6. Silicate ceramics

6.0 Introduction

The main types of *silicate ceramics* are based either on alumosilicates (→ *kaolin- or clay-based* ceramic such as porcelain, earthenware, stoneware and bricks; system K_2O-Al_2O_3-SiO_2) or on magnesium silicates (→ *talc-based* technical ceramics such as steatite, cordierite and forsterite ceramics; system MgO-Al_2O_3-SiO_2). Special groups are zircon- and mullite-based fine ceramics (for electrical insulators) as well as low-thermal expansion ceramics in the system Li_2O-Al_2O_3-SiO_2 (for thermoshock-resistant tableware), which have an extremely narrow sintering interval and are therefore preferentially produced by glass-ceramic techniques (i.e. devitrification of glasses by nucleation and growth). Silicate ceramics are conventionally subdivided into coarse or fine and, according to water absorption, into dense (< 2 % for fine and < 6 % for coarse) or porous ceramics (> 2% and > 6 %, respectively).

6.1 Kaolin- and clay-based ceramics and dental porcelain

In the ternary raw material diagram (kaolin/clay–feldspar–quartz) the composition of all kaolin- and clay-based ceramics lies in the mullite field, that of dental porcelain in the leucite field.

- *Main types of dense silicate fine ceramics*:

    - Hard porcelain (the majority of middle-European porcelains – common firing temperatures approx. 1400 ± 50 °C).
    - Soft porcelain (e.g. old Asian and “vitreous china“, firing temperature 1200–1300 °C, higher content of fluxes).
    - Bone china (English, based on up to 50 % bone ash as a raw material – apart from kaolin, quartz), frit porcelain (French, based on glass frits, 1150 °C) and “parian“ (unglazed ornamental porcelain with a low kaolin content of < 40 %).
    - Dental porcelain (feldspar content approx. 80 %, kaolin < 5 %, firing temperature < 1250 °C).
    - Electrotechnical porcelain for insulators; usually containing alumina (instead of quartz in earlier types of electrotechnical porcelain) in order to increase the mechanical and electrical strength (firing temperature approx. 1250 °C).

- *Hard porcelain:*

    - Porcelain is a densely sintered (defined by a water absorption < 2 %), white and translucent fine ceramic material prepared from natural raw materials; typical raw material mixture for hard porcelain: 50 % kaolin (part of which can be replaced by plastic clay), 25 % quartz and 25 % feldspar (preferentially K-feldspar).
    - Hard porcelain: after firing at 1400 ± 50 °C (with a relatively broad sintering interval) the final ceramic body consists of min. 50 % glass phase, max. 25 % mullite and max. 25 % residual quartz (which can be partly transformed to cristobalite); typical properties: density 2.3–2.5 g/cm^3, tensile modulus 70–80 GPa, Poisson ratio 0.17, flexural strength up to 100 MPa, thermal conductivity 1.2–1.6 W/mK, thermal expansion coefficient $4–6 \cdot 10^{-6}$ K^{-1}.

- At temperatures < 1100 °C the clay minerals (mainly kaolinite) dehydrate (→ metakaolinite above 500–600 °C) and form transient phases by releasing silica (→ defective spinel phase above 900–1000 °C), quartz undergoes polymorphic transitions and mixed K-Na-feldspars (perthites) may homogenize; at temperatures > 1100 °C: formation of feldspar melt causing liquid phase sintering (vitrification), partial dissolution of quartz (→ viscosity increase) and formation of mullite, either directly from the clay minerals (primary mullite) or by reaction of the clay minerals with the feldspar melt (secondary mullite).

- *Other types of kaolin- and clay-based silicate ceramics*:

  - *Earthenware*: porous, non-transparent fine ceramics with a white or colored body; typically fired at 1200 ± 50 °C and glazed with a PbO-containing glaze in a second firing cycle (at approx. 1100 °C); typical raw material compositions are 50–55 % clay, 40 ± 5 % quartz and 5–10 % feldspar; commonly used for tableware and tiles (for the latter, however, firing is a single-step process at about 1100 °C); "faience" is earthenware with a white body, "majolika" with a colored body, "terracotta" is coarse earthenware.
  - *Stoneware*: porous, non-transparent coarse ceramics with a colored body, typically fired at 1250 ± 50 °C (for sanitary ware, floor tiles and sewer pipes with a brown NaCl glaze); note, however, that another variant of stoneware (for tableware, tiles and chemical vessels) is a dense fine ceramic (vitrified stoneware); sanitary ware is between porcelain and stoneware.
  - *Bricks*: porous coarse ceramics, produced from cheap, local clays and loams, typically fired at 900–1000 °C; the loams should not contain pyrite and sulfates → $CaSO_4$ near the body surface (→ hydratation → volume expansion), neither calcite ($CaCO_3$) → may remain unreacted as free CaO after firing (→ hydratation → volume expansion); important properties: frost resistance (requires low porosity) and thermal insulation (requires high porosity).

6.2 Talc-based technical ceramics

All talc-based technical ceramics (ternary phase diagram MgO-Al_2O_3-SiO_2) require precise firing control (narrow sintering interval of a few °C).

- *Steatite ceramics*: basic raw materials – talc and clay (+ feldspar or $BaCO_3$); desired phase – protoenstatite in approx. 30 % glassy matrix; firing temperature 1350–1370 °C; problem to be controlled: transformation of the high-temperature proto- into (low-temperature) clinoenstatite, accompanied with volume expansion.
- *Cordierite ceramics*: basic raw materials – talc, clay and Al_2O_3; desired phase – cordierite in a glassy matrix; self-glazing effect by non-wetting melt exuded onto the surface; low thermal expansion coefficient ($2 \cdot 10^{-6}\ K^{-1}$). Note that only silica glass and Li_2O-Al_2O_3-SiO_2 (glass-) ceramics exhibit lower thermal expansion coefficients (< $0.5 \cdot 10^{-6}\ K^{-1}$) → higher thermal shock resistance.
- *Forsterite ceramics*: basic raw materials – talc and clay (+ $MgCO_3$); firing is less sensitive with respect to temperature (since at 1360 °C only a small amount of eutectic melt is formed and this amount does not change very much with temperature), but very sensitive to changes in composition; high thermal expansion coefficient ($11 \cdot 10^{-6}\ K^{-1}$) enables welding with metals (→ vaccuum electrotechnics).

Complex exercise problem: Use the *ternary phase diagrams* of the systems K_2O-Al_2O_3-SiO_2 and MgO-Al_2O_3-SiO_2 to discuss the phase composition of hard porcelain, cordierite ceramics, forsterite ceramics and steatite ceramics. *Additional explicit questions:*

a.) What are the essential high-temperature reactions for transforming the raw material mixtures into the final phase composition of these ceramic products after firing ?

b.) Which microstructural features contradict the prediction from the equilibrium phase diagrams and what are the reasons for the occurrence of non-equilibrium phases ?