

Special ceramic materials

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Study instructions

You have received study material for the subject Special Ceramic Materials of the 6th semester of the Heat Engineering and Ceramic Materials study program for part-time study.

Prerequisites

To study this subject successfully, you are expected to complete the subject Thermodynamics of Ceramic Systems, Raw Materials for Ceramics Production, and the Technology of Refractory and Thermal Insulation Materials.

The aim of this subject and learning outcomes

The aim of this subject is to acquaint students with theoretical but also practical examples of special, advanced ceramics.

After studying the subject, students should be able to have:

Knowledge outcomes:

- *students will be able to define the structure, composition and the properties of special ceramic materials*
- *students will be able to evaluate the options and procedures for the preparation of materials with defined properties*
- *students will be able to describe the technological steps in production*
- *students will be able to include individual materials into practice*

Skills outcomes:

- *students will have general knowledge (an overall view) in the areas of special ceramics, etc.*
- *students will be able to specify their composition and structural characteristics, describe the production process and their actual application in practice*

When studying each chapter we recommend the following procedure:

At the beginning of each chapter, take sufficient time to study the entire chapter. Read the whole text and make notes of new expressions that you could return to and explain/review their meanings later. It is important to understand the global context. After studying the whole chapter, answer the questions listed at the end and try to remember the key concepts. If you can answer the questions easily, it means you understand the basics of the topic. If you want to expand your knowledge, you can find additional information in the references, in the library or on the Internet.

Communicating with teachers:

Students of part-time studies will be introduced to the time schedule, subject content and links to recommended literature in the introductory lecture. The requirements for acquiring the credit is a semester project on a given topic (Special Ceramic Materials), the form of the final exam is both written and oral. Students have the opportunity of consulting during the week at a pre-arranged time.

Consultations will be held by the guarantor or course lecturer:

- *during common tutorials*

- *individual consultation after arrangement via email or phone*

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SPECIAL CERAMICS



Time for study:

90 minutes



Objective

- to define the concept of ceramics, special ceramics and its basic characteristics
- to describe the basic types and the difference between traditional and special ceramics



Lecture

1.1 INTRODUCTION

Among the key materials of new technologies and technical solutions there also belong so-called "progressive ceramics", "advanced ceramics" and "high-tech ceramics". These new ceramics are definitely different from traditional ceramics. Progressive ceramics = synthetic polycrystalline material with a predominant content of inorganic, non-metallic phases prepared by sintering. The main factors raising interest in these materials are:

- their wide range of exceptional properties,
- the availability of raw materials,
- the lower energy demand for preparation,
- the more favourable ecological aspects of production compared to various metals.

With the development of technology and materials engineering, ceramics have an important role in many areas, including: electronics, communications, aviation, astronautics, environment, energy, etc. Many of the newly proposed and developed ceramic products are of a great importance both for daily and industrial use.

Since the mid-20th century there have been many kinds of ceramics produced with the use of raw materials and with a strictly controlled chemical composition. This represents ceramics which provide products of completely specific characteristics. These ceramics are characterized by their thermal, mechanical, electromagnetic, optical and biological functions. Their production is based on synthetic, even analytical pure raw materials, special forming techniques and a method of firing at a very high temperature. The products of special and structural ceramics show such extraordinary properties that directly caused reversals in certain fields.

□ Special ceramics

Special ceramic materials include the area of materials having their own characteristics e.g., magnetic, electrical, dielectric, pyroelectric, piezoelectric, conductivity, semiconductivity, superconductivity and other areas. A large group is represented by so-called electroceramics and also materials for electrical engineering. Another group is represented by the magnetic properties of the ceramics. The electrical and magnetic properties of ceramics varies considerably due to the

difference in composition and the crystal structure. Many ceramics have a high insulation quality and are used for cable insulation, while some of them have excellent high temperature superconductivity. Certain ceramics are biocompatible and are used for biomedical applications. These materials are used e.g. in orthopaedics, cardio surgery, vascular surgery, plastic surgery and other areas.

□ **Characteristics of special ceramics:**

- ceramic materials are defined as non-metallic materials,
- the preparation of classic ceramics is based on natural raw materials with a different granulometry,
- special (progressive) ceramics puts an emphasis on the creation of structures (microstructure) of a so-called regulated particle-size (grain-size) composition,
- special ceramics are made from synthetically produced materials with a predominant content of an inorganic, non-metallic phase (one phase can be glass),
- special ceramics are prepared by special methods of forming

□ **(Other) Characteristics of special ceramics:**

- a wide range of materials with irreplaceable properties,
- mainly made of synthetic materials,
- production with relatively low energy requirements,
- production is basically environmentally-friendly,
- usable in almost all industrial areas.

1.2 CLASSIFICATION OF ADVANCED CERAMICS

Many authors divide this type of ceramics in different ways. Table 1 gives a more detailed classification of special ceramics according to several criteria. At the same time, there are representatives named after each type of ceramics. Special products of special and structural ceramics can be divided into:

Table 1 Classification of advanced ceramics by selected criteria

According to the chemical composition	
Oxide ceramics	Al ₂ O ₃ , SiO ₂ , ZrO ₂ , MgO, Fe ₂ O ₃ , BeO, CaO, TiO ₂ , SnO ₂ , ThO ₂ , PuO ₂ , UO ₂ and oxides of rare earth elements
Non-oxide ceramics	Carbides (SiC, B ₄ C, TiC, ZrC, Mo ₂ C, VC, WC, ThC, HfC, NbC)
	Nitrides (BN, Si ₃ N ₄ , TiN, ZrN, TaN, UN, ThN, SiAlON),
	Borides (Ti ₂ B, ZrB ₂ , TaB ₂ , HfB ₂ , ThB ₂)
	Silicides (MoSi ₂ , ZrSi, ZrSi ₂ , Ti ₅ Si ₃ , TaSi ₂ , TiSi ₂)
Titanic ceramics (Titanium)	BaTiO ₃ , SrTiO ₃ , CaTiO ₃
Sulphidic ceramics	BaS, CeS, US, ThS, CdS, ZnS
Metal ceramics (Cermets)	Al ₂ O ₃ , ZrO ₂ , MgO, BeO, ThO ₂ , Y ₂ O ₃ + W, V, Mo, Ta, Ti, Zr, Si, Cr, Co, Ni, Nb

According to the application			
	Electrical	Optical	Biological
	Magnetic	Thermal	Nuclear
	Chemical	Mechanical	
The most widely used products with magnetic and electrical properties			
Insulation materials	Al ₂ O ₃ , MgO, BeO, MgAl ₂ O ₄	Substrates for integrated circuits, resistors and electrical connections	
Ferroelectric materials	BaTiO ₃ , SrTiO ₃	Ceramic capacitors	
Piezoelectric materials	PZT	vibrators, oscillators, filters, spark generators, ultrasonic devices, converters	
Semiconductive materials	BaTiO ₃ , SiC, V ₂ O ₅ , (oxides of transition metals)	NTC thermistors: temperature sensors, temperature compensators PTC: temperature compensators, switches, heating elements TF thermistors: thick-film infrared sensors Varistors: surge protectors, lightning arresters	
Ion-conductive materials	Al ₂ O ₃ , ZrO ₂	Dry filling (filler) of Nb batteries, oxygen sensors, pH meters	
Superconducting materials	oxides Ba, rare earth elements	special non-resistive conductors	
Ferrites - soft	Zn-, Mn-, Ni	scan head, temperature sensors	
Ferrites - hard	Ba-, Sr-,	Ferrite magnets, small motors	
Mechanical functions			
Cutting materials	Al ₂ O ₃ , Si ₃ N ₄ , TiC, WC, TiN, etc.	Ceramic, Nitride , Cermet cutting tools	
Abrasion resistant materials	SiC, Al ₂ O ₃ , ZrO ₂ , TiN	liners, gaskets/sealing, fibre guides, blades, ceramic engines, burners, coatings	
Refractory materials	Al ₂ O ₃ , ZrO ₂ , MgO, SiC, Si ₃ N ₄ , SiAlON	heat exchangers, turbine blades, burners, ceramic engines, crucibles/cups	
Chemical functions			
Gas sensors	ZnO, SnO ₂ , Fe ₂ O ₃	detectors, alarms, fans	
Humidity sensors	MgCrO ₂ -TiO ₂	monitoring equipment of microwave ovens/furnaces	
The catalyst carriers	Al ₂ O ₃ , BaTiO ₃	emissions control, adsorption, catalysis	
Electrodes	CaTiO ₃ , SrTiO ₃ , BaS, TiB ₂	for electrolysis, public transport and photochemical processes	

Thermal functions		
Infrared sources	ZrO ₂ , TiO ₂	Infrared devices
Refractory materials	SiC, TiC, B ₄ C, Si ₃ N ₄ , etc.	linings, coatings, thermal conductivity and resistance to thermal shocks
Ceramic based fibres	Al ₂ O ₃ , Al ₃ Si ₂ O ₅ , C	thermal Insulation, composites
Ablative agent/material	SiO ₂ + fibres	shields for modules (spacecraft) and space shuttles
Optical functions		
Translucent (transparent) ceramics	Al ₂ O ₃ , MgO, Al ₃ O ₅ Si ₂	discharge lamps/tubes permeable to IC radiation
Optical ceramics	PLZT	for light modulation, videos, valves
Biological functions		
Replacements	Al ₂ O ₃ , hydroxyapatite, bioglass	dental implants, joints, bone connections
Active sources	Ferrites, radioactive ceramics	external body magnets, temporary radiation sources
Nuclear functions		
Nuclear fuel	UO ₂ , UO ₂ +PuO ₂ , UC	the filling of nuclear reactors
Packaging materials	C, SiC, B ₄ C	the packaging of nuclear fuel
Shielding materials	C, SiC, B ₄ C, BeO	for controlling nuclear reactions



Summary of terms

After studying this chapter the following terms should be clear:

- special ceramics,
- structural ceramics,
- functional ceramics,
- bioceramics,
- granulometry of special ceramics,
- options of preparing special ceramics



Questions and Tasks

1. Define the special ceramics concept.

2. Describe the classification of special ceramics material according to the chemical composition, features and functions.
3. Describe the basic characteristics and requirements for the preparation of raw materials.
4. Name the non-traditional methods of preparing advanced ceramics.

