased ionic character is an unlikely factor in quartz due to the strong covalent energy associated with the Si-O bond. The covalent character of a typical perovskite is less than half that of quartz.¹⁴ Alternatively, the same report attributes the lattice expansion of ceria nanoparticles to the mixed oxidation state of Ce—again an unlikely explanation for quartz behavior since Si is not multivalent. Several reports cite strain related to grain boundaries as a cause of lattice expansion.¹⁵,¹⁶ However, agreement between XRD sizing and TEM data suggests that grain boundaries are rare in the quartz samples reported on here. Finally lattice expansion in nanocrystalline samples has been attributed to a supersaturation of vacancies in the lattice.¹⁷ This explanation
seems unlikely in light of the chemical method of preparation in which molecular units of silicic acid, Si(OH)$_4$, condense in a supersaturated aqueous solution.

Analysis of the thermodynamics involved in the formation of surfaces offers a possible explanation for the lattice expansion exhibited by quartz nanocrystals. Solliard and Flueli suggest that surface atoms will be in a state of dilation or compression depending on whether surface stress, $\sigma$, is greater or less than surface tension, $\gamma$ (not the surface free energy).$^{18}$ In these arguments, stress is the amount of work required to create a new unit of surface area by stretching and tension is the amount of work required to create a new unit of surface area by cleavage.$^{19,20}$ Their experiments showed that gold and platinum nanoparticles have higher surface stress coefficients than surface tensions. This is interpreted as surface dilation which depletes the internal density and incites a lattice contraction. By this logic, the observed lattice expansion in quartz might be explained by a decreased surface stress relative to surface tension. Given the relatively flexible structure of quartz and silica in general, as well as the strong covalent character of the quartz lattice, it seems plausible that the work of tension would outweigh stress. However more detailed experiments, including careful analysis to disprove issues such as vacancies, are required to settle this issue.

3.5 Conclusions

Size selective treatments make it possible to extract lower size distribution nanoscale components from polydisperse ultrafine quartz powders that are generated from hydrothermal synthesis strategies. The combined use of centrifugation and filtration produces three different nanoscale components with average sizes less than 100 nm in
diameter. In addition the size distribution of certain fractions can be reduced to less than 30%. In the case of quartz, the resulting materials exhibit size dependent properties. In particular, synchrotron x-ray diffraction shows a 2.5% lattice expansion for particles with an average size of 37 nm.

3.6 Bibliography


4 High Pressure Behavior of Quartz Nanocrystals

This chapter discusses the behavior of hydrothermal nanoquartz under high pressures inside a diamond-anvil cell (DAC). Three different samples were obtained by size selection methods. These samples are fraction 3, fraction 2, and fraction 1 from the previous chapter, with average sizes of 37-, 84- and 440 nm respectively. Each sample was loaded into a DAC and studied using synchrotron x-ray diffraction up to pressures near 10 GPa. The resulting data is analyzed by fitting to the third order Birch-Murnaghan equation of state. Values for the bulk modulus and the pressure derivative of the bulk modulus are obtained. Within instrumental and experimental error, the value for the bulk modulus of nanoquartz is the same as that of bulk quartz. However, the pressure dependence to the bulk modulus appears to be slightly enhanced at higher pressures.
4.1 Introduction

Previous high pressure studies have shown that nanocrystal size can affect the phase stability, particle shape and mechanical properties of a range of different materials.\textsuperscript{1-5} Through these types of studies, it becomes evident that crystallite size is an important parameter that can be controlled to better understand the fundamental properties of bulk solids. Additionally, the inherent novelty of materials designed along nanometer lengthscales has created possibilities in technology before inaccessible.\textsuperscript{6,7} Because of this, there is an increased need for an understanding of the properties of nanocrystals themselves.

Quartz, a dominant component of the earth's crust and the second most widely used material in the electronics industry, is a likely candidate for size dependent studies.\textsuperscript{8,9} Haines et al. show that solid state amorphization in quartz is sensitive to the extent of hydrostaticity at elevated pressure and Rios et al. show the first order character of the alpha-beta phase transition to decrease in naturally occurring nanocrystalline agate samples.\textsuperscript{10,11} These studies suggest a grain size dependence to quartz phase behavior that has not yet been evaluated. We thus set out to systematically vary the grain size in quartz crystallites and assess this impact on pressure-volume behavior. We report a value for the bulk modulus of nanoquartz that, within experimental error, agrees reasonably well with the bulk value. We also note increased pressure dependence to the bulk modulus as well as an increased unit cell volume of synthetic nanocrystals compared to the bulk volume at ambient as well as elevated pressures.
4.2 Experimental

