Silicate and non-silicate Ceramics

The abundance of oxygen, silicon, and aluminum implies that the earth's crust consists predominantly (more than 97%) of silicate minerals, particularly aluminosilicates. Since the earth's crust is primarily made up of silicates, we can understand why all ceramics are silicate materials.

In industry, silicate ceramics form the majority of the world's ceramics products. They are often described as traditional ceramics products.

Ceramics Main Raw Materials

Each mineral raw material has a specific influence on the rheology of the materials, the development of the microstructure, the phases formation during the heat treatment, and the properties of the finished product. The manufacture of all silicate ceramics requires a large number of raw materials, i.e. clays, feldspars, and silica that considered the most commonly used.

1. Clays

Products such as bricks, white wares, cement, glasses, and alumina are considered traditional ceramics because they are derived from either (1) crude minerals taken directly from deposits or (2) refined minerals that have undergone beneficiation to remove mineral impurities and control the physical characteristics. Most traditional ceramics are fabricated using substantial amounts of clay.

Clays are distinguished from other naturally occurring raw materials by their development of plasticity when mixed with water.

Clay minerals continue to be widely utilized in the production of traditional ceramics and other products due to their ubiquity and low cost combined with properties that include plasticity during forming, rigidity after drying, and durability after firing.

Clays are hydrated silico-aluminous minerals whose structure is made up of sheets by stacking of two types of layers containing, respectively, aluminum (Al-O/OH) in an octahedral structure and silicon (Si-O) in the tetrahedral structure. For this reason, the clay minerals are classified as phyllosilicates because of their layered structure.

When the sheets are separated by films of water, the platelets slide over one another to add plasticity to the mixture. This plasticity is the basis of the use of clay for pottery.

Moreover, when the clay water mixture is dried it becomes hard and brittle and retains its shape. On the firing at temperatures of about 950°C, the clay body becomes dense and strong.

The most common clay that has all these above characteristics is usually called kaolinite clay.

Kaolinite Structure

Kaolinite with formula ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) or ($Al_2Si_2O_5(OH)_4$, is the most common among argillaceous minerals used in ceramics. A projection and structure of its crystalline structure is represented in fig.1. It consists of an alternate stacking of $[Si_2O_5]^{-2}$ and $[Al_2(OH)_4]^{+2}$ layers, which confer to it the laminated character favorable to the development of the plates.

The degree of crystallinity of the kaolinite present in clays is highly variable. It depends largely on the origin conditions and the content of impurities introduced into crystalline lattice.