CHARACTERISTICS OF SPECIAL CERAMICS



Time for study:

120 minutes



Objective

- to define the mechanical, thermal, electric, magnetic and optical properties of special ceramics
- to describe the individual properties, what do they depend on and what affects them



Lecture

1.3 SELECTED PROPERTIES OF CERAMICS

Conductors conduct current and these materials include metals. Semiconductors are special materials that conduct a current only under certain conditions. Non-conductors (insulators) do not conduct a current (only in the case of electrical breakdown). This group of materials is called **dielectrics**. In a technical environment (in practice), we can often meet the term **insulant**. The conductivity of ceramic dielectrics is a function of the chemical composition and microstructure of materials. An important role plays, not only the content and size, but also the orientation of the individual phases in the materials. A significant effect on the electrical conductivity of ceramic materials is its basic phase, the matrix. If the matrix acts as a bonding phase, it determines the electrical conductivity of materials regardless of the conductivity of the dispersed phase. The electrical conductivity of ceramic materials depends on the temperature [2].

□ Polarization and permittivity of ceramic dielectrics

When you insert a ceramic dielectric in a homogeneous electric field of a certain intensity polarization occurs (it polarizes). There is an electric field created in the dielectrics. In other words, if the body of insulating material is put into the electric field, electric power acts on the entire atom or molecule causing a certain shift of electric charges. The atoms and molecules are becoming electrical dipoles and this phenomenon is called electrical polarisation. The electric charges induced in atoms and molecules of the dielectric, are called bound charges, because they do not distract (release) from the body. The charge is negative on the side of the body into which the electric flux line of the external electrical field enters and positive on the side where the electric flux line emerges from the body. Inside the dielectrics are mixed up positive and negative charges, but externally they are not evident. On the contrary, a non-conductor (also an insulant, or dielectrics) has in its structure only bonded electrically charged particles and possible movement is allowed only at the distance equal to the size of the molecules (or atoms) of the substance; therefore these particles cannot carry (be the carriers of) electric current - but even these compounds are not inert towards the electric field. Examples of insulating material are glass, various plastic materials, porcelain, rubber and many other substances. Their structure is characterized in the fact that the atoms and molecules of these

substances are firmly bounded electrons and their negative charge is compensated by positively charged protons [4].

Some ceramics conduct electricity, while some do not. Ceramics, which do not conduct electricity are called insulators. Insulators are classified as:

In short:

ferroelectrics	<ul style="list-style-type: none"> polarization arises spontaneously
piezoelectricity (piezoelectric)	<ul style="list-style-type: none"> polarization is caused by an external mechanical force
pyroelectricity (pyroelectric)	<ul style="list-style-type: none"> polarization arises spontaneously without the application (the influence) of an external electric field

The magnetic properties of materials were discovered in ancient Greece in the mineral magnetite Fe_3O_4 , which is a compound of the iron oxide $FeO \cdot Fe_2O_3$. Much later, by replacing FeO in the Fe_2O_3 compound with other MnO , ZnO , MgO , CuO , NiO oxides, etc., a series of $MeO \cdot Fe_2O_3$ compounds (so-called Ferrites with ferromagnetic properties) were obtained. The magnetic properties of substances are related to the magnetic properties of atoms and molecules. The substance, which is inserted into a magnetic field obtains a magnetic moment. The magnetic characteristics of the substance is the permeability μ .

According to relative permeability values we divide substances into:

non-magnetic	$\mu_r = 1$	vacuum, air
paramagnetic	$\mu_r > 1$	Al, Mn, Pt, Cr, O_2 , N_2
diamagnetic	$\mu_r < 1$	inert gases, water, salt, Au, Cu, Hg
ferromagnetic	$\mu_r \gg 1$	FeO , Cd, alloys, Ni, C

1.3.1 Paramagnetic substances

Substances amplifying the magnetic field are called paramagnetic ($\mu_r > 1$). This group of substances includes atoms with an incomplete shell of electrons even after bonding with valence electrons. These are for example metals of the iron group: aluminium ($\mu_r=1,000023$), manganese, chromium, platinum, and palladium. Paramagnetic magnetization is thus based on the tapping of the magnetic moments of atoms in the direction of the applied magnetic field. The magnetism of paramagnetic substances is inversely proportional to temperature, i.e. with a decreasing temperature, the magnetic field intensity increases [5].

1.3.2 Diamagnetic substances

Substances that weaken the magnetic field are called diamagnetic ($\mu_r < 1$). These are substances with even number of electrons arranged in pairs with a zero magnetic moment (Si^{3+} , Al^{3+} , Ca^{2+} , K^+ , O^{2-}), all inert gases (He, Ne, Ar, Kr, Xe, Rn), most organic compounds, but also certain metals (Cu, Ag, Au, Hg, Bi, bismuth) and water (H_2O) as well. Ceramic materials are therefore generally diamagnetic. If we put diamagnetic material in an external magnetic field, it will not affect the non-magnetic atom in whole, but it will affect the movement of individual electrons, which orbit its core (the core of the atom). A diamagnetic substance repels from the magnet [5].

1.3.3 Ferromagnetic substances

Even a weak magnetic field can cause such an arrangement of atoms, where the magnetic field is amplified and the magnetization of a substance occurs. The magnetic field in the ferromagnetic substance remains, even if the external field disappears. Unlike diamagnetism and paramagnetism (phenomena depending on the atomic structure) ferromagnetism is a phenomenon which depends on the arrangement of atoms (ions) in the crystal lattice. The atoms of ferromagnetic substances themselves are paramagnetic. If we heat (up) a ferromagnetic substance to a certain temperature, called the Curie temperature, it loses its ferromagnetic properties (by a jump) and becomes paramagnetic (e.g. the temperature for magnetite is about 580°C). By cooling it down, below the Curie temperature it becomes non-magnetic ferromagnetic [5].



Summary of terms

After studying this chapter the following terms should be clear:

- tensile modulus, Vickers test, Hooke's Law,
- thermal conductivity, specific heat capacity, thermal conductivity,
- conductor, semiconductor, insulator, energy belt,
- polarization, permittivity, permeability, hysteresis loop,
- refractive index, birefringence (double refraction), dielectric crystal, magnetic crystal.



Questions and tasks

1. Define the mechanical and thermal properties of ceramics.
2. Define and explain the concepts of electrical, dielectric, pyroelectric and piezoelectric magnetic properties of ceramics. What do they depend on, how do they arise and what influences them?

SPECIAL FORMING METHODS



Time for study:

120 minutes



Objective

- to define the basic technological steps with a closer description
- to define basic and special forming methods
- to describe basic technological differences for classical (common) and special ceramics



Lecture

1.4 SPECIAL FORMING METHODS

1.4.1 Casting and die casting

It is designed for thin-walled products, large and/or small, where solid (body) formation is ongoing by the drainage of a highly liquid suspension through a semi-permeable wall (a gypsum or porous polymer). This casting is also called a suspension casting (a slip casting) and is the most common method of wet shaping. A porous mould is covered with ceramic slurry and (while) using capillary pressures acting through the pores, a liquid is absorbed from the slurry mould. On the mould surface, there is gradually growing semi-hard layer until it reaches the desired width of the ceramic material. Usually the drying ceramic part contracts (shrinks) and it can be easily removed from the mould. Other variants of suspension casting are centrifugal casting and die casting into porous moulds. The thickness of the body is a function of time and the in the direction of making the body. There are of course other methods of casting e.g. in a vacuum, under pressure or centrifugation. It always depends on the particular product.

1.4.2 Gel Casting

It is a very attractive shaping process, which is used for the production of the complex and sophisticated shapes of ceramic parts. It has a low proportion of organic additives, thereby reducing the risk of cracking during the removal of binders. This method leaves no impurities after sintering. Using the method of gel casting, the bending strength is several times higher than that of conventional moulding techniques. Ceramics prepared by this method exhibit homogeneity throughout their entire volume. This method is capable of producing materials to 0.2 mm. Similar techniques such as direct coagulation casting (DCC) use (heat or chemically induced) an in-situ transition phase (e.g. the transition to gel) organic or aqueous binders, and allow the casting of suspensions in non-porous moulds (e.g. metallic) → uniform microstructure. A similar process is starch casting (SCC), which is based on the ability of the starch to swell in water at a higher temperature (starch is used as a pore former and the body as a gas generating agent).

