Chapter 2
Ceramic Packaging Materials

Abstract The term 'ceramic' refers to a category of materials that can be all defined as inorganic and non-metallic, and whose chemistry is mainly based on silicon structures. Substantially, these products are subdivided in two categories, depending on the main component: glass on the one hand, and minor ceramic materials like china, porcelain and earthenware on the other side. Common glasses can have different chemical composition, leading to their own colour, thermal or mechanical resistance. Silicon, commonly represented as silica, is found as silica or silicates. With relation to the crystalline structure, silicon's four valences lead to a structural unit in which each silicon atom is located at the centre of a tetrahedron. For this reason, crystalline structures are typical and commonly found in all silicon-based ores. Glass packages are well known because of their optical, thermal and mechanical properties. On the other side, non-glass packages are commonly subdivided in two subgroups: porous earthenware and non-porous porcelain. Each different sub-type shows peculiar properties with notable importance when speaking of food packaging applications.

Keywords Ceramic · Glass · Non-porous porcelain · Porous earthenware · Glass physical properties · Ultraviolet transmission coefficient

Abbreviations

SiO_2 Silicon dioxide
UV Ultraviolet

2.1 Ceramic Packaging Materials: An Overview

In this section, the term 'ceramic' refers to a category of materials that can be all defined as inorganic and non-metallic, and whose chemistry is mainly based on silicon structures. Some minor ceramic materials like china, porcelain and earthenware are also used for the production of containers. However, less relevance

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will be reserved to these products being glass the most important and used material for packaging purposes. Ceramic containers are used for a wide variety of liquid, solid and semisolid foods, but the main use is typically for liquids and the bottle is the most common shape used. However, cups, jars, bowls, vases, amphora, as well as big containers such as tanks, reservoirs, cisterns and vessels are also made by ceramic materials and can get in contact with foods and beverages.

2.1.1 Glass

According to one of the most accurate and available definitions (ASTM 2010), glass is 'an amorphous, inorganic product of fusion that has been cooled to a rigid condition without crystallising'. In fact, the word glass applies more to a physical state of the matter than to a chemical structure; some special organic materials are also named 'glass' or 'glassy' (Mark et al. 1985).

Common glasses can have different chemical composition (Table 2.1), leading to their own colour, thermal or mechanical resistance. Anyway, the major component is always silicon (60–75 %), commonly represented as silica or silicon dioxide (SiO_2). Silicon is the most plentiful element on earth after oxygen; it is found as silica in quartz, sand, cristobalite, and many other minerals. In addition, silicon can be found as silicate—$[SiO_4]^{4-}$—in minerals such as feldspar and kaolinite, where silicon dioxide is joined to some metal oxides. With relation to the crystalline structure, the distinctive form of all silicon-based ores, silicon's four valences lead

Table 2.1 Chemical composition (expressed as %) of common glasses

	Soda-lime glass	Borosilicate glass	Amber	Green	Lead glass	Glass ceramics
Silica	71–73	65–85	72.6	72.1	60	40–70
Boron oxide	–	8–15	–	–	–	–
Sodium oxide	9–15	3–9	12.8	2.9	1.0	–
Potassium oxide	0–1.5	0–2	1.01	0.87	14.9	–
Calcium oxide	7–14	0–2.5	11.1	9.8	–	–
Magnesium oxide	0–6	–	0.23	1.74	–	10–30
Barium oxide	–	0–1	–	–	–	–
Lead oxide	–	–	–	–	24.0	–
Aluminum oxide	0–2	1–5	1.81	1.93	0.08	10–30
Mixture of iron (III) oxide and titanium dioxide	0–0.6	–	0.34	0.37	0.02	–
Chromium (III) oxide	–	–	0.002	0.17	–	–
Sulphur trioxide	–	–	0.08	0.09	–	–
Titanium dioxide	–	–	–	–	–	7–15

to a structural unit, in which each silicon atom is located at the centre of a tetrahedron, having four oxygen atoms at the corners (Fig. 2.1).