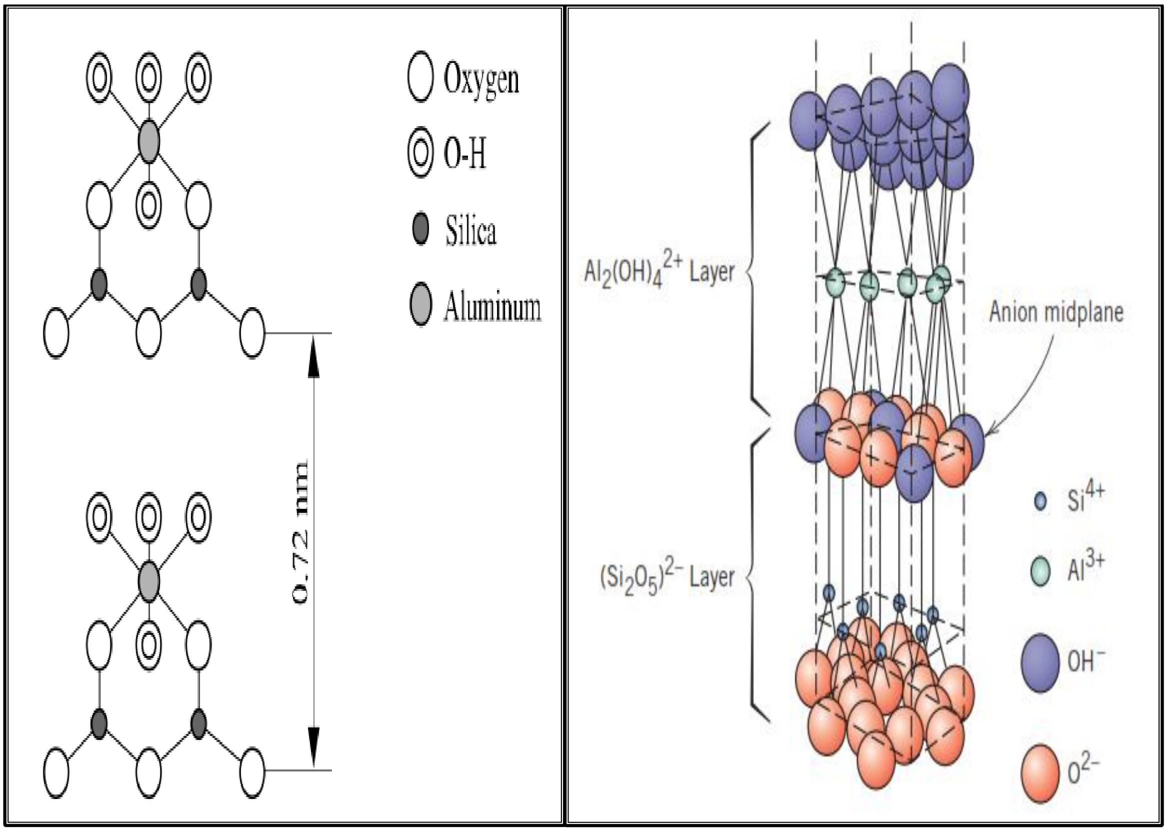

Fig (1): Structure of kaolinite clay.

Transformations of Kaolinite

Kaolinite group clays undergo a series of phase transformations upon thermal treatment in the air at atmospheric pressure and these transformations are described below.

A. Drying

Below (100 °C), water will slowly remove from the kaolin. Between 100 °C and 550 °C, any remaining liquid water, organic materials, and impurities are expelled from kaolinite. During this temperature range, the expulsion of water is reversible: if kaolin is exposed to water, it will be reabsorbed and collapse into fine particulate form, the next transformations are not reversible and represent permanent chemical changes.

B. Metakaolin

Endothermic dehydration of kaolinite begins at (550–600 °C) producing disordered metakaolin, but continuous hydroxyl loss is observed up to 900 °C. Metakaolin is a mixture of amorphous silica and alumina.

$$Al_2Si_2O_5(OH)_4 \longrightarrow Al_2Si_2O_7 + 2\ H_2O.$$

C. Spinel

Between (925–950 °C) converts metakaolin to an aluminum-silicon spinel structure, which also referred to as a gamma-alumina structure

$$2Al_2Si_2O_7 \longrightarrow Si_3Al_4O_{12} + SiO_2.$$

D. Platelet Mullite

Upon calcination above (1050 °C), the spinel phase nucleates and transforms to platelet mullite. Also, during this reaction, crystalline silica in the form of tridymite is released.

$$2Si_3Al_4O_{12} \longrightarrow 2\,(3Al_2O_3 \cdot 2SiO_2) + 5SiO_2$$

E. Needle Mullite

Finally, at (1400 °C) the "needle" form of mullite appears and highly crystalline silica in the form of cristobalite is formed, that offering substantial increases in structural strength and heat resistance but no chemical transformation occurs in this stage.

It should be noted that the impurities present, the degree of the crystallinity, and the speed of the heating influence each of these transformations.

Mullite

Mullite ($3Al_2O_3{\cdot}2SiO_2$) does not exist in nature in large quantities and must be produced synthetically. It has many properties that make it suitable for high-temperature applications.

Mullite has a very small coefficient of thermal expansion (giving it good thermal shock resistance) and creep resistant when subjected to high temperature.

