

Chapter 5

Quartz and Silicas

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Abstract Silica is the most ubiquitous mineral in the earth's crust, existing in a wide variety of crystalline and noncrystalline forms due to the flexibility of the linkage among SiO_4 tetrahedra. The thermodynamically stable, room temperature form of silica is quartz, which is itself a widely available mineral and ingredient in many commercial ceramics and glasses. In addition to historically abundant raw material sources, crystalline and noncrystalline silicas can be produced by a wide range of synthetic routes. For example, synthetic quartz can be produced by hydrothermal growth in an autoclave, and synthetic vitreous silica can be produced from silicon tetrachloride by oxidation or hydrolysis in a methane–oxygen flame. Pure silicas serve as model systems in the study of ceramics and glasses, but at the same time, are used in a wide and steadily increasing variety of sophisticated technological applications, from piezoelectric crystals to optical fibers to waveguides in femtosecond lasers. Increased understanding of these ubiquitous materials is aided by improved experimental tools such as new neutron scattering facilities and increasingly sophisticated computer simulation methods.

1 Introduction and Historic Overview

Quartz and the silicas are composed of silicon and oxygen, the two most ubiquitous elements in the earth's crust [1] (Fig. 1). The widespread presence of the various forms of SiO_2 in common geological materials is a manifestation of this fact. Along this line, many common geological silicates (SiO_2 -based materials such as rocks, clays, and sand) hold a detailed historical record of high-pressure and elevated temperature conditions with significant implications in materials science, engineering, geology, planetary science, and physics [2]. As a result, a discussion of pressure-related structure and properties will be included in this chapter.

Silica (SiO_2) is the most important and versatile ceramic compound of MX_2 stoichiometry. As noted above, it is widely available in raw materials in the earth's surface, and silica is a fundamental constituent of a wide range of ceramic products and glasses;

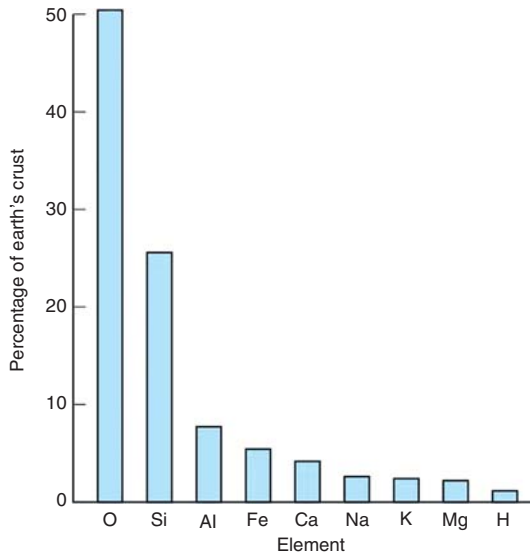


Fig. 1 The relative abundance of elements in the earth's crust illustrates the common availability of quartz and the silicas [1]

its properties permit it to be used in high-temperature and corrosive environments and as abrasives, refractory materials, fillers in paints, and optical components.

Vitreous silica (high purity SiO_2) is a technologically important amorphous material used in a myriad of applications including gas transport systems, laser optics, fiber optics, waveguides, electronics, vacuum systems, and furnace windows. During service, glass may experience elevated conditions of pressures and temperatures that can alter its properties. For instance, a vitreous silica lens may undergo drastic structural changes if pressure and temperature vary greatly in laser optics components. On the other hand, vitreous silica may undergo beneficial structural modifications under controlled conditions, e.g. during waveguide fabrication when femtosecond lasers are applied to induce a desired index of refraction in this glass [3].

2 The Structural Forms of Quartz and Other Silicas

Except for water, silica is the most extensively studied MX_2 compound. One of the challenges in studying silica is its complex set of structures. Silica has several common polymorphs under different conditions of temperature [1] and pressure [4], as seen in Figs. 2 and 3. For instance, cristobalite is the crystalline silica polymorph at atmospheric pressure above $1,470^\circ\text{C}$. It is built on an fcc lattice with 24 ions per unit cell. This structure is, in fact, the simplest form of silica. In addition to five polymorphs (quartz, coesite, stishovite, cristobalite, tridymite) that have thermodynamic stability fields, a large and increasing number of metastable polymorphs have been synthesized. These include vitreous silica, clathrasils, and zeolites [2]. Except for stishovite, all these structures are based on frameworks of