The tetrahedron arranges symmetrically and continuously, each oxygen being connected to two silicon atoms, leading to a well-ordered crystalline organisation. Silica shows a clear polymorphism being able to crystallise at different temperatures and leading to various forms available in the different ores (Demuth et al. 1999):

$$\alpha - \text{quartz} \overset{579^\circ\text{C}}{\Leftrightarrow} \beta - \text{quartz} \overset{857^\circ\text{C}}{\Leftrightarrow} \gamma - \text{tridymite} \overset{1{,}470^\circ\text{C}}{\Leftrightarrow} \beta - \text{cristobalite} \qquad (2.1)$$

The crystalline state of SiO_2 results in very high melting temperature, high toughness, low or null transparency and poor inertness. These features are opposite to expected characteristics of glass packages, when speaking of use and manufacture. Actually, the glass-making process changes inorganic ingredients (Table 2.2) from the crystalline to the amorphous state, through a mainly physical transformation which occurs at temperature above 1,450–1,500 °C. Crystalline structures are lost during this process and tetrahedral units reorganise in an amorphous structure (Fig. 2.2) including atoms of sodium, calcium and magnesium in empty spaces created by the rearrangement. Included metals come from minor ingredients of the

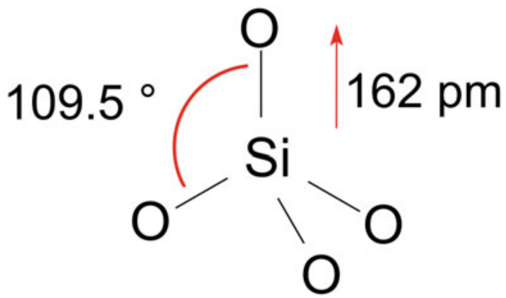

Fig. 2.1 With relation to crystalline form of silicon containing ores, each silicon atom is located at the centre of a tetrahedron, having four oxygen atoms at the corner. BKchem version 0.13.0, 2009 (http://bkchem.zirael.org/index.html) has been used for drawing this structure

Table 2.2 Ingredients used in the glass-making process and relative functions

Ingredient	Function
Silica sand	Former
Boron oxide	Former
Cullet (recycled glass)	Former, fluxes, energy saving
Sodium carbonate	Fluxes
Potassium carbonate	Fluxes
Calcium carbonate	Stabiliser
Magnesium carbonate	Stabiliser
Barium carbonate	Stabiliser
Sodium sulphate	Fining agent
Metal oxides	Colourant, bleaching

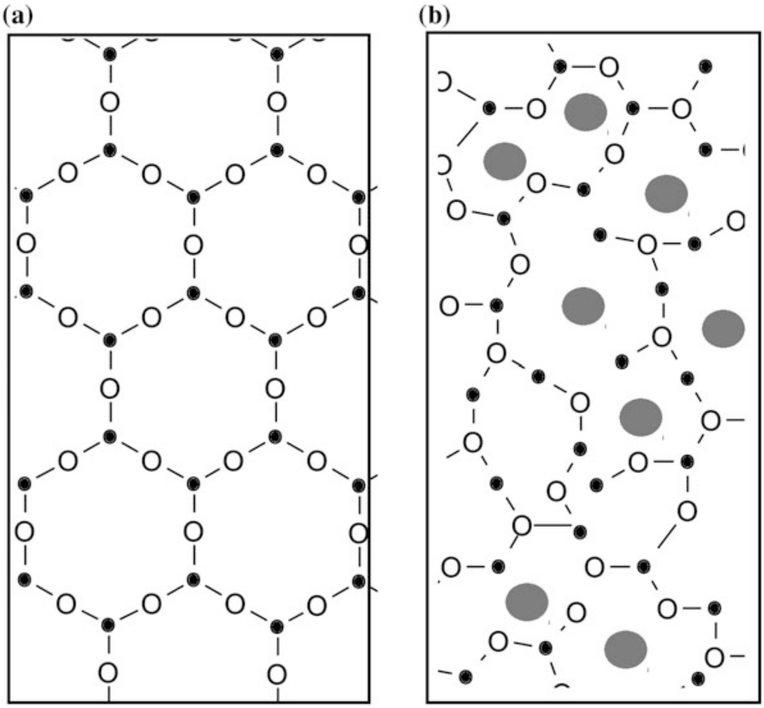

Fig. 2.2 A two-dimensional representation of the crystalline structure **a** (the *black circles* correspond to Silicon, the *clear* and *bigger circles* to Oxygena) of silicone containing ores and the amorphous one **b** (the *full grey biggest circles* to metals, such as sodium, calcium or magnesium) obtained after glass manufacture, which includes atoms of sodium, calcium and magnesium in the empty spaces

glass-making mixture (Lehman 2004; Nixon 2015) which are fundamental in establishing optical, thermal and mechanical properties of the final material (Table 2.3). The ability of the 'Si–O–Si' bond to display angles from 120 up to 180° (Chiang et al. 1997; Varshneya 1994; Rawson 1980) makes possible this amorphous, randomised structure and correlated main properties of glass containers.