Most highly, it does not react readily with molten glass or with molten metal slags and is stable in the corrosive furnace atmosphere. Hence, it is used as a furnace lining and other refractory applications in iron, steel making, and glass industries. There are two commercial approaches to producing mullite: Sintering and Fusing.

Sintered mullite may be obtained from a mixture of the kyanite, a naturally occurring mineral found in metamorphic rocks, bauxite, and kaolin. This mixture is sintered at temperatures up to 1600 ^{0}C. The sintered quality contains (85–90%) mullite with the balance being mainly glass and cristobalite.

By fusing appropriate amounts of alumina and kaolin together in an electric-arc furnace at about 1750 ^{0}C a higher purity mullite can be made. The fused product contains (>95%) mullite, the rest being a mixture of alumina and glass.

Types of Clays Deposits

In nature, clays can be found either in the same location where they were formed or they can be found in a location where they were transported after formation.

Clay deposits that are found where they were formed are referred to as primary or residual deposits. The clays deposited that have been transported after formation are said as secondary or sedimentary deposits.

A. Primary Clays

Primary clay deposits are formed when rock formation is chemically attacked by water. The size and shape of deposit depends on the size and shape of parent rock.

The mineral constituents and impurities of primary clay deposit are also determined by the composition of parent rock, the degree of completion of the reaction, the impurities that are removed by solution during or after reaction, and impurities brought in during or after formation.

Most primary clay deposits contain a high proportion of impurities ranging from (10 to 40%) by volume. Yet, primary deposits tend to be low in iron impurities (Fe_2O_3), TiO_2, and organics.

The major mineral impurities can be removed by beneficiation techniques such as air or water flotation to yield usable clay, while removal of other impurities may require more involved treatment processes.

Clays that are white in color and have minimal iron-based impurities are often referred to as “kaolin” or “china clay”. The color upon firing varies from white to ivory depending upon the impurity content.

The highest quality clays are termed “white burning” because of the lack of coloring from impurities after heating.

B. Secondary Clays

Secondary or sedimentary clays are formed in one location and then transported to the location of the deposit by the action of wind or water. Often, mineral impurities present in the primary deposit are left behind during transport.

Impurity minerals such as quartz and mica are almost completely removed in some cases. However, other impurities such as TiO_2 and Fe_2O_3 are often picked up during transport. Secondary clay deposits tend to have distinct layers because of the repeated cycles of active deposition.

Secondary deposits can also be significantly larger than the primary deposits and contain a wider variety of clay mineral types, since clay can be transported in from different primary deposits. As with the primary clays, the color of raw secondary clays varies with impurities. Many secondary clays can be red or brown in color after the firing depending on the impurities present.

Clays Used in Ceramics Industry

Clays are categorized based on how they are used in the ceramics industry. The two major types of ceramic clay are china clay and ball clay. Other materials include fire clays, bentonite, and talc. Less materials including those classified as shales and stoneware clays are also of interest.

A. China clay

China clays are used to produce traditional ceramics when the color of the finished object and its high temperature performance are important. China clays usually contain large amounts of kaolinite, but can contain considerable amounts of other clay minerals. In all cases, the content of Fe_2O_3, TiO_2 and other potential coloring impurities is low, resulting in bodies that range in color from white to ivory. China clay is mainly found in both residual and secondary deposits.

China clays tend to have a moderate particle size (1–2 μm). Because of the particle size, china clays produce moderate plasticity during forming compared with other clays. Drying and firing shrinkage tend to be moderate. China clays are used in many traditional ceramics, including pottery, stoneware, and porcelains.

B. Ball clay

Ball clays are remarkable because of their high plasticity when mixed with water. The plasticity is a result of the fine particle size of this clay (0.1–1 μm), which is stabilized by a considerable content of organic matter (up to 2 wt%).

