Functional Materials

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He, who wants to see something new, needs to invent it!

Source: FEE Idar-Oberstein
<table>
<thead>
<tr>
<th></th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>U. Müller: Anorganische StrukturchemieTeubner Studienbücher 1991</td>
</tr>
<tr>
<td>2</td>
<td>A.R. West, Grundlagen der Festkörperchemie, VCH Verlagsgesellschaft, Weinheim 1992</td>
</tr>
<tr>
<td>3</td>
<td>H. Briehl, Chemie der Werkstoffe, B.G. Teubner Verlagsgesellschaft, Stuttgart 1995</td>
</tr>
<tr>
<td>5</td>
<td>L. Smart, E. Moore: Einführung in die Festkörperchemie, Vieweg–Lehrbuch 1997</td>
</tr>
<tr>
<td>8</td>
<td>M. Merkel, K.-H. Thomas, Taschenbuch der Werkstoffe, Fachbuchverlag Leipzig 2003</td>
</tr>
</tbody>
</table>
1.1. About Applications of Functional Materials

Some Considerations Previous to the Selection of a Material

1. Is the material generally suitable for the destined application?
   ⇒ Stability against changes in temperature, moisture, oxygen, other gases such as N₂, CO₂, Hg, chemicals, mechanical stress, electrical fields, magnetic fields, plasmas, etc.

2. Are there suitable technologies available to shape the material into its dedicated outer form?
   ⇒ Preparation of thin or thick coatings, processing of extremely hard, moisture-sensitive, temperature-sensitive or brittle materials

3. Do material properties change during processing?
   ⇒ Dependence of material properties on layer thickness or on temperature treatment

4. Is the material environmentally safe? Does it emit pollutants?

5. Is it possible to recycle or dispose of the material in a environmentally sound way, after usage?

Prerequisites to Answer these Questions

⇒ Broad (cross-sectional) knowledge about chemical (catalytic), mechanical, thermal, electrical, magnetic, and optical properties of numerous materials
1.2 Importance of Material Science

Link to Other Sciences and Engineering Branches

- Mineralogy
- Geology
- Biology
- Physics
- Chemistry
- Pharmacy
- Medicine
- Electrical Engineering
- Mechanical Engineering
- Chemical Engineering
1.2 Importance of Material Science

Aim of Material Science

Exact atomic construction of materials ⇒ prediction of all macroscopic properties

The Problem is:

• the exact structure is never known, since every material exhibits impurities, defects and broad particle size distributions
• there is no physical theory that can predict macroscopic properties, such as electrical conductivity, magnetism, absorption spectrum, luminescence, quantum efficiency, etc., to one hundred percent

Therefore Material Science contents oneself with the:

• description of material properties
• investigation of the cause for the properties
• material selection
• material synthesis and optimisation
• analysis of materials
1.2 Importance of Material Science

Importance of Functional Materials

Material development (hardware) is crucial for the speed of technical progress

1. Example: Micro electronics
   - Mainframes with vacuum tubes (1950)
   - Si-wafer for micro electronics (2000)

2. Example: Light sources
   - Fluorescent tubes since ca. 1940
   - (Al,In,Ga)P chip for red LEDs (2000)

Software and drivers can be developed relatively easy and fast in comparison...
1.3 History

Development of Material’s Chemistry/Physics

Material research
„Trial & error“
Oral transmission

Chemistry
Solid state chemistry
High pressure chemistry
Polymer chemistry

Physics
Electromagnetism
Solid state physics
Quantum mechanics
Statistical thermodynamics

Material Science
Selective synthesis
Theoretical understanding of structure and function