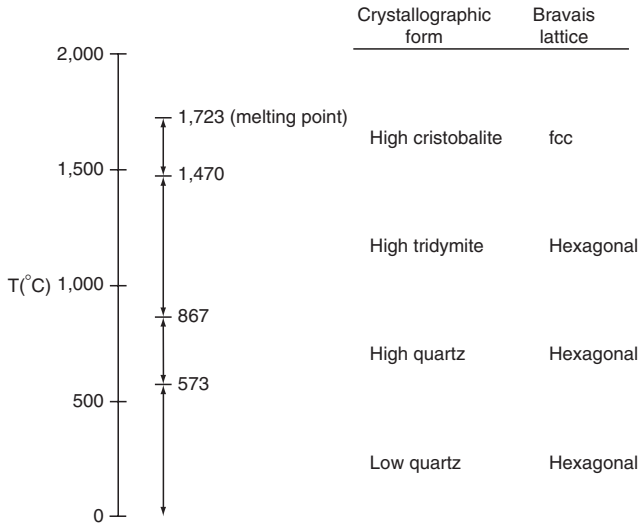


Fig. 2 Principal silica polymorphs at atmospheric pressure [1]

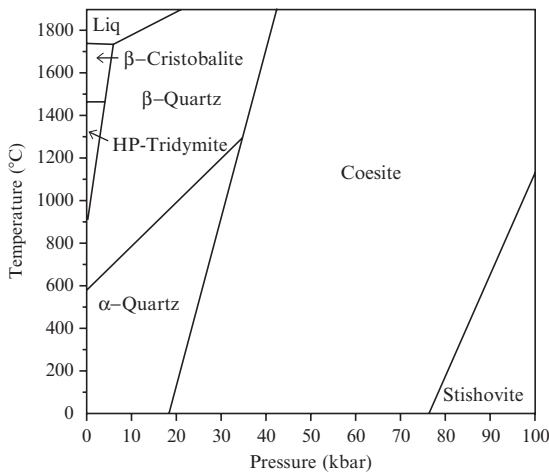


Fig. 3 Phase diagram for the SiO₂ system [4]

SiO₄ tetrahedra. These silica structures have been determined mainly by X-ray and neutron diffraction methods and, more recently, by Si and Al magic angle spinning solid-state NMR studies.

The various framework silica structures arise from the different ways that the (SiO₄)⁴⁻ tetrahedra are linked into 1-, 2-, and 3-dimensional arrangements. Although the basic tetrahedra are present in most silica structures, the connectivity varies widely.

Both ionic and covalent natures of the Si–O bond contribute to the preference for (SiO₄)⁴⁻ tetrahedron formation in both crystalline and glassy silicas. In addition, each O anion is coordinated by two Si cations, corresponding to corner sharing of the oxide tetrahedra, preventing the close-packing of anion layers and resulting in relatively open structures [5].

2.1 Silica Polymorphs

The name quartz comes from the German word “quarz,” of uncertain origin. Quartz and the other main polymorphs of silica are related in the phase diagram [4] shown in Fig. 3. Under ambient conditions, α -quartz is the thermodynamically favored polymorph of silica. At 573°C, α -quartz is transformed into β -quartz, generally similar in structure but with less distortion. This thermal transformation preserves the optical activity of quartz. Heating quartz to 867°C leads to the transformation of β -quartz into β -tridymite, involving the breaking of Si–O bonds to allow the oxygen tetrahedra to rearrange themselves into a simpler, more open hexagonal structure of lower density. The quartz–tridymite transformation involves a high activation energy process that results in loss of the optical activity of quartz. Heating of β -tridymite to 1,470°C gives β -cristobalite that resembles the structure of diamond with silicon atoms in the diamond carbon positions and an oxygen atom midway between each pair of silicon atoms. Further heating of cristobalite results in melting at 1,723°C. A silica melt is easily transformed into vitreous silica by slow cooling, resulting in a loss of long-range order but retaining the short-range order of the silica tetrahedron.

In the last ten years, at least a dozen polymorphs of pure SiO₂ have been reported [6]. Stishovite, another form of silica obtained at high temperatures and pressures, has, rather than a tetrahedral-based geometry, a rutile (TiO₂) structure in which each Si atom is bonded to six O atoms and each O atom bridges three Si atoms [6]. Stishovite (found in Meteor Crater, Arizona) is more dense and chemically more inert than normal silica but reverts to amorphous silica upon heating.

The distinction among polymorphs other than stishovite arises from the different arrangements of connected tetrahedra. Important examples are quartz and cristobalite. The structures of these polymorphs are relatively complicated. These structures are also relatively open, as corner sharing of oxide tetrahedra prevents the close-packing of anion layers as found in the fcc- and hcp-based oxides [5]. One consequence is that these crystalline structures have low densities, e.g., quartz has a density of 2.65 g cm⁻³. This low density facilitates structural changes and phase transitions at high pressures. Finally, the high strength of the Si–O interatomic bond corresponds to the relatively high melting temperature of 1,723°C.