Because of fine particle size, the water demand for ball clays is higher than for most china clays. The fine particle size also gives the ball clay bodies higher green strength and higher fired strength than other clays. In state, ball clays range in color from light brown to nearly black, depending on the organic content. Ball clays are used in traditional ceramic due to workability and strength.

C. Fire clay

The term fire clay refers to secondary clays that are not ball clays or china clays, but can be used to produce refractory bodies. Fire clays are often found in coal deposits, but this is not true for all coal deposits.

The main sub-types of fire clays, in the order of increasing alumina content, are plastic fire clays, flint fire clays, and high alumina fire clays. Refractories made from fire clays set standard for performance in metal processing applications due to their low cost, high corrosion resistance, and excellent thermal stability.

D. Bentonite

Bentonites are highly plastic secondary clays that are used in small amounts as absorbents or as (binders/plasticizers) for different other materials. Bentonites are formed from volcanic ash.

Bentonites swell significantly when mixed with water and because of swelling and extremely high drying and firing shrinkages, bentonite is rarely used as a major constituent in a wide range of traditional ceramics; applications are confined to additives in a multiplicity of processes.

E. Talc

Talc is magnesium silicate structural occurs in secondary deposits and is formed by weathering of magnesium silicate minerals such as olivine and pyroxene. Historically, talc has been used widely in the electrical insulator applications and in paints.

F. Shales

Shale is a term that refers to sedimentary deposits that have been altered by compaction. Weathering of shales is one method for the formation of clays. Shales often contain high levels of iron, giving them a red color when fired.

G. Other Clays

A vast variety of other grades of clay mineral products have been used commercially. The names of these clays can be based on the ultimate application (earthenware clays, stoneware clays, brick clay, porcelain) or the fired properties (vitrifying clays).

Earthenware: refers to products produced from unbeneficiated clays with no additives. Earthenware bodies are typically formed by using a throwing or modeling process. Earthenwares are self-fluxing during firing due to alkali content. Earthenware is fired at low temperatures, typically between (950-1050 °C). It is porous, relatively coarse, red or, even black after firing. The term “pottery” is often used to signify earthenware clays.

Stoneware clays: can be used without beneficiation or any additives to produce ware with high temperature firing (1200 –1300 °C). It is vitrified, or at least partially vitrified, and so it is nonporous and stronger.

Fired stoneware objects usually have buff or gray color and are used as electrical insulators, cookware, decorative items, drain pipes, tiles, and tableware. Stoneware is formed by casting, throwing, or pressing and has lower (Fe_2O_3) than earthenware.

Brick clays: tend to be high in alkalis and iron, but low in alumina. The clays usually have moderate to high plasticity, which facilitates the forming process.

Porcelain: white, thin, and translucent ceramic made from kaolin, quartz, and feldspar. It is an example of vitreous ware. Fired at (1250–1300 °C) produced soft-paste porcelain with low clay content and less plasticity. Hard-paste porcelain with high alumina content derived from clay and feldspar, which permits good plasticity and formability, but requires a high firing temperature (1300–1400 °C).

Vitreous clays: this type of clay depends upon whether clay was melted during the firing process into a glassy (vitreous) substance or not. Vitreous clays are a type of clay that has been fired at high temperatures to create a durable, non-porous material. These clays are characterized by their hardness, strength, and resistance to water absorption.

Vitreous clays contain a high proportion of fine-grained materials, such as silica, which allows them to vitrify or become glass-like when fired at temperatures above 1200 degrees Celsius. This process fuses the particles together, resulting in a dense and hard ceramic material.

Unlike earthenware clays, which are fired at lower temperatures and remain porous, vitreous clays have a low water absorption rate. This makes them suitable for functional pottery and ceramics since they are less likely to absorb the liquid and are more resistant to staining.