Example: Egyptian blue
# 1.3 History

## Progress in Material Handling

<table>
<thead>
<tr>
<th>Date</th>
<th>Material</th>
<th>Date</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>100000 B.C.</td>
<td>Wood, bones, stone</td>
<td>600 A.D.</td>
<td>Chinaware</td>
</tr>
<tr>
<td>9000 B.C.</td>
<td>Fibres</td>
<td>1500 A.D.</td>
<td>Steel, cast iron</td>
</tr>
<tr>
<td>7000 B.C.</td>
<td>Mud brick</td>
<td>1700 A.D.</td>
<td>Böttger porcelain</td>
</tr>
<tr>
<td>6000 B.C.</td>
<td>Ceramics</td>
<td>1820 A.D.</td>
<td>Plastics, rubber</td>
</tr>
<tr>
<td>5000 B.C.</td>
<td>Hemp</td>
<td>1850 A.D.</td>
<td>Concrete</td>
</tr>
<tr>
<td>3500 B.C.</td>
<td>Potter’s wheel</td>
<td>1900 A.D.</td>
<td>Flat glass</td>
</tr>
<tr>
<td>3000 B.C.</td>
<td>Glaze, bronze</td>
<td>1919 A.D.</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>2500 B.C.</td>
<td>Silk</td>
<td>1930 A.D.</td>
<td>Al-alloys</td>
</tr>
<tr>
<td>2000 B.C.</td>
<td>Glass</td>
<td>1950 A.D.</td>
<td>Semiconductor(diodes)</td>
</tr>
<tr>
<td>1500 B.C.</td>
<td>Iron</td>
<td>1960 A.D.</td>
<td>Ti-alloys</td>
</tr>
<tr>
<td>1000 B.C.</td>
<td>Hypothesis of atoms</td>
<td>1986 A.D.</td>
<td>High temperature super conductor</td>
</tr>
<tr>
<td>500 B.C.</td>
<td>Glazed bricks</td>
<td>1993 A.D.</td>
<td>Blue InGaN LEDs</td>
</tr>
<tr>
<td>25 B.C.</td>
<td>Cement</td>
<td>2000 A.D.</td>
<td>Composites, Super alloys</td>
</tr>
<tr>
<td>Around 0</td>
<td>Glass blowing</td>
<td>2007 A.D.</td>
<td>UV-C AlGaN LEDs</td>
</tr>
</tbody>
</table>
1.4 Principals to Classify and Order

Categorisation According to Phase State

<table>
<thead>
<tr>
<th>Solid</th>
<th>Liquid</th>
<th>Gaseous</th>
<th>Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>Non-metals</td>
<td>Natural substances</td>
<td></td>
</tr>
<tr>
<td>Fe, Cu, Ag, Au</td>
<td>Glass, porcelain, plastics, graphite ceramics (ZrO$_2$, Al$_2$O$_3$)</td>
<td>Wood, coke, rubber, asbestos, chalk, marble, gemstones</td>
<td></td>
</tr>
<tr>
<td>Ta, Nb, W, Mo, Ti, Mg, Al, Ga</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na, K, Ba, Sr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd, Pt, Rh, Ir</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Composites (Concrete, glass ceramics, milk carton...
1.4 Principals to Classify and Order

**Structural Materials (Classical Materials)**

⇒ Mechanic properties are most important

- Construction materials
  - Cement, mortar
  - lime, gypsum
- Ceramics
  - Construction ceramics
  - vessel ceramics
  - technical ceramics (engine parts)
- Glass and glass ceramic

**Functional Materials (Modern Materials)**

⇒ Materials, that belong to a certain functional group

- Ceramics
  - Bio-ceramics
  - Electro-ceramics
  - Magneto-ceramics
  - Catalysts
  - Opto-ceramics
- Single crystals
  - Laser-crystals, frequency-doubler (NLO-crystals)
1.4 Principals to Classify and Order

Properties of Materials

**Metals:** High electrical and thermal conductivity, high strength and plasticity  
*Exp.:* Cu as conductive material, hardened steel for tools

**Semiconductors:** Simple adjustability of electrical conductivity by dopants, very brittle  
*Exp.:* Si, Ge, GaAs, \((\text{Ga}_1\text{xIn}_x)\text{N}\) as materials for diodes and solar cells