When crystalline silica is melted and then cooled, a disordered 3-dimensional network of silica tetrahedra (vitreous silica) is generally formed. Glass manufacturing in the USA is a 10 billion dollar per year industry. It directly benefits from studies of quartz as one of the main raw materials of commercial glasses is almost pure quartz sand, with other raw materials being primarily soda ash (Na₂CO₃) and calcite (CaCO₃) [1].

2.2 Quartz

Low (α) quartz allows little ionic substitution into its structure. High (β) quartz allows the charge-balanced substitution of framework silicon by aluminum, with a small cation (Li⁺) occupying the interstices. In the more open cristobalite and tridymite structures, this charge-balanced substitution can be extensive, with many alkali and alkaline earth ions able to occupy interstitial sites. Such materials are called “stuffed

silica derivatives,” with eucryptite (LiAlSiO_4), nepheline ($\text{Na}_3\text{K}(\text{AlSiO}_4)_4$), carnegieite (NaAlSiO_4), and kalsilite (KAlSiO_4) being examples.

Similar to most other silica structures, quartz has a continuously connected network of $(\text{SiO}_4)^{4-}$ tetrahedra and an O/Si ratio equal to 2. This characteristic structure is also seen in cristobalite and tridymite. Interestingly, helices have been reported in quartz with two slightly different Si–O distances (0.1597 and 0.1617 nm) and an Si–O–Si angle of 144° [6]. Enantiomeric crystals of quartz are often obtained and separated mechanically. Each enantiomeric crystal of quartz is optically active.

According to Wyckoff [7], the crystalline forms of silica are the largest group of tetrahedral structures. Each of the three main polymorphs of silica formed at atmospheric pressure in nature (quartz, tridymite, and cristobalite) has a low and high temperature modification. The unit cell of low (α) quartz has three molecules and similar dimensions as the high (β) quartz structure. The difference between low and high forms of quartz arises from small shifts of atom positions. Table 1 lists structural data for both quartz structures.

The atomic arrangements in high and low quartz are very similar. In fact, when a single crystal of low quartz is carefully heated above 575°C , it is known to gradually and smoothly transform into a single crystal of high quartz, with a shift from a 3- to 6-fold symmetry [7]. The oxygen tetrahedron is almost regular (Si–O distance is 0.161 nm) for low quartz and with each oxygen having six adjacent oxygens (0.260–0.267 nm) and two silicon neighbors. Fourier analysis has provided accurate data for both structures [7]. The low and high forms of quartz are related by a displacive transformation with the former having the higher symmetry. Quartz, hexagonal in structure, is the lowest-temperature form of silica [5].

The structure of quartz has been extensively studied [7–10]. Table 2 summarizes structural data for low quartz obtained with the Accelrys *Catalysis 3.0.0* software. The continuous connection of oxygen tetrahedra is apparent from its structure illustrated in Figs. 4 and 5 [11,13].

Figure 5 shows that the linkage of tetrahedra in low quartz is, in fact, a double helix when viewed along the a -axis. This double helix structure was known long before the more celebrated structure of DNA [12,13].

Table 1 Comparison between low- and high-quartz structures [11] (after Wyckoff [7])

	Low temperature or α -quartz	High temperature or β -quartz
Bravais lattice	Hexagonal	Hexagonal
No. of ions	9 (3 Si^+ , 6 O^{2-})	9 (3 Si^+ , 6 O^{2-})
Temperature	$<573^\circ\text{C}^a$	$573\text{--}867^\circ\text{C}^a$
a_o	0.491304 nm	0.501 nm
c_o	0.540463 nm	0.547 nm
cla	1.10 ^b	1.09 ^b
Space group	D_3^4 or D_3^6 ($P3_12$) ^b	D_6^4 or D_6^5 ($P6_22$) ^b
Si–O	0.161 nm	0.162 nm
O–O	0.260–0.267 nm	0.260 nm
Si–O–Si angle	144° ^b	155° ^c
Symmetry	Threefold	Sixfold
Molecules	3	3

Additional data as indicated from different references: ^afrom [1], ^bfrom [8], and ^cfrom [6]

Table 2 Structure of low-quartz^a

Bravais lattice	Unit cell dimensions ^a (<i>a, b, c</i>) in nm	Unit cell major angles ^a (α, β, γ)	Space group number	Symmetry number	No. of ions per unit cell
Hexagonal	0.49130, 0.49130, 0.54052	90.0, 90.0, 120.0	<i>P3₁21</i>	152	9