2. Feldspar

Feldspars constitute an abundant mineral group and make up an estimated (60%) of the earth's crust, and they are present in several sedimentary deposits and are found in all igneous and metamorphic rocks. Feldspars minerals are defined as silicate ceramic and classified according to their composition into:

1- **Orthoclase:** is a mineral rich in potassium with a composition of $K_2O.Al_2O_3.6SiO_2$.

2- **Albite:** is a mineral rich in sodium with the composition of the $Na_2O.Al_2O_3.6SiO_2$.

3- **Anorthite:** is a mineral rich in calcium with the composition of $CaO.Al_2O_3.2SiO_2$.

4- **Petalite:** is a mineral rich in lithium with the composition of $Li_2O.Al_2O_3.8SiO_2$.

Orthoclase and albite are widely used as a flux. Anorthite is rather regarded as a substitute to chalk. Potassic feldspar is appreciated by ceramists because its reaction with silica leads to formation of a liquid whose relatively have high viscosity.

This behavior is considered a guarantee phase against the excessive deformation of pieces during heat treatment. The glass industry uses most of the feldspar produced. Feldspar is a source of Al_2O_3, which improves the mechanical properties of the glass such as its scratch resistance and its ability to withstand thermal shock.

3. Silica

Silica is the most abundant mineral in the earth's crust (show fig.2), existing in a wide variety of crystalline and noncrystalline forms due to the flexibility of linkage among crystal structure, also silica defines as a polymorphic material found in nature in an amorphous form like opal and pebbles or in crystallized forms like quartz, cristobalite, and tridymite.

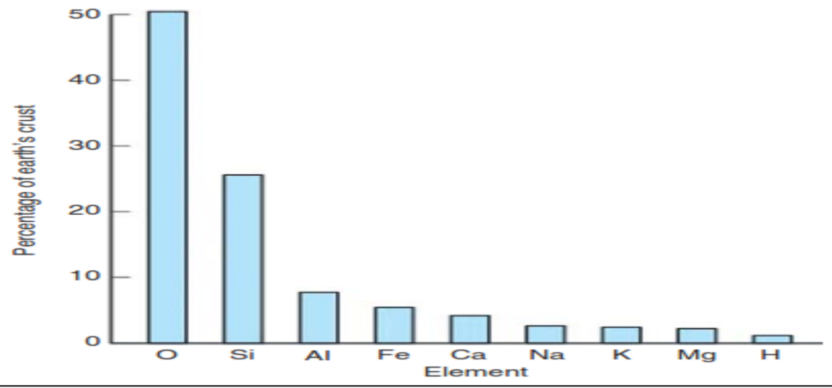

Fig (2): The relative abundance of elements in the earth's crust.

A major source of silica is sand. In ceramics industry, high-quality silica sand with high SiO_2 content (>99.5%) is used. Sand is defined as granular rock particles produced by physical beneficiation of the rocks by the crushing process.

These sands have various chemical compositions, determined by the type of rock being mined. The stable room temperature form of silica is quartz, which is itself a widely available mineral and ingredient in many commercial ceramics and glasses due to its properties that permit it to be used in high temperature and corrosive environments and as abrasives, refractory materials, fillers in paints, and optical components.

Silica undergoes a series of phase transformations upon heating; the form in which silica is found determines the thermal properties of silicate ceramics. Under ambient conditions, α-quartz is the stable thermodynamically favored polymorph phase of the silica at room temperature.

At 573°C, α-quartz is transformed into β-quartz, generally similar in structure but with less distortion results from the volume change (about 2%) due to this transformation. This thermal transformation preserves the optical activity of quartz.

Heating quartz to 867°C leads to the transformation of β-quartz into β-tridymite with a volume increase of (12%), involving the breaking of (Si–O) bonds to allow the formation of a hexagonal structure with lower density. Quartz-tridymite phase transformation involves a high activation energy process that results in the loss of the optical activity of the quartz.

The heating of β-tridymite to (1470°C) gives the β-cristobalite with (FCC) crystal structure that represents the highest crystalline and temperature polymorph of the silica with a volume increase of about (5%). Further heating of cristobalite results in melting at 1723°C. All these phase changes are reversible under suitable conditions of slow cooling as shown in figure (3).