1.4.3 Tape Casting

Tape casting is often called a "doctor-blade process", another method of wet moulding, which is used for the production of thin ceramic sheets and foils. In tape casting, the ceramic slurry is spread over the surface of an unwound paper belt and the thickness of the applied layer is controlled by the blade. Thin ceramic sheets have the greatest utility as supporting plates for electronics, or are used as a dielectric in capacitors.

1.4.4 Drawing (fibre drawing)

Using this method, large or small symmetrical shapes can be formed. The mixture is shaped by the flow of the feed via nozzle caused by pressure. The pressure is exerted by the (mixing) screw or the piston. This method enables the production of a wide range of products from traditional coarse ceramics (profiled bricks) to advanced fine ceramics (corundum or the cordierite bearers of catalytic converters). While using organic binders, a critical step is the defect-free burnout. Co-extrusion can be used for manufacturing laminated or unidirectionally textured composites.

1.4.5 Extrusion

The principle of an extruder device for extruding ceramic slurry is completely identical with the extrusion of plastics. The ceramic suspension can be extruded either by a piston or by a screw type extruder as well. Screw extruders can be provided with one or two piston bolts. The design of the machinery is similar to machines for extruding plastics, but due to the high abrasion of the ceramic suspension, functional surfaces must be provided with a wear-resistant coating. At first, the extruder is filled with a ceramic suspension (slurry). While filling the cylinder of the extruder, there is a sharp increase of pressure and the (subsequent) arrangement of the ceramic slurry in the cylinder. Upon a further increase in pressure, a semi-finished ceramic product will be extruded.

1.4.6 Piston Pressing

It is one of the methods of forming powder mixtures with little or no moistening agent in the piston-sealed-metallic moulds. There are two processes going on during this method:

- the arrangement of the mixture particles,
- the deformation or even the fracture of the particles.

The arrangement of the mixture particles proceeds in the direction of pressing force and this results in an increased bulk density of the moulding (the pressed part). It depends on the particle size, shape and distribution in the mixture. The monodisperse system of spherical particles with various configurations reaches a filling of the mould that corresponds to 52-74% of the material density. The polydisperse system of spherical particles with a suitable granular composition has even more than 90% of the material density. A deformation or fracture of the particles occurs due to their friction (and) mostly at higher pressures. The apparent density of the moulding can be increased (as follows): increasing pressure - the bulk density of the mixture- reducing the strength and hardness of the agglomerate of the particles - the speed of pressing-in.

For this type of pressing, there is the need to achieve an even distribution of the bulk density of the moulding. This depends on the following:

- a) an equal distribution of the filling in the mould (form),
- b) the mode of action of the pressing force,
- c) the ratio of the height,
- d) the diameter and cross-section of the mould.

During pressing the force may act unilaterally, bilaterally or isostatically. The least suitable is a unilateral (force).

1.4.7 Injection Moulding

It is principally the same as extrusion. The mixture consists of a ceramic powder and a binder (usually based on polymers or waxes). The mixture is heated to a temperature at which the binder is liquefied, after injecting it into the mould the binder solidifies (hardens) and after cooling, the raw product is removed. A (necessary) condition (requirement) is the slow burning (out) of the binder before sintering, typically at the temperature range of 300-700°C. This step of the process limits the size of the products. It is suitable for small products with complex geometry.

1.4.8 Hot Pressing

This pressing method takes place under high pressure in a graphite mould at temperatures of 1200-2000°C and in a protective atmosphere (raising the temperature in the graphite increases its tensile strength). This method requires expensive equipment and is suitable for preparing mouldings of oxide and non-oxide powders, which achieve a bulk density close to their own density. This situation occurs at temperatures substantially lower than those for pressureless sintering. It also allows, to some extent, to minimize the crystal growth of the sintered material.

1.4.9 Isostatic Moulding

It is an omnidirectional (in all directions) method, mostly used for granular mixtures with low moisture using high pressures (100-400 MPa). There are two possible methods:

- **in/into the wet form** (the flexible/resilient container with the moulding mixture is together with the sleeve loosely inserted into the liquid in the pressure vessel; (used) for large-sized mouldings of a simple shape),
- **in/into the dry form** (the flexible/resilient pressing container is tightly connected to the pressure vessel; used for forming smaller mouldings of complex shapes (nowadays used for tiles, plates).

❑ Cold Isostatic Pressing (CIP)

This method is suitable for larger and more complex shapes that, on the other hand, should not be too big and too complicated. Hydrostatic pressure is applied using a liquid medium in all directions (pressing a wet form using a rubber bag) or biaxial hydrostatic pressure (pressing in a dry form) → less density gradients. The pressure is usually 200 MPa and when moulding large bodies into the wet form, the pressure is up to 500 MPa.

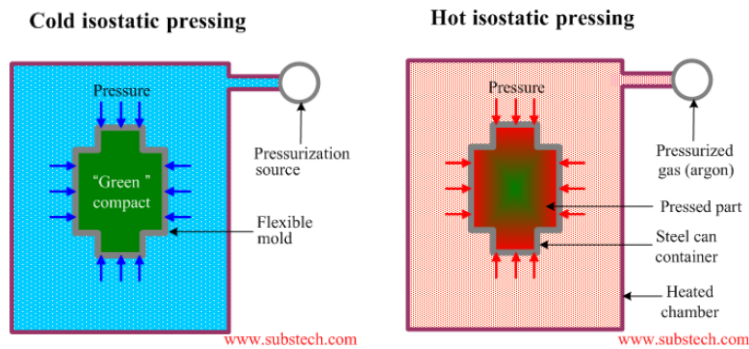


Fig. 14 HIP and CIP pressing (Source: www.substech.com) [7]

Hot Isostatic Pressing (HIP)

This method uses inert gas (e.g. argon) as the moulding media. From the starting mixture, using the piston or isostatic method, first the body of the desired shape must be pressed, optionally burned, and then closed into a casing for pressing (the die insert), which is gas impermeable. These cases are made of refractory metals (e.g.) or the moulding is encapsulated by a surface vitreous (glass) layer. The encapsulated mouldings are placed in a pressure vessel with an inert gas and burn at the required temperature. The heated gas develops a necessary pressure on the mouldings so that they achieve a bulk density close to their (own) density, with little change in the distribution and particle sizes to its original state. It is a pressing method of a controlled microstructure with high mechanical strengths. A pressure of 10-200 MPa is generated by hot gas. These products cannot be too large; rather simple, uncomplicated shapes. This technology can also be used as a post-sintering technique to reduce the size of the closed pores. This is a very expensive process (used only for the high-quality products with demanding applications).



Summary of terms

After studying this chapter the following terms should be clear:

- the shaping of ceramics,
- casting, die casting, gel casting, tape casting, extrusion,
- injection moulding, isostatic moulding,
- CIP, HIP



Questions and tasks

1. Define briefly the technological steps, methods and conditions (requirements) for ceramic moulding.
2. Describe the basic differences between the methods of shaping special and common ceramics.
3. Describe the methods of forming special ceramics.

STRUCTURAL CERAMICS



Time for study:

120 minutes



Objective

- to define the concept of structural ceramics
- to describe the characteristics of structural ceramics
- to define special oxide and non-oxide ceramics
- to define mixed ceramics



Lecture

1.5 OXIDE STRUCTURAL CERAMICS

By the term oxide ceramics we understand a material consisting of one oxide or a mixture of a few oxides. A common feature of these materials is that the basic starting material is a synthetic oxide powder.

1.5.1 Corundum ceramics (based on) Al_2O_3

In the area of technical ceramics, products from oxide ceramics are predominating the world market and that up to 70%. Alumina Al_2O_3 is one of the most important and industrially utilized ceramic. It has rich polymorphism, where in structural and traditional ceramics, polymorphic $\alpha\text{-Al}_2\text{O}_3$ (corundum) is mainly used. The excellent physical properties of this material certainly include its hardness at elevated temperatures, low thermal conductivity, and corrosion resistance. The values of the selected mechanical properties of pure Al_2O_3 are: a melting point at 2054°C , a density 3.5 to 4.0 g.cm^{-3} , a bending strength of 150- 500 MPa, a fracture toughness of 3.5 to $4.5\text{ MPa.m}^{1/2}$ and a modulus of elasticity from 200 to 400 MPa. Alumina products are used as bio implants, ionic conductors, semiconductor devices, nozzles, insulation, wear resistant components, plugs (bodies) in internal combustion engines, cutting tools, wear parts (e.g. the carriers of textile fibres), filters and membranes, the substrates for electronic circuits, armour, etc.

1.5.2 Ceramics based on ZrO_2

The next (and) most widely used material after sintered corundum is ceramics from ZrO_2 . Zirconia among oxide ceramics is irreplaceable for its high melting point of 2710°C and a unique structure that enables the transformation of toughening. In production, the most important raw material is the mineral ZrSiO_4 .