**Ceramics:** Poor electrical and thermal conductivity, suitable for insulating components, high temperature stability, extremely hard, very brittle  
*Exp.:* Capacitors, \(\text{Al}_2\text{O}_3\) and \(\text{MgO}\) as fire-resistant vessels, porcelain

**Polymers:** Normally, poor electrical and thermal conductivity, high mechanical flexibility, low temperature stability  
*Exp.:* Polyethylene as packaging material, epoxy resin for the casing of electrical components

**Composites:** High strength, relatively low density  
*Exp.:* Concrete, graphite-epoxy as components for airplanes
## 1.4 Principals to Classify and Order

### Properties and Applications

**“Electrical” materials**

<table>
<thead>
<tr>
<th>Material type (property)</th>
<th>Compound</th>
<th>Application(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic conductor</td>
<td>Cu, Ag, Au</td>
<td>Electrical engineering</td>
</tr>
<tr>
<td>Low-dimensional metallic conductor</td>
<td>K₂[Pt(CN)₄]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexagonal Cₓ (graphite)</td>
<td>Electrodes</td>
</tr>
<tr>
<td>Semi-conductor</td>
<td>Si, Ge, GaAs, Si, CuInSe₂, GaAs, AlInGaP, AlInGaN</td>
<td>Diodes, transistors, IC’s, Solar cells, LEDs, laser diodes, photo diodes</td>
</tr>
<tr>
<td></td>
<td>Li₀.₀₅Ni₀.₉₅O</td>
<td>Thermistors</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>Photo conductors</td>
</tr>
<tr>
<td></td>
<td>SnO₂:In</td>
<td>Transparent electrodes</td>
</tr>
<tr>
<td>Thermo-electrical materials</td>
<td>Bi₂Te₃, PbTe</td>
<td>Thermo-electrical cooler</td>
</tr>
<tr>
<td>Superconductors</td>
<td>Nb₃Sn</td>
<td>High-field magnets</td>
</tr>
<tr>
<td></td>
<td>YBaCu₃O₇</td>
<td>Resistance-free transport of electricity</td>
</tr>
<tr>
<td>Ionic conductors</td>
<td>NaAl₁₁O₁₇ (β-alumina)</td>
<td>Long-lasting batteries, accumulators</td>
</tr>
<tr>
<td></td>
<td>ZrO₂:Y</td>
<td>O₂-sensors (Lambda-probe)</td>
</tr>
</tbody>
</table>
## 1.4 Principals to Classify and Order

### Properties and Applications

**“Dielectrical”, “magnetic”, and “optical” materials**

<table>
<thead>
<tr>
<th>Material type (property)</th>
<th>Compound</th>
<th>Application(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezo-electrics</td>
<td>Pb(Ti$_{1-x}$Zr$_x$)O$_3$ (PZT)</td>
<td>Electro-acoustics: microphone, speaker</td>
</tr>
<tr>
<td>Pyro-electrics</td>
<td>ZnO</td>
<td>IR-detectors</td>
</tr>
<tr>
<td>Ferro-electrics</td>
<td>BaTiO$_3$, PbTiO$_3$</td>
<td>Capacitors, sensors</td>
</tr>
<tr>
<td>Ferro- and Ferri-magnets</td>
<td>Nd$<em>2$Fe$</em>{14}$B, BaFe$<em>{12}$O$</em>{19}$, SmCo$_5$</td>
<td>Permanent magnets</td>
</tr>
<tr>
<td></td>
<td>Fe, $\gamma$-Fe$_2$O$_3$, CrO$_2$</td>
<td>Audio- and video tapes</td>
</tr>
<tr>
<td></td>
<td>MFe$_2$O$_4$ (Ferrite), ZnFe$_2$O$_4$</td>
<td>Engines, transformers</td>
</tr>
<tr>
<td></td>
<td>Y$_3$Fe$<em>5$O$</em>{12}$ (YIG)</td>
<td>Information storage</td>
</tr>
<tr>
<td></td>
<td>FeBO$_3$</td>
<td>Magneto-optics: modulation of light</td>
</tr>
<tr>
<td>Colour</td>
<td>CoAl$_2$O$_4$, CdS, Fe$_2$O$_3$, TiO$_2$</td>
<td>Colour filter, dispersion paint</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>BaMgAl$<em>{10}$O$</em>{17}$:Eu, Y$_2$O$_3$:Eu</td>
<td>Fluorescent tubes</td>
</tr>
<tr>
<td></td>
<td>Y$_3$Al$<em>5$O$</em>{12}$:Ce, Sr$_2$Si$_5$N$_8$:Eu</td>
<td>white LEDs</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>ZnS:Ag, ZnS:Cu, Y$_2$O$_2$S:Eu</td>
<td>Cathode ray tube</td>
</tr>
<tr>
<td>X-ray luminescence</td>
<td>Bi$_4$Ge$<em>3$O$</em>{12}$, Lu$_2$SiO$_5$:Ce</td>
<td>PET</td>
</tr>
<tr>
<td>Stimulated emission of light</td>
<td>Al$_2$O$_3$:Cr, Al$_2$O$_3$:Ti, Y$_3$Al$<em>5$O$</em>{12}$:Nd</td>
<td>Solid state laser</td>
</tr>
</tbody>
</table>
1.5 Structure-Property-Correlations