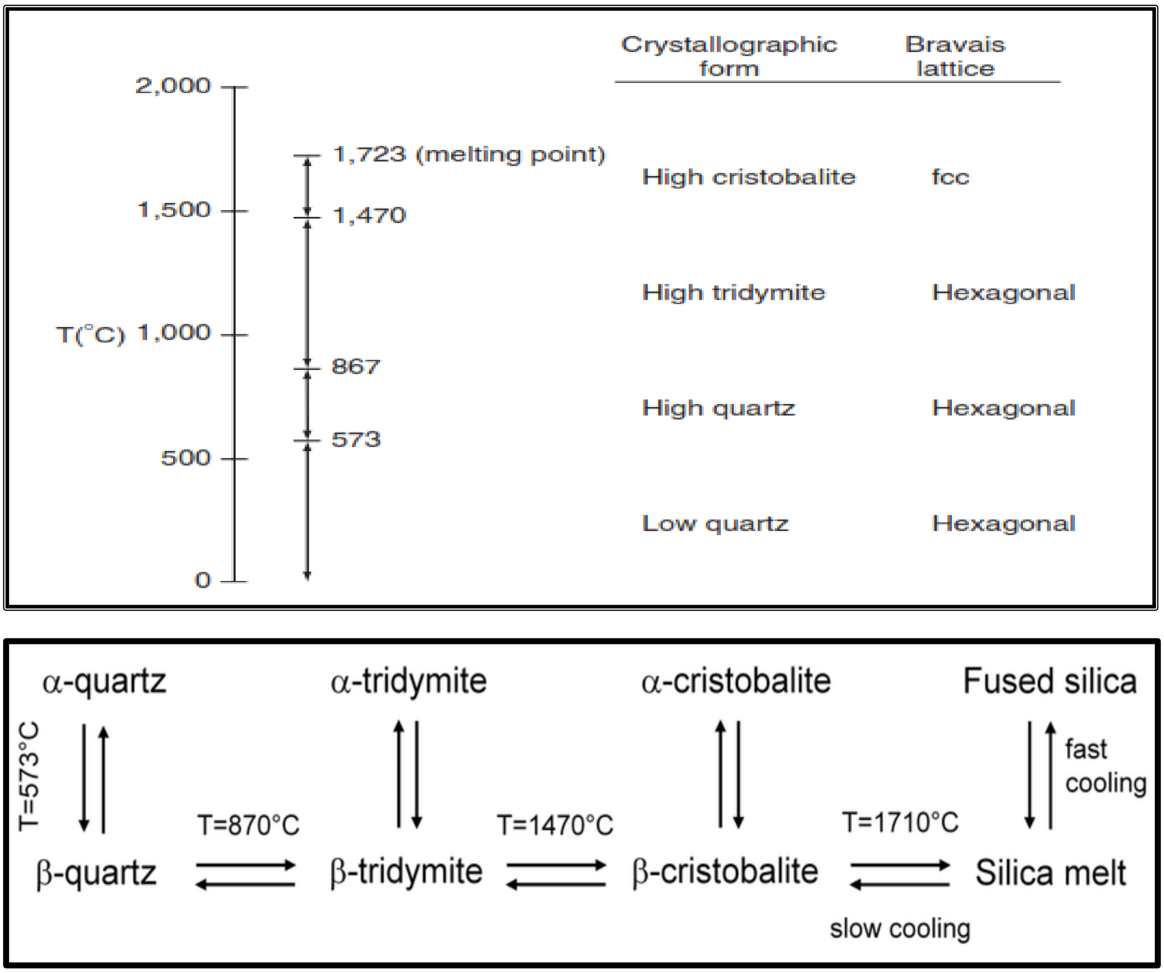

Fig (3): Principal silica polymorphs at atmospheric pressure.