Synthetic quartz nanoparticles are prepared by the hydrothermal treatment of amorphous silica. Reactions proceed under strong base conditions in a Parr 4500 series minireactor for two hours at 573 K. Resulting products are separated into three fractions with average particle sizes, as determined by Transmission Electron Microscopy (TEM), of: fraction 1-- 440 ± 220 nm, fraction 2-- 84 nm with a size distribution from 2 to 174 nm and fraction 3-- 37 nm with a size distribution of 2 to 77 nm. TEM data shows the particles to be relatively isolated as well as faceted.

Pressure is exerted on the sample with the use of a diamond anvil cell (DAC). Figure 4.1 shows an example of a diamond anvil cell similar to the ones used for these experiments. The cells that are actually used have been borrowed from the Alivisatos research group at UC Berkeley and are not shown here. The DAC operates by application of pressure to a sample that is located between two parallel diamond culets (a culet is the name for the smaller flat face of a cut diamond). In general DACs are comprised of two halves. The one shown here is of the piston cylinder type (mini-DAC, High Pressure Diamond Optics) where one half is the “piston” and the other is the “cylinder”. One diamond is mounted at the top of the piston and one at the base of the cylinder. The piston half of the cell fits tightly into the cylinder half such that the diamond faces would come flush together if the cell were closed completely. It is important never to close the cell without some kind of spacer between the diamonds because the weight of the cell itself is enough to cause the diamonds to scratch or crack one another. The diamonds are mounted flat against tungsten carbide backings with Stycast 2850FT black epoxy resin along with 7% catalyst 24LV (by weight) as shown in
the diagram included in Figure 4.1 (High Pressure Diamond Optics). The epoxy is visible about the base of the diamond in Figure 4.1b. The backings fit into each half of the cell and are adjusted to align properly above one another with small setscrews in the sides of the cell halves.

Ruby is generally used inside the sample chamber during experiments for measurement of internal pressure. The fluorescence decay (R₁ line corresponding to radiative decay from ²E to the ground state) from an electronic excitation of ruby (ground state to U band) is highly sensitive to pressure. Its pressure dependent behavior has been calibrated making the material widely used as a pressure gauge for DAC work.¹³,¹⁴ The resulting pressure given from its fluorescence band position varies according to

\[ P = \frac{1904}{B} \left[ \left(1 + \frac{\delta \lambda}{694.24}\right)^{b} - 1\right], \quad [4.1] \]

where \( P \) is the pressure, \( \delta \lambda \) is the R₁ line wavelength shift and \( B \) is an empirical constant that is equal to 7.665 for quasi-hydrostatic conditions and \( B = 5 \) for non-hydrostatic conditions.¹⁵-¹⁷ The value of 694.24 is the position in nm of the R₁ line. R₁ is actually part of a doublet that is easily resolved under hydrostatic pressures. The term hydrostatic refers to an isotropic application of pressure. Ideally the sample is suspended in some sort of homogeneous medium that evenly transfers pressure to the sample from all directions. If pressure is not applied in a hydrostatic way the sample will be in a state of strain far from thermodynamic equilibrium. A decreased resolution of the R₁-R₂ doublet due to broadening is an excellent indicator of non-hydrostatic conditions.
During pressure loading, a gasket sits between the two diamonds. The gasket is basically a small scrap of hardened stainless steel into which a hole is drilled that accommodates the sample. The hole is drilled smaller than the face of the diamond and positioned in the center of the face so that when the cell is closed the sample is enclosed in a tiny space the size of the volume of the hole (the sample chamber).

Pre-indentation is required prior to drilling the hole in the gasket. A solid piece of gasket material is placed between the diamonds; the cell is assembled and the screws are tightened. When the sample is to be pressurized above 15 GPa during experimentation indentation should also proceed to a point above this pressure. This is because there is a solid-solid phase transition in steel at 15 GPa, which will change the compressibility of the gasket. If the experimental pressure will not go beyond 10–15 GPa, then indentation pressures are not as crucial. The gasket should always be indented; however, as softer materials will flow under pressure. If the indentation is not deep enough, typically the drilled hole will close up during the experiment. It can also translate or open wider and the risk is that the hole will move off the edge of the diamond. Trial and error is the best way to determine whether a particular gasket material had been effectively indented. Indentation pressure can be measured by the placement of a ruby chip between the diamonds on top of the gasket while indenting.