**Electronic Structure**

- Free electrons lead to high electrical and thermal conductivity, and to strong absorption
- Unpaired electrons lead to para, and thus to ferro- or anti-ferromagnetic behaviour
- Weakly bound electrons can easily be influenced by electro-magnetic radiation, resulting in altered optical behaviour

**Atomic Structure**

- The crystal structure strongly influences the mechanical, electrical, thermal, catalytic and optical properties
  
  Graphite (layered structure) ↔ diamond (network structure)

- Amorphous materials possess exceptional physical properties, e.g. glass is transparent, but after crystallisation it often becomes impermeable to light
1.5 Structure-Property-Correlations

Nanostructure

- By nanoscale structuring a large number of boundary surfaces is created, i.e. most atoms are located at boundary layers and thus have different physical properties than atoms within the bulk material
- Quantum size effects

Microstructure (texture)

- Mixture and separation on micrometre scale in glasses and alloys
- Primarily influences mechanical and optical properties
- Micro-crystalline materials: sintered micro-crystallites
- Glass ceramics: micro-crystallites in glass matrix
- Composites: Different phases
1.6 Phases and Crystals

Phases and Phase Transitions

Phase: Homogenous material system in a well defined thermodynamic state

Independent state variables: T, p, chemical composition x, magnetic field strength

Dependent state variables (functions): V, U, H, S, F, G, polarisation, magnetisation, electrical resistance

Phase transition: Upon alteration of independent state variables, a non-differentiable point occurs in at least one state function, e.g. G(p,T):

Discontinuity in 1. derivation: Phase transition of 1st order, e.g. melting of Hg at –39 °C
Discontinuity in 2. derivation: Phase transition of 2nd order, e.g. glass transition of poly-styrene at about 100 °C

Polymorphism: Phenomenon, that a homogenous material system crystallises in different lattice types, depending on independent state variables
1.6 Phases and Crystals

Crystals and Mixed Crystals

Ideal crystal: Mathematical, spatially periodical abstraction of real crystals

Substitutional mixed crystals: Atoms are isotypically substituted by “impurity” atoms

Intercalation mixed crystals: “Impurity” atoms are incorporated on interstitials

Real crystal: Ideal crystal + defects + impurities (dopants)

Defects of different dimensions

0-dim. (point defects): Schottky-defects (cation and anion vacancies)
Frenkel-defects (ion $\rightarrow$ interstitials)

1-dim. (line defects): Dislocations (steps, screws)

2-dim. (area defects): Stacking faults, boundary surface, (surfaces, phase boundary, twin boundary, …)

3-dim. (spatial defects): Cavities, pores, inclusions, …
2.1 Mechanical Properties