Zirconia is trimorphous:

	Designation	System	Density (g/cm ³)	Characteristics
ZrO₂	m - ZrO ₂	monoclinic	5.68	thermodynamically stable at room temperature up to 950°C
	t - ZrO ₂	tetragonal	6.10	by transformation from the monoclinic phase upon heating to 1150°C or back to a monoclinic during cooling at 950°C → (by) relative volumetric changes, approx. 5%.
	k - ZrO ₂	cubic	6.27	cubic transformation t ↔ c at approx. 2300°C

Each modification of ZrO₂ differs significantly in its density. The most important is the conversion of the tetragonal phase to monoclinic phase, which is the basis for so-called transformation-reinforced ceramics. The transformation of pure zirconia (zirconium dioxide) from a tetragonal to a monoclinic structure is martensitic and it is associated with an increase of volume (about 9%), so that it is practically impossible to prepare ceramic components (made) of pure zirconia. This transformation does not depend on one temperature, it is athermal, diffusionless and is associated with a large change in the volume and shape of ZrO₂ grains. Therefore, this oxide is partially stabilized at about 10 mole % of other refractory oxides. This significant change in the volume of grains in the ceramic material leads to the formation of cracks. This is possible to achieve by the stabilization of the high-temperature modification of ZrO₂. Practical importance has the stabilization of cubic modification by adding yttrium oxide, calcium and magnesium in the amount of 5-15 wt. %. Zirconia is the most durable material of all materials of oxide ceramics. Zirconia ceramics has excellent chemical and corrosion resistance, excellent toughness for fracture, wear resistance and low thermal conductivity.

Transformation-reinforced ceramics

Table 3 Types of transformation-reinforced ceramics [1]

Ceramics (types and names)	abbreviation
fully stabilized ZrO ₂	FSZ
partly stabilised ZrO ₂	PSZ
ZrO ₂ partly stabilised Y ₂ O ₃	Y PSZ
ZrO ₂ partly stabilised CaO	Ca PSZ
ZrO ₂ partly stabilised CeO ₂	Ce PSZ
tetragonal polycrystalline ZrO ₂	TZP
transformation-reinforced zirconium ceramics	ZTC
corundum ceramics transformation-reinforced ZrO ₂	ZTA

mullite ceramics transformation-reinforced ZrO_2	ZTM
zirconium ceramics transformation-reinforced Al_2O_3	ATZ

1.6 NON-OXIDE CERAMICS

This very wide range of materials, may also be considered as non-metal and/or metal materials without a sharp boundary between the two groups. These are materials with a high melting point above 1800°C and that exhibit a high degree of hardness and good thermal and electrical conductivity. These are most often nitrides and carbides, and even diamonds. A special group consists of so-called sialons (SiALON ceramics) formed by a solid solution of Si_3N_4 - Al_2O_3 . The diagram in Figure 20 shows the possible systems of binary compounds which the components may form.

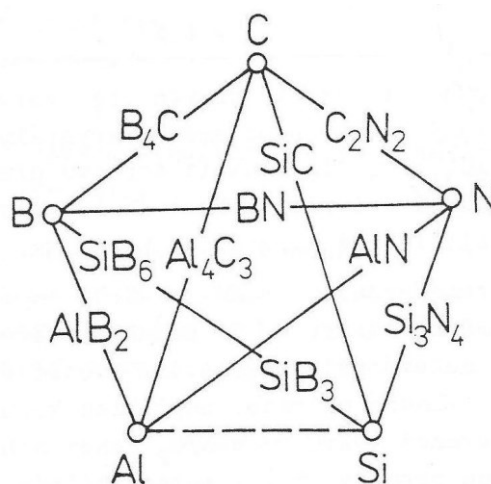


Fig. 20 A system containing non-metallic and difficult to melt compounds [9]

1.6.1 Silicon Carbide Ceramics (SiC)

Silicon carbide behaves almost the same way as a diamond. It is not only the lightest, but also the hardest ceramic material with excellent thermal conductivity, low thermal expansion and is very resistant to acids and alkalis. It is the basic material for the production of refractory shaped building materials and monolithic mixtures, the heating resistor elements of electric furnaces, abrasives, the structural material of mechanics and the heat-resistant parts of gas turbines, engines, etc. The properties of ceramic materials based on silicon carbide remain constant up to temperatures above 1400°C . High Young's modulus > 400 GPa ensures excellent dimensional stability. Due to these properties, silicon carbide is predetermined for use in construction material. Silicon carbide well handles corrosion, abrasion and erosion and has superior resistance to friction wear as well. These components are used for example in chemical plants, mills, expanders and extruders or nozzles.

Silicon carbide SiC is a polymorphic substance. Low temperature modification β - SiC is cubical and above a temperature of 2100°C it changes to a high-temperature modification of α - SiC, which is hexagonal. SiC ceramics have a high degree of hardness (9.5. according to the Mohs scale). Structural ceramics SiC are prepared using different procedures and are therefore recognized as [1]:

- SSiC (sintered silicon carbide)
- SiSiC (silicon-infiltrated silicon carbide)

1.6.2 Silicon nitride ceramics

Silicon nitride (Si_3N_4) offers an excellent combination of material properties. These materials are almost as light as silicon carbide (SiC), but their microstructure provides excellent thermal shock resistance, whereas their fracture toughness provides resistance to impact and shock. Silicon nitride is present in more than one crystal structure modification:

- α - low temperature,
- β - high temperature (β is rather softer than α , but it has higher toughness in fractures, and a higher strength).

Ceramic materials made of Si_3N_4 are prepared at high temperatures from 1750°C to 1900°C in a protective atmosphere of nitrogen. Simple shapes are manufactured by hot pressing HPSN, for mass production there is used compression moulding. Another method is the reaction sintering of RBSN. The most common use of Si_3N_4 ceramics is found in the engineering industry in the form of cutting blades for machining hard metallic materials. It is due to their high durability and the improved surface of the workpiece without the need for cooling. The next area of the using Si_3N_4 ceramics is in the automotive industry for bearings, valves, turbochargers, spark plugs, etc.

Types of silicon nitride [8]:

- reaction bonded silicon nitride RBSN
- sintered silicon nitride SSN
- hot pressed silicon nitride HPSN extruded at high temperatures
- silicon nitride produced by the hot isostatic pressing method

1.6.3 Ceramics of aluminium nitride

Aluminium nitride (AlN) is the only technical ceramic material that offers an extremely interesting combination of very high thermal conductivity and excellent electrical insulation properties. Solid AlN is produced by sintering at a temperature of 1600°C - 1900°C in an atmosphere of nitrogen. The use of AlN is limited to a temperature of 800°C due to strong oxidation above this temperature. Thanks to its excellent insulating properties and high thermal conductivity ($170\text{-}190 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) it was first used in microelectronics [26]. This makes aluminium nitride destined for use in high performance and microelectronic applications. AlN is largely used in optoelectronics as a dielectric layer in optical storage media, a circuit carrier (substrate) in semiconductors, as the heat sink in LED lighting technology or in high-performance electronics.

1.6.4 SiAlON ceramics

Sialons are ceramic alloys based on the elements of silicon carbide (Si), aluminium (Al), oxygen (O) and nitrogen (N) which were developed in 1970 as a result of Si_3N_4 production. There are three basic forms of Sialons known as Si_3N_4 alloys. The basic structural unit of Si_3N_4 is SiN_4 tetrahedron, which is analogous to SiO_4 of the constructional components in silicates. The tetrahedrons are combined into a solid three-dimensional network sharing the corners, where the Si-

N bonds are short and very strong. This solid compact structure is responsible for many important properties of Si_3N_4 .

The α/β SiAlON ceramics are among the most up-to-date materials used in technical ceramics and are associated with silicon nitrides. They occur only in certain compounds of raw materials and consist of at least three phases: α -SiAlON, β -SiAlON and an amorphous or partially crystalline grain boundary phase. The class of α/β -SiAlON materials is characterized by a unique combination of an even higher hardness than that of a normal silicon nitride, with the same toughness level. The α -SiAlON phase is very hard, whereas the β -SiAlON phase - as a normal silicon nitride - exhibits a high level of fracture toughness. The hardness of α/β -SiAlON materials and their abrasion resistance can be further enhanced by using a hard material, such as silicon carbide. During the manufacturing of so-called Sialon ceramics, HIP technology does not have to be used, since the compaction of the sample in the sintering process takes place in the presence of the liquid phase even without pressure. These materials have very high toughness and they even retain other beneficial properties at high temperatures. With Sialon ceramics using the HIP method the hardness or fracture toughness does not increase.

1.6.5 Titanium carbide ceramics

Titanium is a metal, which crystallizes in a hexagonal system at temperatures higher than 900°C , in a cubic space-centred structure. TiC is extremely tough refractory ceramic material. Visually, it appears as a black powder with a face centred cubic lattice. It is produced by the reduction of carbon TiO₃ (not all at once, but gradually through different transition oxides at high temperatures about 2000 - 2200°C), by reducing and carburizing the mixture of highly pure TiO₂, and the black soot or graphite powder in an induction furnace in a vacuum or hydrogen atmosphere (there is no need to prevent the access of air from the surrounding area). The vacuum method is, however, preferred, since TiC contains a higher amount of bound C and does not contain nitrogen.

Compact shapes can be prepared by pressure sintering. An addition of 6-30% of titanium carbide, increases the resistance of tungsten carbide to abrasion, corrosion and oxidation. This will, however, form a solid solution that is more fragile and more susceptible to breakage than the original material. A nano TiC powder is used as an abrasion-resistant material for the manufacture of grinding bodies, crucibles and for the production of knives. Commercially it is used for the production of cutting tools. It is commonly also used for the preparation of cermets, which are often used in machines with a high cutting speed. The cutting plates with no tungsten in their content may be made of a cermet of titanium carbide in a Ni-Co matrix, thereby an increase in the cutting speed, accuracy and in the smoothness of the workpiece is possible. Transparent TiC is a very good optical material. Sometimes also referred to as high-tech ceramics and is used as a protective shield for space shuttles during flights through the atmosphere [26]. When polished, it can be used in the manufacture of watches due to its scratch resistance.