Gasket holes are formed after the indentation. The size of the drill bit should be somewhat smaller than the dimension of the culet. For a 350-μm culet, a 250-μm bit is sufficient. The gasket material should be mounted in a way that it will not move or vibrate during drilling. The drilled hole should be carefully centered in the indentation and should be as vertical as possible. Any roughness or scraps left at the edges should be
cut away or smoothed before loading the cell. It is useful to use a sharp pointed object such as a fine needle to mark the center of the indentation before the gasket is removed from the face of the diamond (just after indenting). This helps guide the drill bit and keep it stationary while drilling. Bits should be handled very carefully and their rotation should be examined before drilling. A bit that wobbles or swivels about the center axis of rotation during drilling will not work. Using a perfectly straight bit can circumvent much frustration.

Samples are loaded as dry powders and ethylcyclohexane (4:1 methanol/ethanol can also be used) is then added as a hydrostatic pressure-transmitting medium. It is useful to balance the gasket material on the diamond using small pieces of clay. Generally a fine-tipped tool (micro-manipulation tools are available from Hampton Research) dipped into the sample powder will withdraw a sufficient amount of sample. The sample is then pressed into the sample chamber (gasket hole). A stereomicroscope is used to magnify the loading of the sample. Small amounts of finely ground ruby powder are then added toward the edge of the sample chamber. Ideally, individual crystals a small fraction of the size of the chamber are loaded in 3-5 locations near the edges. For a 250 mm diameter chamber, this is quite difficult. If the powder is sufficiently fine, a small amount can typically be flicked or dispersed across the top of the chamber and with luck it will not “block” the sample.

Once the cell is closed with the sample inside, pressure is applied by tightening the cell. Four screws fit into the slots shown in Figure 4.1c. They are tightened to finger tight and then further tightened in ¼ turns successively. Two of the screws are right-handed and two are left-handed so that it is easier to keep track of the order of tightening.
It is very important to tighten the screws evenly. Over tightening one side of the cell results in nonparallel alignment of the diamond faces. The diamonds are then in danger of puncturing the gasket, contacting one another and breaking.

Once the cell is loaded sample evaluation can be performed in situ. The design of the cell is such that each half contains a tiny hole through which light sources can be directed. This hole can be seen as the tiny white spec in the center of the top half of the cell shown in Figure 4.1a. For the pressure measurement, the entire DAC can be place inside a microscope fluorescence apparatus. The illumination (514.5 nm Ag laser) is coaxial with the detection line through the objective of the microscope. The laser is focused vertically through the hole in the center of the DAC. For x-ray experiments, the layout of the apparatus is such that data is collected in transmission. The position of the cell is rotated 90° to that shown in figure 4.1c with the x-rays incident horizontally and a large array detector parallel to the face of the DAC at the opposite end.

For these experiments high-pressure studies of fractions 1 and 2 are performed in a screw type piston-cylinder diamond anvil cell equipped with 500-μm-anel diamonfs. A membrane style DAC (pressure is applied by the injection of argon into the interstitial space between the DAC and an external cage) with 350-μm-anel diamonds is used for fraction 3. Synchrotron x-ray patterns are obtained on beamline 7.3.3 at the Advanced Light Source, Lawrence Berkeley National Laboratories. The beam is focused using a Pt coated silicon mirror to a spot size of 75 × 120 μm. A cryo-cooled double-bounce Si (111) crystal generates monochromatic x-rays of 11 keV. Diffraction patterns are collected using a MAR 345 image plate detector that is calibrated using either alumina or lanthanum hexaboride powders. All x-ray patterns are integrated using FIT2D\textsuperscript{19-21} and
peak positions are fit to Voigt line profiles using PeakFit (Jandel Sci. Software). X-ray reflections are clearly indexed to the trigonal alpha-quartz structure.
Figure 4.1 The diamond anvil cell. Panel A shows a top view of the top half of the cell (on the left) with the bottom half shown to the right. Panel B gives a closer view of the bottom half of the cell showing the black epoxy that glues the diamond to the backing. The diagram shows a cross sectional view of the cell with the gasket positioned between the diamonds, as it would be when containing a sample with the cell closed.
4.3 Results and Discussion