Important Mechanical Quantities

⇒ Elasticity, plasticity, breaking strength, ductility, hardness (Mohs, Brinell, Vickers, Knoop, Rockwell, Shore, … → scales of hardness)
⇒ Different ways of mechanical deformation

One dimensional test

![Diagram of tensional stress](Image 1)

- Tensile stress: \( \sigma = F/A \)
- Elongation: \( \varepsilon = \frac{l}{\Delta l} \)
- Elastic modulus: \( E = \frac{\sigma}{\varepsilon} \)

Shear experiment

![Diagram of shear stress](Image 2)

- Shear stress: \( \tau = F/A \)
- Shearing angle: \( \varphi \)
- Shear modulus: \( G = \frac{\tau}{\varphi} \)
## 2.1 Mechanical Properties

### Important Mechanical Quantities

**Compression experiment**

![Compression experiment diagram](image)

- **Pressure**
  - $p$

- **Relative change in volume**
  - $\Delta V/V$

- **Compressive modulus**
  - $\kappa = p/(\Delta V/V)$

The moduli $\kappa$, $G$, and $E$ are not independent from one another but linked.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's modulus $E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>0.1 GPa</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2 GPa</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3 GPa</td>
</tr>
<tr>
<td>Pb</td>
<td>18 GPa</td>
</tr>
<tr>
<td>β-Sn</td>
<td>54 GPa</td>
</tr>
<tr>
<td>Al</td>
<td>69 GPa</td>
</tr>
<tr>
<td>Window glass</td>
<td>70 GPa</td>
</tr>
<tr>
<td>SiO$_2$ (quartz)</td>
<td>74 GPa</td>
</tr>
<tr>
<td>Au</td>
<td>80 GPa</td>
</tr>
<tr>
<td>Cu</td>
<td>110 GPa</td>
</tr>
<tr>
<td>Steel</td>
<td>207 GPa</td>
</tr>
<tr>
<td>Y$_3$Al$<em>5$O$</em>{12}$</td>
<td>283 GPa</td>
</tr>
<tr>
<td>W</td>
<td>355 GPa</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>373 GPa</td>
</tr>
<tr>
<td>SiC</td>
<td>470 GPa</td>
</tr>
</tbody>
</table>
2.1 Mechanical Properties

**Influence of Temperature on Moduli**

Typical dependence \( \kappa, G, E \)

Polymers, highly elastic \( \Rightarrow \) v. d. W. forces
Metals, elastic \( \Rightarrow \) metallic interactions
Ceramics, brittle \( \Rightarrow \) ionic interactions

Cause: Potential shape, e.g. Lennard-Jones potential

Elastic shape formations by deflection of the atoms from their equilibrium position.
2.1 Mechanical Properties

Elasticity and Plasticity

Tension-Strain-Diagram (typically) (for construction steel S235)

**Elastic deformation:** \( \sigma = \varepsilon \cdot E \) (Hook’s law)

**Inelastic deformation:** Hooke’s law is not valid, anymore (hysteresis)

**Plastic deformation:** permanent deformation \( \Rightarrow \) ductility
2.1 Mechanical Properties

Ductility Describes the Capability of a Material to Be Plastically Deformed without Breaking

\[ D = \frac{(L_b - L_0)}{L_0} \]

with \( L_0 = \) length of sample without strain
\( L_b = \) length of sample after breaking

Materials are ductile, if \( D > 0.5 \) \( \Rightarrow \) most metals

Plastic deformations rely on translational motions of slippery dislocations!
2.1 Mechanical Properties

Hardness Describes the Resistance of Materials against the Intrusion of Objects into their Surface

Mohs-Hardness (scratch-test)