^aFrom Accelrys software [11]; P = Primitive

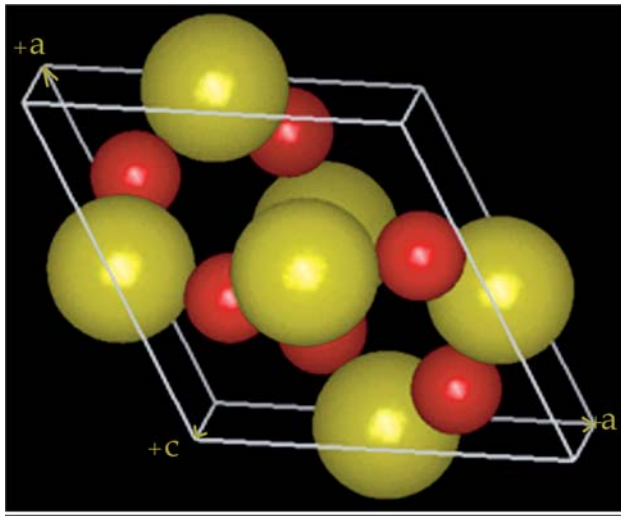


Fig. 4 Atomic arrangement in low-quartz (looking down the *c*-axis). (Small dark and larger light spheres represent oxygen and silicon ions respectively). The relative sizes of these ions correspond to the significant degree of covalency in the Si–O bond [11]

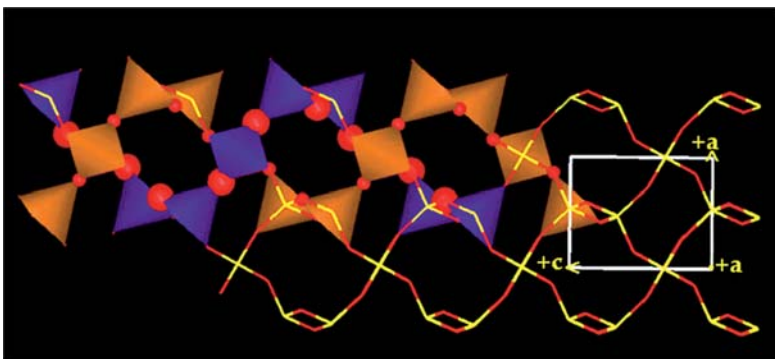


Fig. 5 Illustration of the double helix formed by SiO_4 tetrahedra in low-quartz (viewed down an *a*-axis) [11,13]

2.3 Cristobalite

Cristobalite, the highest-temperature polymorph of silica, was named after the place where it was discovered, the San Cristobal mountain in Mexico. Interestingly, silicate phases including cristobalite have also been found in cosmic dust collected by space vehicles [9]. The high cosmic and terrestrial abundance of silicas makes knowledge of their physical and chemical properties especially important in fields such as geology, chemistry, and physics. Cristobalite, like tridymite and keatite, is isostructural with ice polymorphs (i.e. cubic ice Ic).

Cristobalite has the Si atoms located as are the C atoms in diamond, with the O atoms midway between each pair of Si [13]. Like other crystalline polymorphs of silica, cristobalite is characterized by corner-shared SiO_4 tetrahedra. In addition, Liebau [9] noted that cristobalite, like quartz, exists in two forms having the same topology, with variations mainly in the Si–O–Si bond angles. Thermodynamic variables (such as pressure and temperature) and kinetic issues will determine which of these phases is formed. The interconversion of quartz and cristobalite on heating requires breaking and re-forming bonds, and consequently, the activation energy is high. However, the rates of conversion are strongly affected by the presence of impurities, or by the introduction of alkali metal oxides or other “mineralizers.”

Cristobalite has been well-characterized since the late fifties [7,9]. The high-cristobalite structure is characterized by a continuously connected network of $(\text{SiO}_4)^{4-}$ tetrahedra and is summarized in Table 3. The atomic model of the high-cristobalite structure in Fig. 6 [11] was generated with Accelrys *Catalysis 3.0.0*. Also, the Si–O distances have been noted to range between 0.158 nm and 0.169 nm.

2.4 Vitreous Silica

Crystalline silicas contain ordered arrangements of anion tetrahedra, whereas glassy silica has a high degree of randomness. Comparisons of these networks indicate that both have the basic tetrahedral unit, the same O–Si–O bond angle (109.5°), an O/Si ratio of two, and full connectivity of tetrahedra. An equivalent short-range order has been found in both crystalline and glassy silica, as shown schematically in Fig. 7.