2.1.1.1 Thermal Properties of Glass Packages

Glass is an amorphous material and it does not display a sharp melting temperature. In fact, it progressively softens until a true liquid state is achieved; subsequently, it becomes solid over a temperature range when cooling. In the most common glass used for packaging (a soda-lime glass based on a mixture of sodium carbonate and calcium carbonate), the higher the concentration of alkali, the lower the tetrahedral connectivity. This arrangement decreases the glass transition temperature (Chiang et al. 1997; Varshneya 1994) leading to lower temperatures of melting and

Table 2.3 Physical properties of soda lime versus borosilicate glasses (Lehman 2004; Nixon 2015)

Ingredient	Soda-lime glass	Borosilicate glass
Coefficient of linear expansion (°C^{-1}) α (0–300 °C)	8.6×10^{-6}	3.25×10^{-6}
Strain point (°C)	511	510
Annealing range (°C)	480–575	560
Soften point (°C)	575	821
Temperature limits (°C)		230 (normal service)
Maximum thermal shock (°C)		160
Density (g cm^{-3})	2.44	2.23
Young's modulus (GPa)	10.2	9.1
Shear modulus (modulus of rigidity) (GPa)	4.2	3.8
Refractive index (λ = 589.3 nm)	1.515	1.474

deformation, which are very useful behaviours for glass containers manufacture. Furthermore, glass melting and moulding can be indefinitely repeated without any loss of the original properties, giving great and unsurpassed opportunities of recycling to this material.

Glass has the lowest coefficient of thermal expansion among any packaging material (about 6–8 × 10^{-6} °C^{-1}). On the other side, this feature might augment the risk of failures when a glass container, closed with metal or plastic closures, undergoes to thermal treatment like pasteurisation or sterilisation. The most important thermal property of glass bottles or jars is the capability to withstand sudden thermal changes. Even if glass has low thermal conductivity (0.96 W m^{-1} °C^{-1} at 30 °C), a temperature variation deeply modifies the inner stress equilibrium. When glass is quickly cooled, tensile stresses are established on the surface from which the heat is removed first; tensile stresses are compensated by compressive stresses in the inner structure. On the contrary, when glass matrices are quickly heated, compressive forces are set up on the surface where its temperature increases first, with tensile forces on the opposite. Upon the temperature equilibrium is slowly achieved, however, these stresses disappear. Since glass is more sensitive to tensile stresses than to compressive ones, as many materials, sudden cooling steps are the most dangerous processes. The thermal strength of glass objects is influenced by the chemical composition; the presence of boron and aluminum oxides increases hugely the heat resistance (Table 2.3), like in Pyrex® or Corning® glasses respectively.

2.1.1.2 Mechanical Properties of Glass Packages

Glass containers are known as fragile objects: despite the high strength of the covalent bond between silicon and oxygen, an initiated fracture quickly propagates in glass items (Zhao et al. 2006). In fact, the continuous structure of interconnected tetrahedral SiO_2 can prevent plastic flows of the material; the same thing can be affirmed for stress absorption. Moreover, the breakage occurs when widely varying stresses are observed. Glass objects always have superficial or internal defects (cracks, flaws), even if not always visible, leading at their tip to a stress amplification. For these reasons glass bottles are tested for internal pressure resistance, vertical load strength and resistance to impact.

Vertical loads are quite common in glass packages uses, e.g. during stacked storage or during closure application. Applied pressures can achieve 7 MPa in the last situation, generating tensile stresses on the shoulder and on the bottom. It has to be noted that glass bottles contain very often carbonated beverages, leading to differential pressure stresses across container walls (0.5–1.0 MPa). The weight and thickness of the final object can increase the resistance to such stresses with more efficacy than glass composition (Hambley 1986); heavy glass bottles, like those for sparkling wines, can resist internal pressure up to 7 MPa.