Empirical scale of comparison

<table>
<thead>
<tr>
<th>Mohs-Hardness</th>
<th>Material for comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Talcum Mg₃[Si₄O₁₀(OH)₂]</td>
</tr>
<tr>
<td>2</td>
<td>Gypsum CaSO₄·2H₂O</td>
</tr>
<tr>
<td>3</td>
<td>Calcite CaCO₃</td>
</tr>
<tr>
<td>4</td>
<td>Fluorite CaF₂</td>
</tr>
<tr>
<td>5</td>
<td>Apatite Ca₅(PO₄)₃(F,Cl)</td>
</tr>
<tr>
<td>6</td>
<td>Orthoklas K[AlSi₃O₈]</td>
</tr>
<tr>
<td>7</td>
<td>Quartz SiO₂</td>
</tr>
<tr>
<td>8</td>
<td>Topaz Al₂SiO₄(F,OH)₂</td>
</tr>
<tr>
<td>9</td>
<td>Corundum Al₂O₃ (~ Cr, W, Ir)</td>
</tr>
<tr>
<td>10</td>
<td>Diamond C_{cubic}</td>
</tr>
</tbody>
</table>

Brinell-Hardness HB (pressure-test)

\[
HB = \frac{F}{(\pi / 2)D(D - \sqrt{D^2 - D_i^2})}
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>HB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymers</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Brass (Cu-Zn)</td>
<td>50</td>
</tr>
<tr>
<td>Mundane steel</td>
<td>200</td>
</tr>
<tr>
<td>Annealed steel</td>
<td>500 - 1000</td>
</tr>
<tr>
<td>Diamond</td>
<td>7500</td>
</tr>
</tbody>
</table>
2.2 Thermal Properties

Thermal Properties of Solids Depend Strongly on Bonding Energies of the Atomic Components

<table>
<thead>
<tr>
<th>Type of bonding</th>
<th>Bonding energy [kJ/mol]</th>
<th>Covalent part of ionic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>600 – 1500</td>
<td></td>
</tr>
<tr>
<td>Covalent</td>
<td>500 – 1250</td>
<td></td>
</tr>
<tr>
<td>Metallic</td>
<td>100 – 800</td>
<td></td>
</tr>
<tr>
<td>H-bonds</td>
<td>&lt; 170</td>
<td></td>
</tr>
<tr>
<td>Van der Waals</td>
<td>&lt; 50</td>
<td></td>
</tr>
</tbody>
</table>

The bonding strength influences the phonon frequencies (lattice vibrations) and thus the following temperature-dependant properties:

- Molar heat capacity and specific heat capacity
- Thermal conductivity
- Thermal expansion coefficient

\[ KO = \exp^{-0.25(\Delta X)^2} \]
2.2 Thermal Properties

Molar Heat Capacity

\[ c_{vm} = \left( \frac{\delta U_m}{\delta T} \right)_{V,N} \]

\[ c_{pm} = \left( \frac{\delta H_m}{\delta T} \right)_{p,N} \]

In solids: \( c_{vm} \approx c_{pm} \)

Temperature-dependence of heat capacity

At high temperatures: \( c_{vm} = 3R \approx 25 \text{ J/K} \cdot \text{mol} \)  
(Dulong-Petit’s rule)  
Metals ~ above 100 °C  
Ceramics ~ above 1000 °C

At low temperatures: \( c_{vm} \sim T^3 \)

At 0 K: \( c_{vm} = 0 \)
2.2 Thermal Properties

Molar Heat Capacity

Lattice vibrations in solids  
\( (k = \text{wave vector}, \ u = \text{deflection}) \)

Debye-Theory: Assumptions

- Atoms vibrate as couples (phonons)
- The distribution of frequencies is discrete
- Maximal wavelength depends on the size of the crystal = 2 * length
- Minimal wavelength is given by the lattice spacing
- For every wavelength there is a longitudinal and two transversal modes, thus 3N modes for N atoms
- The energy of every vibration is given by \( E = hv \)
- The excitation into a higher vibrational state is subject to Boltzmann-statistics, i.e. \( \exp(-\Delta E/kT) = \exp(-h\Delta v/kT) \)
2.2 Thermal Properties

Molar Heat Capacity

Debye-Theory – Results

At low temperatures:

\[ c_{\text{vm}} = \left( \frac{T}{\Theta_D} \right)^3 \]

with \( \Theta_D = \frac{\hbar \nu_D}{k} = \text{Debye-temperature} \)

and \( \nu_D = \text{Debye-frequency} \)

Explanation: At low temperatures, according to Boltzmann-statistics, only low-lying frequencies are excited. With increasing temperature, more and more frequencies can be excited.

