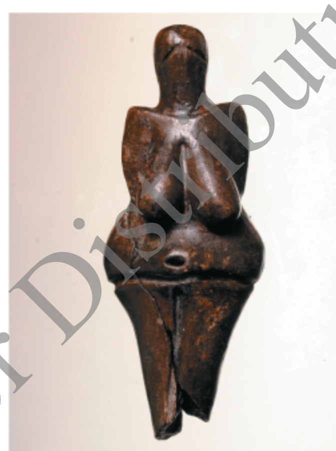
12.7: Ceramics, Cement, and Glass

The silicate structures we examined in Section 12.6 are common in ceramics, cement, and glass. These substances are used in buildings, electrical devices, pottery, and kitchenware. If you look around wherever you are sitting at this moment, you are likely to see examples of these materials. In this section of the chapter, we examine each of these amazing classes of materials individually.

Ceramics

Ceramics are traditionally defined as inorganic nonmetallic solids that are prepared from powders usually mixed with water, formed into the desired shape, and then heated. They are extensively used to make bricks, tiles, pottery, dishware, and insulating elements in electrical devices. Ceramics display a range of properties but are usually hard, strong, nonconductive, and brittle. The word ceramics originates from the Greek *keramikos*. Keramikos is an area of Athens that was the potters' quarter of the city, and the Greeks were among the first accomplished potters. However, pottery itself predates recorded history; the oldest known example is the Venus of Dolni, a figurine that dates to 29,000–25,000 BCE. Ceramics can be categorized into three types: silicate ceramics, oxide ceramics, and nonoxide ceramics.

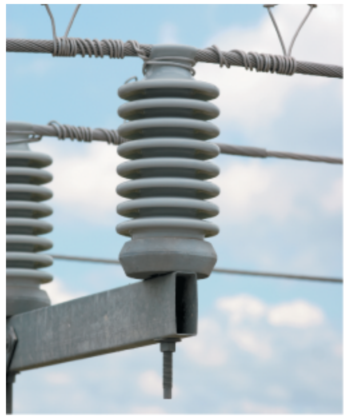


The Venus of Dolni dates to 29,000–25,000 BCE and is the oldest ceramic object known. It was discovered in 1925 in the Czech Republic.

Silicate Ceramics

Many ceramics are composed of *aluminosilicates*, a class of minerals in which some of the silicon atoms in the silicate structure are replaced by aluminum. The weathering of naturally occurring aluminosilicates produces **clays**, which are essentially powdered forms of the minerals mixed with water. When heated, reactions occur that transform the clay into the ceramic substance.

For example, the clay kaolinite, $Al_2Si_2O_5(OH)_4$, undergoes irreversible chemical and structural changes when heated (or fired) above 1500 °C. These changes transform the clay into a white ceramic solid containing an extended network of Si-O and Al-O tetrahedra. Kaolonite is the most important component of porcelain, a ceramic substance that originated in China during the Han dynasty about 2000 years ago. The term *china* today still refers to the fine plates, saucers, and cups made from porcelain and related ceramic materials. Silicate ceramics also find extensive use as insulators in electrical applications.



Ceramic electrical insulator

Oxide Ceramics

Among the most common oxide ceramics are Al_2O_3 and MgO. These materials demonstrate the advantages and disadvantages of the use of ceramic materials for industrial purposes compared to metals. Al_2O_3 melts at 2072 °C, compared to aluminum metal, which melts at 660 °C. MgO melts at an even higher temperature (2852 °C). Both are physically and chemically stable at high temperatures. The high melting point and chemical stability make Al_2O_3 and MgO outstanding *refractory materials*—materials that can be used in high-temperature applications.

For example, aluminum oxide and magnesium oxide are used in industrial furnaces, high-speed cutting tools, crucibles, heating elements, and fire proofing. Engineers have long desired to take advantage of the high-temperature stability of ceramics to make ceramic engines. A ceramic engine can run at a higher temperature, which makes it more efficient and requires less cooling. However, certain less desirable characteristics of ceramics have made that pursuit difficult. Ceramic materials tend to be brittle and subject to thermal shock (they can crack upon fast changes in temperature). Whereas metals can bend and stretch under stress, ceramics break. Even though ceramics have found some limited use as components of engines, a completely ceramic mass-produced engine remains elusive.