Three related structural parameters for characterizing the atomic-scale structure of vitreous silica are the Si–O–Si bond angle between adjacent tetrahedra, the rotational angle between adjacent tetrahedra, and the “rings” of oxygens, as illustrated in Fig. 7 [5]. Each of these parameters has a constant value or set of values in crystalline silica,

Table 3 Characteristics of high-cristobalite^a

Bravais lattice	Unit cell dimensions ^a (<i>a,b,c</i>) in nm	Unit cell major angles ^a (α,β,γ) in degrees	Space group number	Symmetry number	No. of ions per cell
FCC	0.716, 0.716, 0.716	90.0, 90.0, 90.0	$Fd\bar{3}m$	227	24

^aFrom Accelrys software [11]

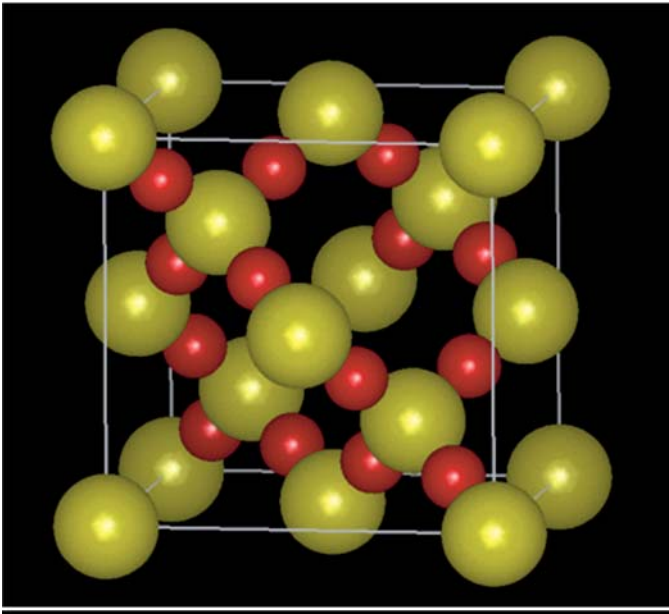


Fig. 6 Atomic arrangement in the high-cristobalite unit cell viewed down an a -axis. Small darker and large lighter spheres represent oxygen and silicon ions respectively. As in Fig. 4, the relative sizes of these ions correspond to the significant degree of covalency in the Si–O bond [11]

but varies over a wide range in vitreous silica. Table 4 summarizes these traits. The predominant Si–O–Si angle in quartz and cristobalite is 143.61° and 148° , respectively, and for tridymite it is 180° (one among a large group of angles). Vitreous silica, however, has a wide, continuous range of values between 120° and 180° (mean of less than 150°). The rotational angle between tetrahedra is either 0° or 60° for crystalline silica and is random in glass [2,5].

The common inorganic glasses used for windows and common glassware are silicates with significant amounts of oxides, other than SiO_2 , present, such as Na_2O and CaO . Scientific glassware is generally a borosilicate containing B_2O_3 , along with the soda and lime components. The boric oxide is a glass former, contributing to the oxide network polymerization, and glass modifiers (Na_2O and CaO) disrupt or depolymerize the network, reducing the melting and glass transition temperatures. Silica, as a chemical component in these glasses, is rather nonreactive to acids, H_2 , Cl_2 , and most metals at ordinary or slightly elevated temperatures, but it is attacked by fluorine, aqueous HF, and fused carbonates among others [14].

The general feature of vitreous silica as a continuously connected “random” network of SiO_4 tetrahedra was first defined by Zachariasen [15]. This nature of vitreous silica was verified by Warren et al. [16] within the limits of the X-ray diffraction techniques of that day. Several, subsequent studies have investigated the structure of vitreous silica and generally confirmed the open structure proposed by Zachariasen. Mozzi and Warren [17] substantially refined the X-ray work done by Warren et al. [16]

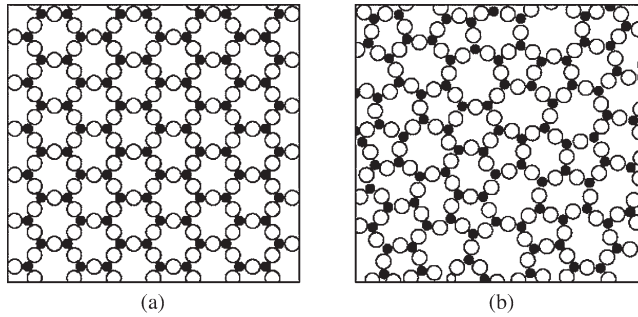


Fig. 7 Schematic 2-dimensional comparison of the structure of crystalline vs. noncrystalline silica [1]

Table 4 Some characteristics of crystalline and noncrystalline silica [2,5,11]

	SiO ₂ glass	SiO ₂ crystal
Number of nearest neighbors	Si: 4 O: 2	Si: 4 O: 2
Bond Angles	109.5° (O–Si–O) 144° ± 15° rms[9]	109.5° (O–Si–O) 180° (tridymite) ^a 150.9°–143.61° (quartz) ^b
Rotation angle between tetrahedra	(Si–O–Si) Random	Approx. 148° (cristobalite) ^b 0° or 60°

^aOnly one among a large group of angles

^bFrom [2]

identifying the average Si–O–Si bond angle at 144° and the overall distribution of that angle varying between 120° and 180°. Subsequent modeling studies largely confirmed the Mozzi and Warren results [18–20].