Materials with weak bonds: low Debye-frequencies
Materials with strong bonds: high Debye-frequencies

At high temperatures:

\[ c_{\text{vm}} = 3R \approx 25 \text{ J/K\cdotmol} \]

Explanation: All 3 N vibrational modes are excited. Every vibrational mode contributes the amount of \( k \) (1/2 k from potential energy and 1/2 k from kinetic energy) to the heat capacity.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \Theta_D ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>225</td>
</tr>
<tr>
<td>C (diamond)</td>
<td>1800</td>
</tr>
<tr>
<td>Fe</td>
<td>465</td>
</tr>
<tr>
<td>Pb</td>
<td>94.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>281</td>
</tr>
<tr>
<td>CaF(_2)</td>
<td>474</td>
</tr>
<tr>
<td>FeS(_2)</td>
<td>645</td>
</tr>
</tbody>
</table>

\[ \nu = \frac{1}{2\pi} \cdot \sqrt{\frac{D}{m}} \]

\( D = \text{force constant} \)

\( m = \text{mass} \)
2.2 Thermal Properties

Molar Heat Capacity

Exceptions in solids
Metals (with electron gas)
At extremely low temperatures, free electrons contribute extensively to the heat capacity, because of $c_{el} \sim T$

Formation of point defects in crystals (e.g. Frenkel- or Schottky-defects) lead to an increase in heat capacity

Disorder in amorphous materials, s.a. glasses, leads to differences in the vibrational spectra and thus to a alteration of the heat capacity, especially at temperatures above 50 K

Phase transitions (structural, magnetic) lead to anomalies of the heat capacity close to the transformation temperature
# 2.2 Thermal Properties

## Molar Heat Capacity and specific Heat

Specific heat \( c = \text{heat capacity/molar mass} \ [\text{J/K} \cdot \text{g}] \)

<table>
<thead>
<tr>
<th>Material</th>
<th>Heat capacity [J/K·g]</th>
<th>Material</th>
<th>Heat capacity [J/K·g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.90</td>
<td>Al(_2)O(_3)</td>
<td>0.84</td>
</tr>
<tr>
<td>Cu</td>
<td>0.39</td>
<td>C (diamond)</td>
<td>0.52</td>
</tr>
<tr>
<td>B</td>
<td>1.03</td>
<td>SiC</td>
<td>1.05</td>
</tr>
<tr>
<td>Fe</td>
<td>0.44</td>
<td>Si(_3)N(_4)</td>
<td>0.71</td>
</tr>
<tr>
<td>Pb</td>
<td>0.16</td>
<td>SiO(_2) (quartz)</td>
<td>1.11</td>
</tr>
<tr>
<td>Mg</td>
<td>1.02</td>
<td>Polyethylene, high density</td>
<td>1.84</td>
</tr>
<tr>
<td>Ni</td>
<td>0.44</td>
<td>Polyethylene, low density</td>
<td>2.30</td>
</tr>
<tr>
<td>Si</td>
<td>0.70</td>
<td>Polystyrene</td>
<td>1.17</td>
</tr>
<tr>
<td>Ti</td>
<td>0.53</td>
<td>Nylon-6,6</td>
<td>1.67</td>
</tr>
<tr>
<td>W</td>
<td>0.13</td>
<td>H(_2)O</td>
<td>4.18</td>
</tr>
<tr>
<td>Zn</td>
<td>0.39</td>
<td>N(_2)</td>
<td>1.04</td>
</tr>
</tbody>
</table>
2.2 Thermal Properties