Figures 1 and 2 show a continuous decrease in lattice spacing with increasing pressure for the smallest sized sample, fraction 3. The patterns in figure 1 have been background subtracted and peaks related to the diffraction from the sample gasket and ruby have been removed. As the pressure increases the (202) reflection shifts toward one of the gasket peaks until, at a pressure of roughly 2 GPa, it completely overlaps and can no longer be assigned. Additionally, the (110), (112) and (202) reflections all fade out with higher pressures due to reduced signal to noise. For fractions 1 and 2 the signal to noise was much improved due to both larger sample volume as well as larger crystallite size. Figure 2 shows the linear shift in peak position of the major reflections for fraction 3. Fractions 1 and 2 exhibit analogous behavior with successively shifted diffraction peaks corresponding to linear decreases in d-spacings.
Figure 4.1 Pressure evolution of synchrotron x-ray diffraction from nanoquartz. The patterns shown are for fraction 3, which has an average nanocrystal size of 37 nm. Intensities are normalized and offset by 1. Reflections from ruby and the sample gasket have been subtracted.
Figure 4.2 Pressure evolution of the d-spacings of nanoquartz. The sample is the same as the one shown in Figure 4.1
Figure 4.3 Pressure dependent synchrotron x-ray diffraction of fraction 2. The average crystallite size for this sample is 84 nm. The intensity has been offset by one and peaks due to diffraction from the sample gasket and/or ruby have been subtracted.
Figure 3, which includes data from both fraction 2 and fraction 3 (with sizes of 84- and 37-nm respectively), shows the pressure-volume behavior of nanocrystalline quartz. Volumes are calculated using the average of the lattice parameter, a, and the individual value of c from the remaining relevant reflections. 'a' is determined from the (100), (110) and (200) reflections, and is determined from the (101), (112) and (202) reflections. The resulting volumes are then averaged and the error in volume is taken as the standard deviation on that average. In the case of fraction 2 (and for fraction 1, figure 4.4), the (102), (111) and (201) reflections are also used to determine c.

The deformation of a crystal in response to an external pressure can be more easily understood by considering the familiar expression for the response of a spring under one-dimensional compression: Hooke's Law. According to this law, the change in length of a spring, L, under an external force is given by \( \frac{1}{2} kL^2 \), where k is a force constant specific to the type of material from which the spring is made. The analogous equation for a three-dimensional crystal would similarly depend on its elemental composition as well as on its symmetry and bonding. This relationship is given by the stress and strain tensors. An equation for the change in volume of a crystal under hydrostatic compression can be formulated based on the relationship between stress and strain for a given crystal structure.

4.3.1 The Birch-Murnaghan equation of state

Francis Birch developed a model based on the expression given by F. D. Murnaghan for the finite strain in a crystal. {Birch, 1947 #157} It begins with the construction of the volume change associated with applied pressure. Under a uniform
compression, which shortens every direction in the crystal by a factor of \((1-\alpha)\), the volume change associated with this compression, \(V/V_0\), is equal to \((1-\alpha)^3\). Murnaghan developed an expression for the finite strain of a cubic crystal in terms of Cartesian coordinates: \{Murnaghan, 1937 #169\}

\[
\varepsilon_{rs} = \delta_{rs} \varepsilon + \beta_{rs} (1 - 2 \varepsilon)
\]

where \(\varepsilon\) is related to \(\alpha\) by

\[
(1 - \alpha)^3 = (1 - 2 \varepsilon)^{\frac{3}{2}} = \frac{V}{V_0},
\]

\(r\) and \(s = 1, 2, 3\) and \(\beta_{rs}\) is a strain coefficient. He further recognized the fundamental relationship between stress and strain in terms of strain energy:

\[
T_{rs} = \rho \left( \frac{\partial \phi}{\partial \varepsilon_{rs}} - 2 \varepsilon_{rp} \frac{\partial \phi}{\partial \varepsilon_{pr}} \right),
\]

where \(\rho\) is the initial unstrained density. A third order Taylor expansion of strain energy about \(\varepsilon = [(V_0/V)^{2/3} - 1]/2\) gives the Birch-Murnaghan equation of state:

\[
P = \frac{3}{2} K_0 (x^{\frac{2}{3}} - x^{\frac{1}{3}}) [1 + \frac{3}{2} (K_0' - 4)(x^{-\frac{5}{3}} - 1)]
\]

where \(P\) is the pressure, \(K_0\) is the bulk modulus, \(x\) is the ratio \(V/V_0\), and \(K_0'\) is the pressure derivative of the bulk modulus.\(^{22}\) This third order approximation of the pressure required to affect a certain volume change was developed based on a