1.6.6 CERMET

Cermet is a sintered carbide comprising hard particles based on titanium. The name "CerMet" is a combination of the words ceramics and metal [8]. Originally cermets consisted of TiC and nickel. Modern cermets do not contain nickel and their sophisticated composition is formed with basic building elements-the particles of carbonitride titanium Ti (C, N), the particles of the secondary

hard phase (Ti, Nb, W, C, N) and a cobalt rich binder. Ti (C, N) provides (to a respective class) higher abrasion resistance; the secondary hard phase increases the plastic deformation resistance and the proportion of cobalt has a decisive influence on toughness. Compared to conventional sintered carbide, cermet has higher wear resistance and less tendency to build up the material on the workpiece cutting edge. On the other hand, cermet also has a lower level of internal compressive stress and hence a lower resistance to the formation of thermal cracks. In order to increase their wear resistance, it is also possible to coat cermets using the PVD method. Cermets can be used for troubleshooting in the machining of iron-based materials.

1.6.7 Titanium carbide ceramics

After the diamond and cubic BN, B_4C is the third hardest material. These ceramics are moulded by hot pressing at temperatures of 1900-2200°C in a vacuum or argon. Its production is very expensive and it is used in nuclear power engineering for absorbing neutrons. In the military industry, it is used for the lightweight armour of an aircraft and for the production of bulletproof vests [26, 1]. Due to its high degree of hardness, the powder of B_4C is used as an abrasive in polishing and lapping, or when adjusting diamond tools. B_4C powders are usually made by the carbothermic reduction of the boric oxide B_2O_3 or H_3BO_3 boric acid with petroleum coke or graphite in a resistance or arc furnace. Subsequently, the resulting BN is crushed, milled, washed in acid and separated. Coatings and fine powders are produced via precipitation from the gaseous phase by the reaction of BCl_3 (resp. BBr_3 , BH_3 , B_3H_6) and methane. Dense B_4C is prepared by hot pressing at temperatures of 1900-2200°C in a vacuum or argon. The production of parts made of B_4C is expensive.



Summary of terms

After studying this chapter the following terms should be clear:

- transformation-reinforced ceramics
- modifications of ZrO_2 ,
- Si_3N_4 synthesis,
- types of SiC,
- SiALON,
- Cermet



Questions and tasks

1. Describe the differences between oxide and non-oxide ceramics.
2. Describe the properties, the application of ceramics based on Al_2O_3 , ZrO_2 and transformation-reinforced ceramics.
3. Describe the properties, production and application of SiC, Si_3N_4 , TIC, AlN, BN.
4. Define SIALON and Cermet.

FUNCTIONAL CERAMICS



Time to study:

120 minutes



Objective

- to define functional ceramics and their representatives
- to describe the characteristics of functional ceramics
- to describe the features and the representatives of capacitor ceramics



Lecture

The name functional ceramics is due to their active properties designed for special applications which take advantage of their electrical, magnetic and optical properties. In this group of ceramics with electrical properties are included conductors and semiconductors, insulators and piezoceramics, as well as the ceramics for optical applications and ceramics with magnetic properties, called ferrite ceramic. We divide them into magnetically soft ferrites and magnetically hard ferrites.

1.7 DIELECTRIC CERAMICS

Porcelain → so-called hard: it contains the glass phase with quartz crystals, corundum and mullite. It has high dielectric strength, but the disadvantage is the greater dielectric loss when above 400°C it is no longer an insulator, and it loses its insulation properties. Insulators are used for low voltage, high voltage, very high voltage, cable terminations (ends) and the like. Higher parameters have, for example, corundum porcelains with typical properties as: a density 2.3 to 2.5 g/cm³, Young's modulus of 70-80 GPa, a bending strength of up to 100 MPa, a thermal conductivity of 1.2-1.6 W/m.K⁻¹ and thermal expansion of 4-6.10⁻⁶.K⁻¹.

Ultraporcelain → one of the masses in the system of BaO – Al₂O₃ – SiO₂: made of Al₂O₃, kaolin, BaCO₃, with the addition of CaCO₃, firing at 1360°C. It has high mechanical strength and hardness (close to corundum) and good electrical properties. Application: highly stressed components of/for HF devices.

Porcelit → low-loss porcelain. It is made of silica, kaolin, and alkaline earth oxides. It has good electrical properties and resistance to thermal shocks. It is used for capacitors in HF circuits.

Stoneware → has the same composition as porcelain. The main raw materials are stoneware clays. Due to the lower firing temperature (1150-1350°C) it has worse mechanical strength. Advantage: good formability of the raw mix → large, complicated products → large insulators, carriers of resistive wires.

1.7.1 Magnesium ceramics

The group of technical ceramics called magnesium ceramics can include ceramics intended mainly for low temperature applications (e.g. electrical engineering). The main representatives of this group are (these) ceramics:

- **Steatite** (high mechanical strength and a low dissipation factor, used in high-frequency/radio frequency technology)
- **Cordierite** (a low coefficient of expansion, which is the cause of resistance to thermal shock and low size component dependence on temperature),
- **Forsterite** (vacuum tightness, a low dielectric loss at high frequencies and the possibility of soldering metals due to high thermal expansion, used in (vacuum) electrical engineering).

Steatite → materials: talc (calcined, non-calcined), clay, feldspar or BaCO_3 Low Voltage Steatite ($\epsilon_r = 6$) has the composition in the system of M-A-S. The calcined (burned) product contains MS and another crystalline phase and little glass. It has about two times higher strength than porcelain and better electrical properties. It is used in high power electronics such as supporting insulators, (route sheet), insulating components for low and high voltage, and is also suitable for higher temperatures. Low-loss steatite is used for high frequency electronics, and it has good mechanical properties and low power losses ($\text{tg}\delta$). Steatite has been used for many years in large industrial systems, home electronics, aviation, the automotive industry and specialised electro-technical tools such as cathode ray tubes.

Cordierite ($\text{M}_2\text{A}_2\text{S}_5$) → raw materials: talc, clay and Al_2O_3 . It is a compound having a low expansion coefficient. Sintered cordierite ceramics are used for components in electrical engineering. For NN insulators, resistors (the supports for resistances) and components exposed to thermal shocks. It has an outstanding resistance to sudden temperature changes and good electrical insulating properties. The porous material is used for heating plates, supports and heating spirals.

Forsterite (M_2S) → raw materials: talc and clay + MgCO_3 ; a highly heat resistant compound. With forsterite, there is no problem with the firing as with the previous materials. Forsterite features excellent high-thermal insulation properties, and low loss. It is vacuum-tight with large thermal expansion. It has an excellent electrical properties even at high temperatures. It is used for insulators in vacuum devices.

Mullite ceramics → ($\epsilon_r = 8$), raw materials: sillimanite, andalusite, disthene → (by) firing mullite + SiO_2 . It has characteristics somewhere between porcelain and corundum. Application: pyrometer protection tubes, combustion tubes, etc., often already replaced with corundum.

Lithium ceramics → (L - A - S). During the firing process there forms LAS_4 (α -spodumen), or LAS_2 (α -eucryptit) or possibly (Na, Li) $\text{AlSi}_4\text{O}_{10}$ (petalite). They all have a low or negative thermal expansion coefficient → possible to obtain materials independent of temperature in terms of size. Today, the materials of such a composition are obtained mainly as glass ceramics with a variety of shapes.

1.7.2 Ceramic capacitors

Another group are materials that can be defined as substances with permittivity $\epsilon_r > 12$. According to the dependence of relative permittivity ϵ_r on temperature, ceramics are capacitors divided (by their dielectric polarization mode) into:

1.8 CERAMIC CAPACITORS

□ Type I (low-loss)

- These are substances with a defined value of temperature coefficient (with) capacity α_c and with ϵ_r in the range of 12 – 300 and with a linear dependence of ϵ_r on temperature.

Rutile ceramics → a value greater than 10 among conventional substances is rare. The first exception was found in crystalline TiO_2 in the form of rutile, and so-called rutile ceramics. Rutile with clay and flux is formed into various shapes of capacitors. It is burned at 1250 - 1350°C; so-called "rutilit" is used for LF and HF circuits. With the addition of MgO, BaO into the mixture there arises titanates formed by firing and by the change of composition, while essential properties can be continuously modified. The permittivity of industrially produced rutile ceramics ranges from 60-85. It has a negative temperature coefficient which is inappropriate for some applications. By adding components such as MgO, BaO, the substances react in the mixture and become titanates, which are in terms of temperature coefficient ϵ_r the active phase, while reducing the actual permittivity. The system TiO_2 - MgO can, with the appropriate choice of composition, vary all the important parameters of the dielectric. The next used titanate is CaTiO_3 , which occurs in the nature as perovskite. CaTiO_3 has the permittivity of 150 with a strongly negative temperature coefficient. Therefore, it is used for regulations and is applied in the systems of MgTiO_3 - CaTiO_3 , CaSnO_3 - CaTiO_3 and CaZrO_3 - CaTiO_3 . Compounds have a positive temperature coefficient on the first place. They are suitable for capacitors, electronic circuits, mainly resonance (types). They include capacitors based on rutile, further titanates, zirconates and silicates.