Until the 1950s, the Russian school of glass science favored a theory of the structure of vitreous silica based on the coincidence of the broad X-ray diffraction peaks for vitreous silica and the sharp peaks of cristobalite. The glass pattern was ascribed to line broadening due to the extremely small “particle size” [21] of such crystallites. However, for vitreous silica, this “microcrystallite” theory has largely been supplanted by the random network theory of Zachariasen. After more than seven decades, the Zachariasen model continues to be a very useful first-order description of vitreous silica. X-ray [17] and neutron [22] studies have generally supported this conclusion. On the other hand, silicate glasses with significant modifier content have provided evidence of subtle ordering effects analogous to crystalline silicates of similar composition. CaO–SiO₂ glass in comparison to wollastonite is an excellent example [23,24]. Figure 8 shows a computer-generated model of vitreous silica using well-established interatomic potentials for Si–O [25,26].

The short-range structure (i.e., length scale below 0.5 nm) of vitreous silica has been studied in terms of the structure factor and the radial distribution functions using neutron and X-ray diffraction experiments. Experimental radial distribution functions indicate that the separation distance between Si and O falls in the 0.159–0.162 nm range. The nearest neighbor distances O–O are 0.260–0.265 nm and the Si–Si distances are 0.305–0.322 nm [27,28].

High pressures can affect the properties of vitreous silica. For example, the nature of silica within the soil is a question of continuing inquiry in geology. Siliceous rocks that undergo meteorite impacts often form a detailed record of the high-pressure shocks on the surfaces. The response of vitreous silica to stress is also critical to technology, from tool making to the control of microstrains in modern nanolayered materials. High-pressure studies have unveiled a number of phenomena in silica glass, including the discovery of new phases, amorphization transitions, and unusual behavior under dynamic compression [29]. Thus, understanding the response of vitreous silica to high-pressure conditions has important implications for geology, planetary science, materials science, optics, and physics.

An indication of the effect of high pressure on the structure of vitreous silica is illustrated by the distortion of the ring size distribution. Shackelford and Masaryk [30] showed that the sizes of interstitial sites in vitreous silica follow a lognormal distribution. Similarly, the distribution of ring sizes in two-dimensional models of this material also follows the lognormal distribution [31]. Contemporary, rigorous three-dimensional simulations of vitreous silica (such as Fig. 8) clearly demonstrate this distribution. Figure 9 shows how this skewed distribution broadens significantly upon the application of high pressures. The average ring size in such structures at ambient conditions is six-membered (a loop of six connected silica tetrahedra), and the number of rings larger and smaller than six drops off sharply. Under high pressure, however, the number of six-membered rings is diminished and the relative numbers of larger and smaller rings (for example, eight- and four-membered rings) increase.

3 Key Properties of Quartz and Other Silicas

Quartz is abundant and hence inexpensive, relatively hard and chemically inert. Similar to other ceramics, high hardness is a useful property of quartz. Knoop hardness data for a number of ceramic materials including quartz are given in Table 5 [32]. The densities of a number of ceramic materials including quartz are given in Table 6 [32].

Extensive reviews have been reported on the mechanical behavior of vitreous silica [33]. The Young's modulus at 25°C is 73 GPa, the shear modulus is 31 GPa, and Poisson's ratio is reported as 0.17. Vitreous silica and silicates are notable solids because of their unique set of properties such as its ability to transmit visible light, ultraviolet and infrared radiation, good refractory and dielectric properties, chemical inertness, and low thermal expansion with resulting high thermal shock resistance. In the infrared region, water incorporated in the structure as hydroxyl (OH⁻) has strong absorption bands at specific wavelengths. The Si–O vibration has two strong absorption bands that affect the transmission of silica. Transmission curves are typically compared

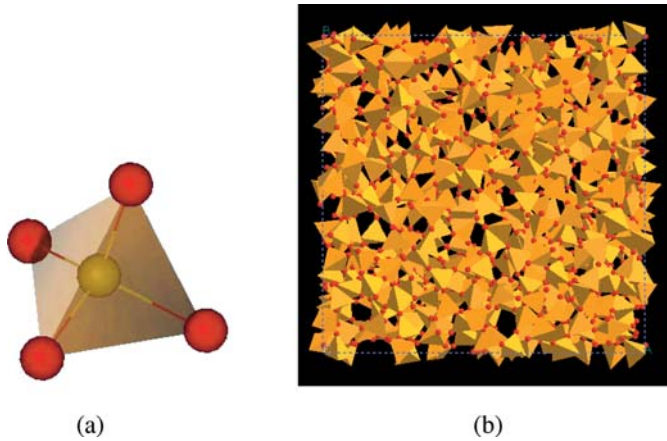


Fig. 8 The structure of vitreous silica is composed of a (a) basic building block, the $(\text{SiO}_4)^{4-}$ tetrahedron (corner spheres denote oxygen and the central sphere silicon), which forms (b) a 3D noncrystalline network of fully connected tetrahedra [26]

