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\textsubscript{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\textsubscript{2} in common geological materials is a manifestation of this fact. Along this line, many common geological silicates (SiO\textsubscript{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\textsubscript{2}) is the most important and versatile ceramic compound of MX\textsubscript{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;
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°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