□ Type II (high dielectric)

- These are substances with a high permittivity $\epsilon_r = 500 - 15000$ with a non-linear dependence of ϵ_r on temperature and on the intensity of the electric field, with undefined α_c and large dielectric loss.

BaTiO_3 is the basis of an important group of ferroelectric dielectrics and so is then PbTiO_3 . BaTiO_3 has high mechanical strength and high ϵ_r . At the temperature of the Curie point $\epsilon_r = f(T)$ is strongly dependent on conditions using spontaneous polarization. However, BaTiO_3 alone is only seldom used, because in the field of operating temperatures the maximum ϵ_r is not utilized (it is at low temperatures). The value for BaTiO_3 is 12000. The behaviour of ferroelectric substances is associated with the crystal structure. The ideal structure is a face centered cubic lattice. Ions Ba and Pb increase the unit cell and alter its symmetry to a tetragonal. Ion Ti^{4+} is ejected from a central position inside the cell, thus creating a permanent dipole. Above the temperature of the Curie point (120°C) the structure is as a BaTiO_3 cubic, whereas under it it is tetragonal. This group also includes compounds of KNbO_3 , KTaO_3 , WO_3 , and LiTaO_3 . Ferroelectric materials are characterized by a hysteresis loop on the (dependency) curve of the "intensity of the electric field - polarization".

For practical purposes it is advantageous if it can regulate the properties of titanate dielectrics. Adding other substances to BaTiO_3 forms solid solutions. The best additions are SrTiO_3 , PbTiO_3 , BaSnO_3 , CaSnO_3 , CaTiO_3 , MgTiO_3 , MgZrO_3 , etc. The first intervention (i.e. the maximum displacement) is achieved by combining them with BaTiO_3 , which forms solid solutions (SrTiO_3 , PbTiO_3 , BaSnO_3 , CaZrO_3). The flattening of the curve can be achieved by other agents, e.g. CaTiO_3 , MgZrO_3 . The permittivity then is less dependent on temperature and its value is also reduced. It is possible to obtain ceramics with high ϵ_r in a narrow range of temperatures. It is called (we call it) "permutit" → miniature capacitors with high capacity.

□ Type III

The substitution of very high permittivity ϵ_r was allowed by a semiconducting ceramic capacitor based on BaTiO_3 , SrTiO_3 , and their solid designs. By annealing of the ceramic body in a reducing atmosphere, the BaTiO_3 changes to semiconductor type N and by subsequent oxidation annealing on the surface of the ceramic body there is created a thin insulating layer (the core remains semiconducting). Such capacitors have a high surface capacity and are referred to as a capacitor type 3, known as supermit products (based on SiTiO_3), and often supplemented by rare earth elements. Applications for microwave electronics, telecommunication purposes (satellites), radar applications, diagnostic tools → all in the area of cm to mm wavelengths. In this respect, ceramic dielectrics are irreplaceable, allowing the miniaturization and integration of microwave circuits.



Summary of terms

After studying this chapter the following terms should be clear:

- dielectric,
- permittivity,
- capacitor type I, II and III,
- rutile ceramics,
- Curie temperature,
- hysteresis loop



Questions and tasks

1. Define functional ceramics and its properties.
2. Define the concept of special ceramics.
3. Describe ceramics for electronics applications.
4. Explain the concept of capacitor ceramics type I, II and III.
5. Name the compounds that represent the group of functional ceramics, their preparation and characteristics.
6. Describe the hysteresis loop for ferroelectrics.

SEMICONDUCTOR CERAMICS



Time for study:

90 minutes



Objective

- to define semiconducting ceramic materials
- to describe their working principle
- to describe the difference between the semiconductor of type N and type P

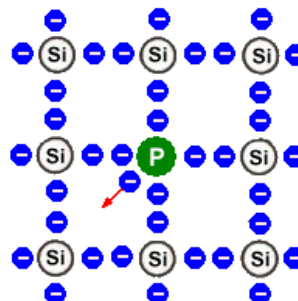
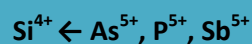


Lecture

Semiconductors are solid substances whose electrical conductivity depends on external or internal conditions, and they can be easily influenced by the change of those conditions. A semiconductor is characterized by a defective structure. Ceramic semiconductors are considered as materials in which there is the transfer of an electric charge mediated by "electron" or "holes" (transfer by ions = ion conductivity). Basically, these are oxides with a defective structure, in their pure state are among insulators. The most common semiconductors include Si and Ge. Today, semiconductor components (diodes, transistors, integrated circuits or microprocessors) belong to the basic building elements of all electronic equipment and devices. Among the conductive ceramics can be counted: items for heating resistors, resistors with a positive or negative temperature coefficient of resistance, resistors with a voltage dependence of resistance, ionic conductors, sensors and superconductors [24].

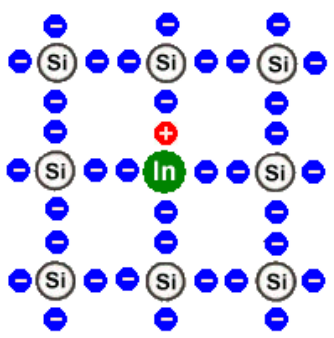
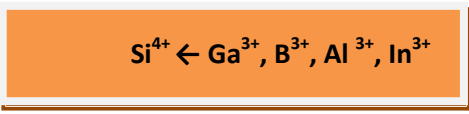
□ N-type Semiconductors

The conductivity of N-type (negative) is formed when a part of Si atoms are replaced by an additive (e.g. P, As etc.), i.e. those having pentavalent atoms.



□ P-type Semiconductors

The conductivity of a P-type (positive) is formed, when Si plus additives with the atoms of a trivalent element with three valence electrons are incorporated into the crystal lattice.



□ **Thermistor**

It is an electrical component, where electrical resistance is dependent on temperature. Thermistors are manufactured from the oxide of various metals. It is produced by so-called powder metallurgy. Then, under high pressure it is compressed to a desired shape and sintered at a high temperature (over 1000°C). It is compressed into various shapes of rods, beads, discs or pads of small dimensions (in the order of 1-10 mm). The thermistors have high internal resistance, therefore the resistance of their supply connections is negligible. They serve as temperature sensors. They can be used for example to limit the current in the circuit when the passage of a larger quantity of current causes a warming of the components due to higher resistance.

Classification of thermistors:

- **Posistors** - PTC thermistors, where the resistance will increase with warming
- **Negistors** - NTC thermistors, where the resistance will decrease with warming

□ **Pozistor**

It is a bipolar electrical component, a type of thermistor with a positive temperature dependence (i.e. with increasing temperature there decreases resistance). They are made of polycrystalline ferroelectric ceramics (barium titanate BaTiO₃). The resistance of a posistor with the rise in temperature at first slightly decreases over the Curie temperature, and then sharply increases by (about) three orders of magnitude (3 times) and then slightly decreases again. Pozistors are used as automatic switches responsive to temperature changes, for example as protection against the overheating of electric motors, as sensors such as detectors of various changes in temperature or regulatory elements.

□ **Varistor**

It is a non-linear semiconductor, where the resistance depends on the voltage. It is made by sintering the grains of SiC, at 1200°C or by sintering the oxides of some metals e.g. zinc. The prerequisite is the presence of three-dimensional defects. Varistors are used to stabilize DC voltage (as overvoltage protection).



Summary of terms

After studying this chapter the following terms should be clear:

- hole conductivity,
- electron conductivity,
- negative conductivity,
- positive conductivity



Questions and tasks

1. Explain electron, hole and ion conductivity.
2. What is meant by a type N semiconductor and a type P semiconductor?

CERAMICS WITH ION CONDUCTIVITY



Time for study:

60 minutes



Objective

- to define ceramics with ion conductivity
- to describe ion conductivity
- to name the types of solid electrolytes



Lecture

1.9 CERAMICS WITH ION CONDUCTIVITY

In recent years, ceramics with high ion conductivity were prepared and the possibilities of their highly effective applications were found. Today, many technically used ceramics with ion conductivity, those with the highest conductivity (above $1 \cdot 10^{-2} \Omega^{-1} \text{cm}^{-1}$), are referred to as "superionic conductors". Generally, the electrolytes are defined as solutions or melts, which conduct electricity. In the electrolytes a current is not transmitted by electrons as in metals, but by ions. Crystalline ionic compounds may also conduct electric current for example by the transmission of ions through unoccupied nodes (vacancies) of their crystal lattice. Unlike electrons they are larger, their mobility is smaller, and thus the conductivity of electrolytes is lower than of metals. Such materials (usually solid solutions) are called solid electrolytes. All ionic conductors have certain structural preconditions to allow the easy mobility of ions in the following ways:

→ either it derives directly from the structure of the basic components

If it follows directly from the structure of the basic ingredients, there are substances 1-2-3 with a different character of ionic movement. In the first case, the ions move through kind of tunnels in the structure (e.g. β -eucryptit), a two-dimensional movement in the plane (u β - Al_2O_3), a three-dimensional structure AgI, in which the small ions move

→ or introducing vacancies (point defects), which facilitate the movement of ions

Among the ionic conductors, in which there is an increased amount of structural defects there are mainly oxides with a partial heterovalent substitution (if ions of different valences in so-called heterovalent substitution are substituted, the electrical neutrality of the structure must be ensured by another type of substitution). There are deliberately created vacancies in the structure (Schottky defects). In the electric field then ions easily pass into the empty positions (for the same ion), so that the vacancies pass through the whole crystal.