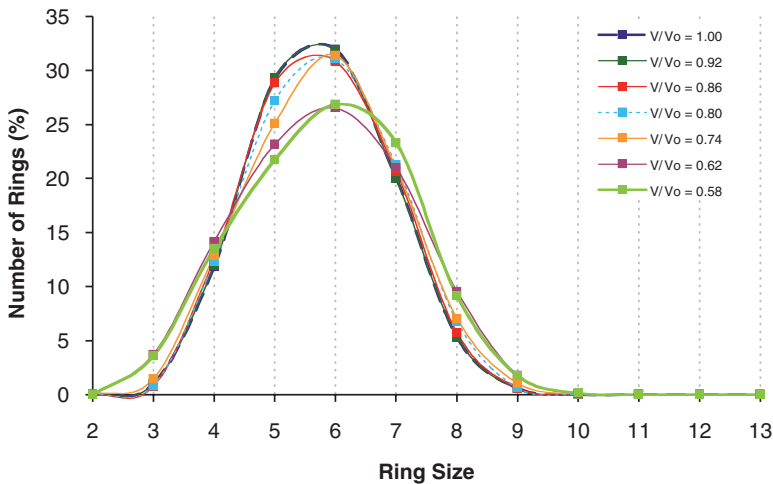


Fig. 9 The distribution of ring sizes in vitreous silica follows a lognormal distribution. The distribution broadens under increasingly high pressures

for several types of vitreous silica. Ultra-pure vitreous silica with elevated high transparency is required in telecommunication fiber optics.

Different sources of radiation can affect the physical and optical properties of vitreous silica. For instance, a dose of 1×10^{20} neutrons cm^{-2} has been reported to increase the density of vitreous silica by about 3% (to 2.26 g cm^{-3}) [27]. Similar increases in density are reported in quartz, tridymite, and cristobalite after comparable irradiation levels. On the other hand, ionizing radiation such as X-rays, γ -rays, electrons, or protons carry

Table 5 Knoop hardness for quartz and some common ceramic materials [32]

Material	Knoop hardness (100 g load) (in kg mm ⁻²)
Boron carbide (B ₄ C)	2800
Silicon carbide (SiC)	2,500–2,550
Tungsten carbide (WC)	1,870–1,880
Aluminum oxide (Al ₂ O ₃)	2,000–2,050
Zirconium oxide (ZrO ₂)	1,200
Quartz (SiO ₂)	
Parallel to optical axis	710
Perpendicular to optical axis	790
SiO ₂ glass	500–679

Table 6 Densities for quartz and some common ceramic materials [32]

Material	Density (g cm ⁻³)
Boron carbide (B ₄ C)	2.51
Silicon carbide (SiC)	
Hex.	3.217
Cub.	3.210
Tungsten carbide (WC)	15.8
Aluminum oxide (Al ₂ O ₃)	3.97–3.986
Zirconium oxide (ZrO ₂)	5.56
Quartz (SiO ₂)	2.65
SiO ₂ glass	2.201–2.211

enough energy to produce absorption centers, known as color or defect centers, in vitreous silica. A characteristic band at 215 nm is produced by long exposures to X-radiation [27]. This band is also reported in irradiated α -quartz and is often associated with the existence of E' centers, a type of defect assumed to be a pyramidal SiO₃ unit having an unpaired electron in the Si sp³ orbital. Various types of defect centers in silica glass can be classified as either intrinsic (melt-quench) or extrinsic (radiation-induced).

4 Processing Quartz and Other Silicas

Silica, the main component of silicates, is widely used as mentioned earlier. In its crystalline and noncrystalline polymorphs, silica is used industrially as a raw material for glasses, ceramics, foundry molds, in the production of silicon, and more recently in technical applications such as quartz oscillators and optical waveguides for long-distance telecommunications. Of the crystalline forms, only α -quartz is commonly used as sand or as natural and synthetic single crystals. Cristobalite is often utilized as the synthetic phase in glass-ceramics.

