12. Functional ceramics

12.0 Introduction

Of course even *structural ceramics* fulfill certain functions, usually based on the ability of ceramics to withstand mechanical and thermal loading, sometimes in chemically aggressive environments, including body fluids (bioceramics). So-called *functional ceramics* are ceramics designed for special applications requiring electric, magnetic or optical properties.

Basic electric and magnetic material properties: electric conductivity or resistivity (Ohm's law), electrical strength (breakdown voltage gradient), permittivity ε, permeability. Additional material parameters in alternating fields: complex permittivity and permeability, dielectric loss factor $\varepsilon'' = \varepsilon' \tan\delta$, where ε' = real part of $\varepsilon^* = \varepsilon' - i\varepsilon''$, loss angle δ, loss tangent $\tan\delta = \varepsilon''/\varepsilon'$ (→ similar relations for permeability). Further characteristics for nonlinear materials with hysteresis loops: initial permittivity or permeability (in small electric and magnetic fields), maximum permittivity or permeability, saturation polarization or magnetization, remanent polarization or magnetization, coercive force, loop shape and area.

Polarization mechanisms in dielectrics (with approximate frequency and EM wave ranges): Electronic (10^{15} Hz, UV/VIS), ionic (10^{12} – 10^{13} Hz, IR), orientational (high: 10^{12} – 10^{13} Hz, low: 10^3 – 10^6 Hz, MW/RF), space charge polarization due to interfaces with distance ranging from several mm (10^{-3} Hz; electrode polarization) down to several μm (10^3 Hz; dielectric response due to material heterogeneities → Maxwell-Wagner-Sillars theory). Only orientational and interfacial polarization influence the electric circuit characteristics of insulators (ε_r = < 10) and linear dielectrics (ε_r = 10–300) from 10^{-3} to 10^9 Hz and determine the properties of non-linear dielectrics (ε_r > 10000); easy polarizability → high permittivity. Electronic and ionic polarization influence the optical properties of glasses and ceramics.

12.1 Electrically insulating ceramics

Constitutive equation – Ohm's law → electric conductivity λ_e [$(\Omega\cdot\text{m})^{-1}$]; *material classes*: insulators < 10^{-10} $(\Omega\cdot\text{m})^{-1}$, semiconductors 10^{-7}–10^5 $(\Omega\cdot\text{m})^{-1}$ and conductors > 10^4 $(\Omega\cdot\text{m})^{-1}$; relative permittivity ε_r of insulators ε_r < 10. Typical applications of ceramic insulators: electronic circuit substrates, power transmission lines, spark plugs.

12.2 Ferroelectric ceramics

Ferroelectric materials exhibit polarization even in the absence of an electric field (spontaneous polarization) → hysteresis loop → non-linear dielectrics with very high permittivity (ε_r > 10000), exhibiting a maximum at the Curie temperature T_C (transition from the ferroelectric low-temperature to the paraelectric high-temperature phase). Typical structure: ABO_3 (perovskite); ferroelectric ceramics must exhibit anisotropic texture.

Two traditional classes of ceramic capacitors: TiO_2-based "type 1" capacitors (linear dielectrics with low losses; permittivity of only 10–300, but almost constant with temperature) and $BaTiO_3$- or PZT-based "type 2" capacitors (non-linear, lossy dielectrics; high permittivity, but strongly temperature-dependent). $BaTiO_3$ is tetragonal (and ferroelectric) at room temperature and cubic (and thus paraelectric) above T_C = 120 °C. Substitution of Ba^{2+} by Sr^{2+} or Pb^{2+} or of Ti^{4+} by Zr^{4+} or Sn^{4+} leads to a shift of the ε_r maximum in the frequency dependence; the height of the maximum can be influenced by other ions and the temperature dependence by controlling the stoichiometry → binary phase diagram $BaO-TiO_2$.

PZT ceramics are solid solutions of $PbZrO_3$ (T_C = 230 °C) and $PbTiO_3$ (T_C = 490 °C), preferentially with a composition of $Pb(Zr_{0.52},Ti_{0.48})O_3$ (T_C = 300 °C); similar: relaxor ferroelectrics ($PbNbO_3$ with Mg^{2+} or Zn^{2+}). Other applications use the piezo- and pyroelectricity of these ceramics (piezoelectric transducers in sensors / microphones and actuators / loudspeakers, pyroelectric IR radiation sensors etc.). Pore-free PLZT ceramics $(Pb,La)(Zr,Ti)O_3$ is transparent with a field-dependent birifringence → electro-optical applications). Key problem in processing PZT and PLZT ceramics: Pb volatilization.

12.3 Ferrimagnetic ceramics

Ferrites are mixed metal oxides containing iron oxide (Fe_2O_3) as their main component. Ceramics with only diamagnetic ions (Si^{4+}, Al^{3+}, Ca^{2+}, K^+, O^{2-}) cannot be ferrimagnetic. The three most important classes of commercial ferrites are

- *Soft ferrites* (coercivity H_C < 10 A/cm) with cubic *spinel structure*, e.g. Mn-ferrite ($MnFe_2O_4$ or $MnO \cdot Fe_2O_3$), Ni-ferrite, Mn-Zn-, Ni-Zn- and Mg-Mn-Zn-ferrites; oxide spinels are completely miscible → wide range of compositions and properties.
- Soft ferrites (coercivity H_C < 10 A/cm) with cubic *garnet structure* (for microwave applications, i.e. f >> 100 MHz), e.g. yttrium iron garnet $3Y_2O_3 \cdot 5Fe_2O_3$ ("YIG").
- *Hard ferrites* (coercivity H_C > 100 A/cm) with hexagonal *magnetoplumbite structure* (hexaferrites for permanent magnets), e.g. Ba-hexaferrites ($BaO \cdot 6Fe_2O_3$).

Like ferromagnetic materials (mainly metals), ferrimagnetic materials (mainly ceramics) exhibit spontaneous magnetization in the absence of an external field, domain structure, hysteresis behavior in the B-H-plot and a phase transition to the paramagnetic phase at the Curie temperature (in analogy with ferroelectric ceramics). Crystal structures of ferrites are tolerant to variations in chemical composition → wide range of properties.

12.4 Other functional ceramics

- *Semiconductors*: with positive or negative temperature coefficient of resistivity (PTC – cold conductors or NTC – hot conductors, respectively); varistors (e.g. ZnO) as surge protectors, termistors and oxygen sensors.
- *Ionic conductors* (e.g. β-alumina $Na_2O \cdot 11Al_2O_3$ for sodium-sulfur batteries – cationic conductor, or cubic ZrO_2 for solid-oxide fuel cells (SOFC) – anionic conductor).
- *Superconductors* (e.g. the high-temperature superconductor $YBa_2Cu_3O_{7-x}$).
- *Electro-optical ceramics* (e.g. for radiation sensors) and *scintillators* (emit light when struck by high-energy α- or β-particles or high energy photons, e.g. X-ray or γ-rays).

12.5 Principles of microwave technology for ceramic engineers

Microwaves (MW) are between radio frequency (RF) waves and infrared (IR) waves in the electromagnetic spectrum (frequencies 0.3 – 300 GHz, free-space wavelengths 1 m – 1 mm). Usual *operating frequency* 2.45 GHz (wavelength 12.2 cm); good MW absorbers: water, SiC; rate of energy absorption dependent on the loss factor; penetration depth; applications in ceramic technology (e.g. drying or sintering).