The greatest mobility will have mobile ions with the smallest charge, and it means they are monovalent. The movable ion is easiest to move through the centre of the planes, and ions will be most mobile with a small coordination number and a weak binding force. This is due to either the character of the compounds or a suitable doping event, creating a combination with tunnels in the

structure. Mobility does not depend directly on the size of the ion, because very small ions are bounded more tightly. The solid electrolyte and thus fast ionic conductivity are therefore an optimal compromise between spherical factors and binding energy. Compounds and solid solutions have prevailing constant ion conductivity only within a certain range of external conditions (temperature, charge carriers, etc.).

1.9.1 Types of electrolytes

YSZ → pure ZrO_2 is monoclinic and is a mixed (ion-electrical) conductor. Zirconia is the most widely used solid electrolyte using stabilizing additives usually doped with 8-10% Y_2O_3 [12] MgO, Ca. A solid electrolyte is the cubic phase, but it can also be tetragonal, whose conductivity is about half that of the cubic phase. Cubic ZrO_2 is highly stable, contains a large electrolytic domain and has considerable oxygen conductivity (0.1 S/cm at 1000°C). The most widely used is cubic ZrO_2 doped with 8% Y_2O_3 (YSZ). The absolute value of ionic conductivity depends on the concentration of stabilizing substances, on the manner of the sample preparation, in particular on the influence of the grain boundaries composition and the size of the crystals. Solid electrolyte variant PSZ (partially stabilized ZrO_2) or TZP (pure fine tetragonal phase) is due to its mechanical properties and is used as mechanically resistant material for engineering applications. A solid zirconia electrolyte [33] is preferred for the potentiometric measurement of redox systems and for refractory applications.

CeO → is an electrolyte mostly doped (with) Sm_2O_3 or Gd_2O_3 . CeO belongs among the metal oxides of rare earth elements. Its crystalline structure has the shape of a cubic grid. It is the most reactive oxide. The melting point is 2750°C and the thermal conductivity is 12 W/m.K⁻¹.

δ - Bi_2O_3 → is a third type of solid electrolyte with a cubic fluorite structure and high oxide conductivity. It reaches about 1S/cm at 800°C. A significant disadvantage is the easy reduction of δ - Bi_2O_3 and transformation to the monoclinic phase, accompanied by a great change in volume [13, 14].

Th₂ → (after the chemical modification it is a low emitter) doped with the same oxides as ZrO_2 .

Anionic solid electrolytes → fluoride solid electrolytes: small 3-dimensional ion F^- and arrangements in certain structures, there are significant for example: CaF_2 , BaF_2 , PbF_2 , event. $KBiF_4$, $NH_4Sn_2F_5$.

Cationic solid electrolytes →

- Al_2O -
- NASICON (compounds)
- Lithium conductors

Inorganic conductors with the cations Ag^+ and Cu^+ (3D) → Ion conductive cubic modification AgI and other compounds with mobility Ag^+ ion (Ag_2S , Ag_2Se , Ag_2Te , Ag_2HgI_4 ...). Copper halogens (CuI , $CuCl$, $CuBr$) are ionic conductors at about 300°C.

Conductive glass → glass containing Ag^+ , Cu^+ , Pb^+ cationic glass and the second group with F^- and Cl^- .

□ **The application of solid electrolytes:**

- electrolysis with electrolyte $\text{ZrO}_2 - \text{Y}_2\text{O}_3$ as a cleaning electrochemical pump for a deoxygenating protective atmosphere
- primary cells, from cationic solid electrolytes they can be assembled on electrochemical cells (batteries), which are characterized by high stability during storage and are designed as hermetic resilient energy machines e.g. pacemakers
- secondary cells (batteries with fixed electrolytes e.g. Li/SO_2 system)



Summary of terms

After studying this chapter the following terms should be clear:

- electrolyte,
- solid electrolyte,
- ion conductor,
- cationic electrolyte,
- anionic electrolyte



Questions and tasks

1. Define ceramics with ionic conductivity.
2. Explain the principle of ionic conductivity, and what does it depend on?
3. Define types of solid electrolytes and their utilization.

PIEZOELECTRIC MATERIALS



Time for study:

90 minutes



Objective

- to define the principle of piezoelectric and pyroelectric phenomena,
- to describe types of ceramics with piezoelectric and pyroelectric properties,
- to describe the optoelectric properties of ceramics



Lecture

1.10 PIEZOELECTRIC CERAMIC MATERIALS

It is a special group of ceramic dielectrics. Ceramics themselves do not have piezoelectric properties. If we crush a piezoelectric crystal, for example a single crystal ZnS, and sinter a plate from a powder providing electrodes, it will not have the effect of deformation by an electric field and even the electrodes will have no charge due to the influence of the deformation. Only ceramics made of a ferroelectric material will show piezoelectric properties after polarization.

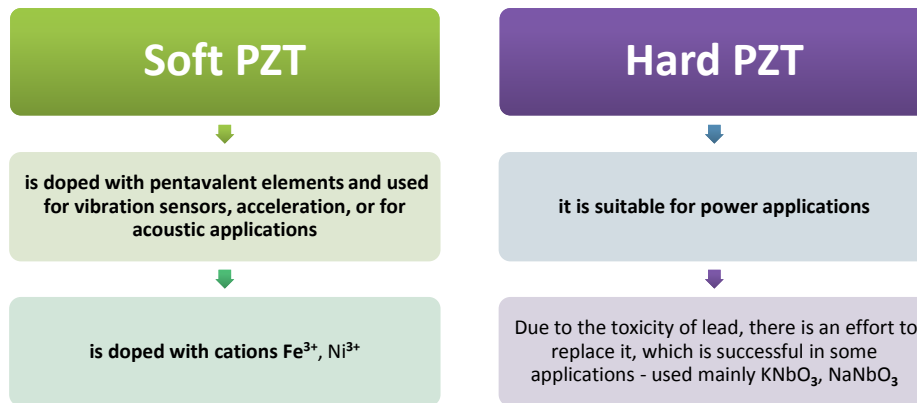
□ The piezoelectric effect

It develops as a consequence of deformation in the direction of the one crystallographic axis where an electric charge of the opposite sign appears on the ends (the inverted piezoelectric phenomenon is deformation due to the insertion of an electric field on the crystal). Piezoelectricity is based on the ability of certain crystals to generate an electric charge under mechanical stress in compression or tension.

1.10.1 PZT ceramics

Today's systems are almost unreservedly based on lead-zirconate-titanate (PZT, $\text{Pb}(\text{TiZr})\text{O}_3$) i.e., they consist of the mixed crystals PbZrO_3 and PbTiO_3 with widely variable properties; a Curie temperature of 220°C to 490°C.

PZT ceramics can be divided into two groups:



New types: niobium (NaNbO_3 , PbNb_2O_6) with a Curie temperature of about 360°C . Today, the most promising are solid solutions between PbZrO_3 and PbTiO_3 (called PZT), improved with other dopants, and today mainly lanthanum (i.e. PLZT ceramics), mainly for electro-optical elements. Applications: piezoelectric transducers/converters (microphones, speakers), the resonant elements of an electronic circuit, electro-optical elements and pyroelectric sensors. Piezoelectric materials can be used as transducers/converters between mechanical and electrical energy. For example submarines are detected by means of ultrasonic waves, where as a result of flow, the material shrinks and expands again, which is subjected to mechanical waves towards the surface, where it is captured by ceramic plates, and converted to an electrical pulse [34]. The utilization of piezoelectricity was dramatically expanded in the automotive industry (e.g. the airbag), computer technology or healthcare (e.g. sonograph).



Summary of terms

After studying this chapter the following terms should be clear:

- piezoelectric effect,
- pyroelectric effect,
- PZT ceramics,
- PLZT ceramics



Questions and tasks

1. Define ceramics with piezoelectric properties.
2. Define ceramics with pyroelectric properties.
3. What is PLZ and PLZT ceramics and where is it used?
4. Define the properties of optoelectric ceramics.

FERRITE CERAMICS



Time for study:

120 minutes



Objective

- to define ferrite ceramics
- to describe ferromagnetic phenomenon
- to describe the difference between ferroelectric and ferromagnetic materials



Lecture

Ferromagnetic substances are those having a relative permeability $\mu_r \gg 1$. The magnetic field strongly modifies upon insertion of such a material in its place. This phenomenon is used in the construction of permanent magnets and electromagnets for various purposes.

In the periodic table there are only four elements which exhibit purely ferromagnetic phenomenon: Fe, Ni, Co, Gd. The most famous representatives are called Ferrites, chemical oxides of iron and barium or strontium which after sintering have the character of ceramic materials. Furthermore, there are also so-called AlNiCo magnets, flexible magnets, magnets based on rare earth elements, non-metallic ferromagnets (semiconductor compounds of iron and oxygen or other elements). Ferromagnetic phenomenon was observed even in some alloy elements.

1.10.2 Ferrites

Ferrites are dark grey or black ceramic materials. They are very hard, brittle and chemically inert. Most modern magnetically soft ferrites have a cubic (spinel) structure. Ferromagnetic substances have two spontaneously magnetized subgrids (A, B) which are not equivalent to both, and cations types and crystallography. Ferrites are materials that have similar characteristics as ferromagnets, however, they have uncompensated magnetic moments and therefore are close to antiferromagnetic substances. They are not even magnetically equal. The spontaneous magnetization of the two grids cancel each other out, and the resulting magnetic moment is the difference between the two subgrids.