Within experimental error the bulk modulus of nanoscale quartz does not differ from previously reported values for extended quartz crystal systems. As is apparent in Figure 4.3, pressure/volume data from fractions 2 and 3 significantly overlap with each
other making it difficult to distinguish two separate trends. Because of this it is assumed that in terms of pressure/volume behavior, the two fractions fall in an equivalent size regime. Thus, a third order Birch-Murnaghan nonlinear least squares fit was performed on the two sets combined. The dashed line in Figure 4.4 is the result of this fit which gives \( K_0 = 35.2 \pm 2.5 \) GPa. Hemley et al. report a bulk modulus of 38.7 GPa (the solid line reproduced in Figure 4.4) in work that also used the third order Birch-Murnaghan equation of state to fit a substantive number of data from several different reports, all looking at quartz single crystals.\(^{23}\) Within experimental error, the value reported in this work for the bulk modulus of quartz nanocrystals agrees well this previous result.

### 4.3.2 Enhanced pressure derivative of the bulk modulus of nanoquartz

Birch-Murnaghan fits of nanoquartz PV behavior, while producing \( K_0 \) values corroborative with bulk data, produce estimates of the pressure derivative, \( K'_0 \), in excess of the bulk. It is apparent in figure 3, that both fractions 2 and 3 show a clear deviation from the previously reported fit at higher pressures (> 4 GPa). This is attributed to a higher \( K'_0 \), 8.9 ± 1.5, for quartz nanocrystals, in contrast with that reported by Hemley et al. of 4.9.\(^{23}\) The third fit included in figure 3 (dotted line) is added to clarify the effect of change in bulk modulus relative to its pressure derivative. By increasing the bulk modulus roughly 10 GPa, while keeping \( K'_0 = 4.9 \), the Birch-Murnaghan equation of state predicts a shift of the curve to higher volumes. While an increased \( K_0 \) might more accurately describe the nanoquartz volumes at higher pressures, it can be seen from figure 3 that such a shift would not account for the lower pressure behavior. Indeed, a nonlinear least squares fit of the Birch-Murnaghan equation of state converges to a bulk modulus not far from the value of the extended crystal yet very different in its pressure derivative,
\( K_0' \). The difference in \( K_0' \) suggests a size effect in the pressure dependence of the bulk modulus.

Figure 4.4. Change in relative volume with increasing pressure. Open circles represent data points for fraction 2; closed squares correspond to fraction 3. The solid line is a calculated second order Birch-Murnaghan (BM) equation of state (EOS) using values, \( K_0 = 38.7 \) GPa and \( K_0' = 4.9 \). The dashed line is the nonlinear least squares fit of the BM EOS to the combined data from fractions 2 and 3. This fit converged to values of \( K_0 = \ldots \)
35.2 ± 2.5 GPa and $K_0' = 8.9 \pm 1.5$ with $\chi^2 = 0.991$. The dotted line corresponds to a calculated BM EOS where $K_0 = 50$ GPa and $K_0' = 4.9$.

The reason fractions 2 and 3 do not give separate values of $K_0'$ is likely due to their broad size distributions. The evident size effect in $K_0'$ raises the question of why fractions 2 and 3 do not exhibit clearly different pressure/volume trends. The explanation may be that while their average sizes are distinct, the size distributions overlap to the extent that the two trends are blurred into one. Broad size distributions occur in the samples used for these experiments due to difficulties associated with separation of nucleation and growth inherent in the hydrothermal preparation of high surface energy nanocrystals. This issue has been addressed previously and it is useful to note here that improvements on size control and size distribution may be possible and would likely result in a more well defined size effect of $K_0'$ for nanoquartz.$^{12}$

4.4 Conclusions

This work illustrates the hydrostatic volume change of quartz nanocrystals and compares this pressure dependent behavior to a well-established pressure/volume equation of state. These results show that the compressibility of synthetic quartz nanocrystals, within experimental error, agrees well with that of the bulk. The third order Birch-Murnaghan equation of state fits the experimental data with $\chi^2$ values of 0.991. It is also clear that there is an increased pressure dependence of the bulk modulus in the nanocrystal system. The broad size distributions of fractions 2 and 3 have the effect that their individual pressure volume trends are indistinguishable in the studied pressure
range. Future studies will require more finely size-selected populations of quartz nanocrystals. This work is an important step toward further size dependent investigations.

4.5 Bibliography


(4) Tolbert, S. H.; Alivisatos, A. P. Science 1994, 265, 373.


(18) Both the piston-cylinder and membrane DACs were purchased from Diacell Products, Ltd., Leicester UK, www.diacell.co.uk (David@diacell.com)