Beyond the abundant natural sources of quartz and other silicas, techniques for synthetic production of these materials have provided a significantly wider range of applications [27,34]. Large, high-quality crystals of quartz can be grown by the well-established technique of hydrothermal growth in an autoclave filled with a solution of

sodium carbonate at elevated temperature and pressure. Quartz particles are fed into the bottom of the growing chamber, while seed crystals are fed into the top in a metal frame. A temperature gradient establishes a greater solubility at the higher-temperature bottom of the chamber, leading to a continuous transfer of material upward to the growing single crystals. Uniform quality crystals are routinely produced with well-controlled shapes and sizes. Specific seed crystal orientations are used to produce desired products such as particular oscillator configurations.

Vitreous silica has a unique set of properties for applications where optical transmission, chemical inertness, and thermal stability are crucial. The abundance of vitreous silica in nature is widespread in biogenic sources such as sponges and diatoms, in crystalline opals, and as glass cycled by organisms through the environment (e.g., silicification of plant tissues for structural integrity and protection from insects [35]). This important glass can also be readily found in abiogenic sources such as volcanic glasses, resulting from extensive quenched magmas, tektites (spherical or teardrop-shaped silicate glass bodies linked with impact craters), and lechatelierite (pure silica glass), resulting from lightning strikes of unconsolidated sand or soil that form fulgurites. Glassy silica is also formed by a combination of temperature and pressure resulting from meteoritic impact [27].

Vitreous silica is high purity SiO_2 glass that can withstand service temperatures above $1,000^\circ\text{C}$. As a metastable phase of silica, vitreous silica can be readily obtained in nature and synthetically. Silica glass can be produced in a pure and stable form, displaying useful properties, but is rigid and difficult to shape even at $2,000^\circ\text{C}$. Hence, it is not accessible to mass production plastic-forming methods. However, techniques have been developed to produce vitreous silica in various shapes and sizes [36–39].

First, quartz crystals can be melted to produce silica glass by either the Osram process or the Heraeus method [27]. In the Osram technique, fragmented quartz is fed to a tubular furnace and melted in a crucible protected by an inert gas, where tubing is drawn from the bottom of the crucible. In the Heraeus method, quartz crystals are fed in an oxy-hydrogen flame through a rotating fused quartz tube and withdrawn slowly from the burner as clear fused (vitreous) silica accumulates. The quartz crystals are generally washed in hydrofluoric acid and distilled water to remove surface impurities, followed by drying and heating to $\sim 800^\circ\text{C}$, before being immersed in distilled water. Purity of the natural sand is very important in glass and ceramic materials, and transition metal oxides should not exceed 200 ppm.

In vapor phase hydrolysis [37,38], synthetic vitreous silica is prepared from silicon tetrachloride by oxidation or hydrolysis in a methane–oxygen flame. The resulting soot is sintered to form silica glass. Water, formed from the oxidation of methane, subsequently combines with the chloride, leading to the production of hydrochloric acid and oxygen. Subsequent work on these materials can lead to a variety of useful products, including telescope mirror blanks, lamp tubing, crucibles, and optical fibers (the largest commercial use for vitreous silica in telecommunications).

Finally, vitreous silica can be manufactured by the sol–gel technique developed by Zarzycki [39]. Gels are formed by the destabilization of colloidal sols or by the hydrolysis of metal organic compounds. This latter routine is the most common technique that yields a silica–alcohol–water gel. Subsequently, the gel is dried and fused to produce silica glass. The manufacture of 3D articles by this method is limited due

to the difficulty in drying porous gels without large shrinkage and cracking and the associated high costs of the raw materials. Silica gel can also be used as a drying agent and as supports for chromatography and catalysis [6].

5 Future Trends

Various silicas, including quartz, are especially interesting in that they represent a family of materials that are familiar, while also providing state-of-the-art applications. As an example of the commonplace, the largest part of the industrial sand and gravel production in the United States (39% in 2004 corresponding to more than ten million tons) is glassmaking sand [40]. This important raw material is the relatively high-purity quartz with only small amounts of alumina and iron oxide impurities permitted. Health and safety regulations are expected to cause future sand and gravel operations to be relocated to areas more remote from high-population centers.

As noted earlier in this chapter, vitreous silica is used increasingly in a number of advanced applications such as fiber optics, laser systems, and waveguides. In addition, vitreous silica continues to be an excellent model system for the study of the structure of noncrystalline solids. One can expect that the continuing refinement of our understanding of this structure will be aided by the availability of a new generation of diffraction systems at the Spallation Neutron Source (SNS) at the Oak Ridge National Laboratory and the GLAD diffractometer at the Argon National Laboratory. Much of the focus of these structural studies as well as future technological applications will be the “medium-range” nano-scale that exists between the short-range order of the silica tetrahedron and the long-range randomness of vitreous silica. Computer simulations have played a key role in predicting the nature of such length scales in this important glassy material [11,26,41]. Further improvements of interatomic potentials and computing power will certainly expand our understanding of this material and perhaps one-day allow the design of ceramics and glasses with specific, desirable properties not currently available.

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