Ferromagnetic substances are a function of the chemical composition and crystalline structure. The condition of their formation is that at least one type of cation substance has unpaired electrons in its electron shell and it has a suitable crystal structure.

The general composition of these ferrites is MeFe_2O_4 where Me represents one or more metals such as Mn, Zn, Ni, Co, Cu, Fe or Mg. The most common combinations are MnZn or NiZn. These compounds have good magnetic properties under certain T_c . Monocrystalline ferrites can be

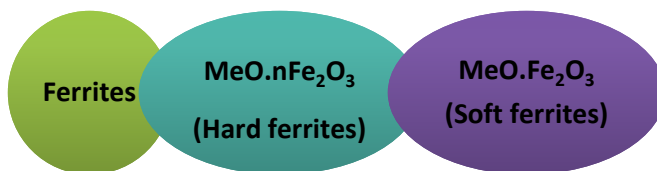
manufactured for (some) special applications, but most ferrites are produced as polycrystalline ceramics.

As an example there can be given the zinc ferrite $ZnFe_2O_4$. All ions of Zn are placed in tetrahedral positions and those of iron in octahedral positions. Such a spinel structure is described as normal. Zn ions have no magnetic moment, while Fe ions have a random orientation so that their magnetic moments cancel each other. Therefore, this substance is not ferromagnetic. By contrast, the ferrite Fe_3O_4 (known as the magnetite mineral) has a so-called inverse structure, typical for ferromagnetic spinels. Tetrahedral spots are occupied by trivalent ions, while other ions Fe^{2+} and Fe^{3+} are located in the octahedral positions (the number is doubled).

Ferrites for technical purposes usually contain more ions. They are solid solutions and their magnetic properties can be regulated by an isomorphous exchange of the components.

- Among the most common divalent cations are Mn, Fe, Co, Ni, Cu, Mg, Zn, Cd, having a close ionic radius, which is a necessary condition for substitution.
- Divalent ions can also be replaced by a combination of $Li^+ + Fe^{3+}$.
- Trivalent iron ions in the spinel structure may also be replaced with Al^{3+} , Ga^{3+} or Cr^{3+} .

□ Dividing ferrites



Ferrites are compounds of $MeO.Fe_2O_3$ or $MeO.nFe_2O_3$. In contrast to ferromagnetic metals, ceramic ferrites have much higher resistance, so that the energy losses arising from the effect of the eddy current in the cores of coils and transformers are significantly smaller in ferrites than in metals.

□ Magnetically soft ferrites ($MeO.Fe_2O_3$)



- The most common commercially used softmagnetic materials are spinel ferrites, Mn_2Zn and Ni_2Zn .

Mn-Zn-ferrite

- magnesium-zinc ferrites are preferred for lower frequencies
- Mn_2Zn ferrites exhibit higher permeability (μ_i) and degree of (Bs) and are suitable up to 3 MHz
- characterized by higher permeability and lower coercive field strength
- having high magnetic permeability and low dielectric losses they are therefore considered the most significant
- (with) an actual porosity (of) PS = 5% it has the permeability of 2.000, when the PS = 1 to 2% it is 20.000, and when the PS = 0.5% it is 40.000

- Such ferrites sinter at high temperatures and have a coarse-grained microstructure. At high temperatures there can occur the reduction of Zn concentration on the surface of the fired bodies and the layer of reduced permeability value forms, which is etched away.
- These high sintered ferrites are used in tape recorders.

Ni-Zn-ferrite

- With an initial perm. 5000, magnetic properties are more stable and less temperature-dependent than they were previously
- NiZn ferrite generally is preferred for a higher frequency transformers, inductors and power efficient applications,
- The microstructure and properties of ceramic ferrites depend on the conditions of processing.
- NiZn ferrites have very high resistance and are the most appropriate for the frequencies above 1 MHz.
- Pure Zn-ferrite is paramagnetic, and larger cations of Zn²⁺ occupy only tetrahedral positions, while Fe ions have only octahedral positions which leads to weak magnetic connections between Fe ions.
- However, the addition of Zn improves the properties of both the above mentioned ferrites.

□ **Magnetically hard ferrites MeO. 6Fe₂O₃**



- e. g. cobalt, tungsten and chromium steel, hard ferrites.
- They have a broad hysteresis loop and large residual magnetism.
- These ferrites are used as permanent magnets.
- They form the basic grid of hard ferrites oxygen anions, in the thickest hexagonal arrangement.
- In every fifth plain, one oxygen anion is replaced by a divalent metal cation.
- The cations of Fe⁺ are located in the spaces between grid areas and (on) the five non-equivalent crystallographic sites.
- In one unit cell, there are 16 Fe ions in parallel orientation and 8 ions of iron in the opposite orientation, with these ferrites the preferred orientation is in the direction of hexagonal c-axis.
- The magnetic moment can be oriented either parallel or antiparallel to the c-axis.
- Ferrite magnets can be produced by means of powder metallurgy as anisotropic or isotropic.

Anisotropic magnets have good magnetic properties only in one direction, i.e. in the preferential axis of magnetisation. They are pressed in the magnetic field giving exactly the prior direction of magnetization. They can be magnetized only in this preferred axis. Possible applications are similar to the isotropic magnets, however, with the same volume a higher magnetic flux can be achieved and according to the type, it usually has the value of permanent magnetic induction higher (about) 1.5 - 2 times. For anisotropic magnets the prior direction of magnetization is identical to the direction of the orientation of magnetization.

Isotropic magnets have almost the same magnetic properties in all directions. They are made of isotropic materials, are pressed without the presence of a magnetic field resulting in numerous possibilities of magnetization. Isotropic magnets have no preferred axis of magnetization and can therefore be magnetized as required in one of the three axes. Compared to anisotropic permanent magnets, they are cost-effective.

□ **Typical use of magnets and electromagnets**

- magnetic recording media,
- credit and magnetic cards,
- TVs and computer monitors,
- speakers and microphones,
- electric motors and generators,
- transformers



Summary of terms

After studying this chapter the following terms should be clear:

- ferromagnetic material,
- Weiss domains,
- magnetic induction,
- magnetic field,
- magnetically soft ferrite,
- magnetically hard ferrite,
- PZT, PLZT ceramics



Questions and tasks

1. Define ferrite, its properties, distribution and preparation.
2. Define a ferromagnetic and ferrimagnetic substance.
3. Define an anisotropic and isotropic magnet.
4. Describe the hysteresis loop of a ferrite.
5. Where are the ferrite ceramics used?

SUPERCONDUCTING CERAMICS



Time for study:

60 minutes



Objective

- to define superconducting ceramics
- to describe how superconductivity arises in a material



Lecture

The word superconductor is used for materials which, when cooled below a certain temperature, exhibit the following two characteristics:

- zero resistance when conducting an electrical current
- perfect displacing of the magnetic field from its volume [38]

Superconductors are called perfect diamagnets. The temperature at which occurs the transformation phase or the transition of the substance from the normal state to a superconducting is called critical temperature T_c . A superconductor, after cooling below the critical temperature displaces the lines (the flux lines) of the magnetic field from its volume. This occurs concretely because the external magnetic field induces superconductive currents on the surface which create a magnetic field of the same size as the external field, but with opposite sign. This completely cancels the magnetic field inside the superconductor. If the magnetic field is generated by a magnet located near a superconductor, it leads to their mutual repulsion. Unlike the repulsion between the two magnets, which occurs when they are turned with identical poles, in the case of a magnet and superconductor there occurs repulsion between them independent of the magnet orientation. When cooled (down) to a temperature near absolute zero, metals suddenly lose their electrical resistance and become superconductive. Superconductivity is such the effect when thin layers of atoms interconnect their valence electrons, distort the crystal structure and form sort of tunnels, which can then let the electrons or electron pairs pass through without being disturbed. Lattice oscillations (vibrations) then actually do not disturb or decelerate the movement of electrons but even support the movement.

Gradually, large quantities of materials with superconducting properties were discovered, however, and they all reached these properties only at very low temperatures. In 1986, Alex Müller and George Bednorz prepared the first of a series of so-called ceramic superconductors which had a $T_c = 35$ K and then there followed the discovery of superconductors at temperatures higher than the temperature of the liquefaction of nitrogen (77 K). The phenomenon was named high temperature

superconductivity. La-Ca-Ba-Cu-O showed a superconducting transition above 30 K, and in 1987, in the system Y-Ba-Cu-O it showed a transition at $T_c = 90$ K. During a subsequent search for other superconducting materials based on copper oxides with even a higher transition temperature there were gradually, during several years (e.g. in 1988 in Japan and USA) found superconducting substances in the system Bi-Sr-Ca-Cu-O with a transition temperature of about $T_c = 110$ K (an important substitute of very expensive yttrium with bismuth), and $T_c = 125$ K for substances of the system Hg-Ba-Ca-Cu-O.



Summary of terms

After studying this chapter the following terms should be clear:

- superconductivity
- superconductor
- the critical temperature
- current density



Questions and tasks

1. Define the superconductivity of ceramics.
2. Explain what causes superconductivity?
3. Describe the preparation and use of superconductive materials.

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