2.1.1.3 Optical Properties of Glass Packages

Glass packages are well known and appreciated for their transparency in the visible wavelengths range and to microwaves, leading to low energy dissipation, i.e. to negligible reduction in transmitted energy. Moreover, glass objects show very low ultraviolet (UV) transmission coefficients: this feature, often considered marginal, is more useful when speaking of quality protection of foods and beverages. These good properties are due both to the chemical nature of the ingredients and the acquired amorphous structure. The glass clearness may be modified by selecting appropriate metal oxides as minor ingredients, as well as the colour. Concerning UV transmission, the presence of alkaline oxides improves UV barriers provided by pure silica which, by itself, has a cut-off value around 150 nm.

2.1.2 Ceramics and Earthenware

Various materials, obtained by cooking a mixture of clay and water, are traditionally used to contain foods and beverages; they are variously indicated (not always properly) as ceramics, china, porcelain, pottery, stoneware, earthenware (Table 2.4). Clays are fine-grained soil, combined with hydrous aluminum phyllosilicates or other silicate minerals, traces of metal oxides and organic matter. Silicate minerals, the largest component, are easily available materials: they constitute approximately 90 % of the Earth's crust. These minerals are classified on the basis of their silicate structure, which may contain different ratios of silicon and oxygen.

Earthenware jars have been extensively used as food and beverage containers in ancient times by Greeks and Romans (Twede 2002). However, ceramic materials are still widely used for tableware, cookware and storage vessels. Several different types of these materials can be produced by selecting appropriate clays, water mixtures and the firing process.

Table 2.4 Tentative definitions of ceramics

Ceramic	Any article made of natural clay, non-metallic minerals mixed in various formulas with water and sometimes organic materials, shaped, processed or consolidated at high temperatures. Ceramic materials in contact with foods are used in all forms of pottery from crude earthenware to the finest porcelain
Pottery	It usually falls into three main classes: porous-bodied pottery, stoneware and porcelain. Raw clay is transformed into a porous pottery when it is heated at about 500 °C. Pottery commonly describes functional clay objects that serve a purpose in daily life (as plates, cups or vases)
Terracotta	Terracotta ('baked dirt' from the Latin *terra cotta*) is a type of red earthenware usually unglazed. The typical firing temperature is around 1000 °C. The iron content gives the fired body a brownish colour, which varies considerably being yellow, orange, red, *terracotta*, pink, grey or brown
Earthenware	It is made from either red or white clay baked at low temperature, typically 1,000–1,080 °C. Since it has not been fired to the point of vitrification, earthenware is porous and must be glazed in order to be watertight. It is generally more fragile than other types of pottery
Stoneware	Stoneware is composed of fire clay and ball clay as well as feldspar and silica. It is fired at high temperatures, typically 1,148–1,316 °C (2,100–2,400 °F), and is inherently non-porous. The white, grey or brown clay vitrifies during firing; so, the surface will be watertight. Stoneware is harder, stronger and more durable than earthenware
Porcelain	Porcelain is a white clay body used in making functional and non-functional pieces. Basically, the chemical composition of porcelain is a combination of clay, kaolin (a primary clay known for its translucency), feldspar, silica and quartz, but other materials may be added
Fine China	The fine china is fired at a lower temperature—around 1,200 °C (2,200 °F). Fine china is much softer than porcelain, making it much more suitable for applications such as plates and cups
Bone china	Bone china is a type of soft-paste porcelain made white and translucent by the addition of calcined animal bone to the body. The quality of the finished product is based on how much bone is in the mixture: a high-quality bone china should contain 30 to 40–45 % bone. Bone gives the fired body high levels of translucency and a unique milky white colour

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A sharp classification is made into porous earthenware and non-porous porcelain (Chandler 1967; Hlavac 1983). Porous earthenware can be glazed for giving impermeability and brilliance obtaining china, porcelain and others products. A common way of manufacturing these containers involves drying of the wet shaped body, cooking at 800–1,000 °C. Finally, the manufacture is completed after a glazing or enamel coating through a 12 h—treatment at higher temperature (1,300–1,500 °C). Potteries of different glazing treatments are believed to play a fundamental role for attaining natural ripening in traditional oriental fermented foods.

Microporous earthenware are even more interesting because they may be tailored with controlled glazing or heating treatments to offer unique gas and moisture permeation properties (Seo et al. 2005). Carbon dioxide/oxygen permeability ratios close to unit may offer a new potential for respiring products packaging when these values are close to 1 (Kader et al. 1989). In addition, fermentation processes may be easily controlled (Yun et al. 2006). Furthermore, included metals have been supposed to act as low far—infrared emitters, leading to the inhibition of microbial growth (Vatansever and Hamblin 2012).

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