Aluminum oxide crucible

Nonoxide Ceramics

The nonoxide ceramics include substances such as Si_3N_4, BN, and SiC. Silicon nitride is a network covalent solid with a structure similar to silica; the silicon atoms sit in the center of nitrogen tetrahedra that are linked together. Silicon nitride is used extensively in engine parts and nonmetallic ball bearings. Boron nitride is isoelectronic with C_2 (i.e., BN and C_2, have the same number of valence electrons) and forms structures similar to carbon. For example, BN can form layered sheets (similar to graphite) that are covalently bound within the sheets but have only dispersion forces between the sheets. As a result, this form of BN makes a good high-temperature lubricant.

Cement

Cement was first discovered by the Romans, who used lime, volcanic ash, and clay to make a pourable slurry that hardened into a rock-like substance. The Romans used cement to construct the 43.3-m diameter dome of the Pantheon, a 2000-year-old edifice. This dome remains the largest unreinforced concrete dome in existence. The majority of the cement used today is Portland cement. The original Portland cement was patented in 1824 by an English bricklayer named Joseph Aspidin (1788–1855). The hardened cement resembles a prestigious building stone from the Isle of Portland in southwest England and derives its name from this resemblance.

The Roman Pantheon, still a popular tourist attraction, sits in the center of the heart of ancient Rome.

Portland cement is a powdered mixture consisting mostly of limestone ($CaCO_3$) and silica (SiO_2), with smaller amounts of alumina (Al_2O_3), iron(III) oxide (Fe_2O_3), and gypsum ($CaSO_4 \cdot 2\,H_2O$). The powdered mixture reacts with water in a number of complex reactions that produce a final rock-like substance. Unlike clays, which lose water upon setting, Portland cement reacts *with* water as it hardens. The hardening process involves the formation of Si-O-Si bridges that produce fibrous structures. These structures bond strongly to each other (and most other substances).

Portland cement is combined with sand and pebbles to make **concrete**, the most widely used building material in the world. Concrete dramatically revolutionized construction. Before concrete, buildings were made exclusively by arranging the materials piece by piece. With the development of concrete, buildings could literally be poured into place. Concrete is used extensively to make foundations, walls, buildings, bridges, aqueducts, roads, and dams. About half of all the structures humans construct are made of concrete.

Glass

Glassblowing involves blowing air into a hot piece of glass to form spherical shapes.

Silica melts when heated above 1500 °C. After melting, if cooled quickly, silica does not crystallize back into the quartz structure. Instead, the Si atoms and O atoms form a randomly ordered amorphous structure called a **glass**. Silicate glass is transparent, impervious to water, and an outstanding material for making windows and drinking vessels. The Egyptians and Greeks likely made glass objects; however, the Romans in the first century AD were the first to extensively develop glassmaking. They discovered that adding sodium carbonate to silica dramatically lowers its melting point, allowing glass to form at much lower temperatures. In addition, they developed glassblowing, which involves melting glass and then using a tube to blow the glass into spherical shapes.

shapes.

When SiO_2 is made into a glass, the result is called **vitreous silica** or **fused silica**. This type of glass is hard, resists high temperatures, has a low thermal expansion, and is transparent to both visible light and ultraviolet light. Vitreous silica is too expensive for most common applications (because of the high temperatures required to produce it). The most common modern glass is **soda-lime glass**, which is also referred to as *window glass*. Soda-lime glass is about 70% SiO_2 with the balance being mostly Na_2O and CaO. This type of glass is transparent to visible light (not ultraviolet) and has a high thermal expansion, but it is less expensive to make and form into desired shapes than vitreous silica.

One disadvantage of soda-lime glass is its tendency to crack under thermal shock. Adding boric oxide (B_2O_3) to the glass mixture instead of CaO produces **borosilicate glass** (also known as **Pyrex®**), which expands less when heated. As a result, vessels made of Pyrex® can withstand heating and cooling cycles that would shatter soda-lime glass. The beakers, flasks, and other glassware found in most chemistry labs are made of borosilicate glass.

Leaded glass (often called *crystal* even though it is not a crystal) results when PbO is mixed with SiO_2 and a couple of other minor components. This type of glass has a higher index of refraction (it bends light more than ordinary glass), which results in more brilliant looking glassware. It also makes a ringing sound when tapped, which is a common test to distinguish lead crystal from ordinary glass. Recent concerns about the toxicity of lead in leaded glass have led to the development of lead-free alternatives (often called lead-free crystal) for stemware and drinking glasses, which has properties similar to those of leaded glass but without the negative health risks.

Leaded glass has a higher index of refraction than ordinary glass, making it look more brilliant.

> The amount of lead that leaches into a drink from leaded glass over a short period of time is likely inconsequential. However, storing drinks in leaded glass for long periods of time can lead to elevated lead levels in the liquid.