Heat Transfer

1. Thermal Radiation
   - Electromagnetic radiation (microwaves, IR, VIS, UV, etc.)
   - Heat flux in all phases, even in vacuum

   \[ \dot{Q} = \varepsilon \sigma A T^4 \]
   with \( A = \text{area}, \ \varepsilon = \text{emission intensity}, \ \sigma = \text{Boltzmann-constant} \)
   i.e. \( \sim T^4 \)

2. Convection
   - Transport of particles
   - Heat flux in liquids and gases but not in solids or vacuum

   \[ \dot{Q} = \alpha A (T_1 - T_2) \]
   with \( A = \text{area}, \ \alpha = \text{thermal transfer coefficient} \ [\text{Wm}^{-2}\text{K}^{-1}] \)
   (describes the flow conditions around a body)

3. Thermal conduction
   - No macroscopic material flow
   - Heat flux in all phase but not in vacuum
2.2 Thermal Properties

Heat Conductivity

Thermal transport in solids

- Phonons
- Free electrons
- At extremely high temperatures: IR-radiation (→ incandescent bulb) ~ $T^4$

Temperature gradient $\frac{dT}{dz}$

Heat flux $J_Q = \frac{1}{A} \cdot \frac{dQ}{dt}$

Non-metallic solids (ceramics)

- Phonons are responsible for heat conductivity
- Heat conductivity of almost perfect single crystals is much higher than of polycrystalline materials (spreading of phonons at grain boundaries), materials with a lot of defects or impurities and glasses (spreading of phonons through disorder)
- Often, the heat conductivity decreases with increasing temperature, since ever more defects are generated

$J_Q = \frac{1}{A} \cdot \frac{dQ}{dt} = -\lambda \frac{dT}{dz}$

$\lambda$ = heat conductivity coefficient
2.2 Thermal Properties

Heat Conductivity

Metallic solids
- Heat conductivity is dominated by free electrons and is thus significantly higher than for non-metals
- As first approximation, heat conductivity is proportional to electric conductivity:
  \[ \lambda = L \sigma T \] (Wiedemann-Franz-law) with \( L = 2.3 \times 10^{-8} \, \text{J} \Omega / \text{s} \cdot \text{K}^2 \) (Lorentz constant)

Semi-conductors
- Heat transport by electrons and phonons
- At low temperatures, phonons dominate heat transport
- With increasing temperature, more and more electrons are promoted into the conduction band, which leads to a considerable increase in thermal conductivity

Polymers
- Poor heat conductors, since, in general, no free electrons are available and a significant amount of energy is stored in local movements of chain segments, so that the transport of heat is severely hindered

High thermal conductivity is of importance for the cooling of light and radiation sources, LEDs, displays, micro processors, etc.
## 2.2 Thermal Properties

### Thermal Conductivity $\lambda \ [\text{Js}^{-1}\text{m}^{-1}\text{K}^{-1}] = [\text{Wm}^{-1}\text{K}^{-1}]$

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity $[\text{J/m}\cdot\text{s}\cdot\text{K}]$</th>
<th>Material</th>
<th>Thermal conductivity $[\text{J/m}\cdot\text{s}\cdot\text{K}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>238</td>
<td>Al$_2$O$_3$</td>
<td>16</td>
</tr>
<tr>
<td>Cu</td>
<td>402</td>
<td>C (diamond)</td>
<td>23</td>
</tr>
<tr>
<td>Fe</td>
<td>79</td>
<td>C (graphite)</td>
<td>335</td>
</tr>
<tr>
<td>Mg</td>
<td>100</td>
<td>Clay (oven)</td>
<td>0,27</td>
</tr>
<tr>
<td>Pb</td>
<td>35</td>
<td>SiC</td>
<td>88</td>
</tr>
<tr>
<td>Si</td>
<td>150</td>
<td>Si$_3$N$_4$</td>
<td>14,6</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>Na-lime glass</td>
<td>0,96</td>
</tr>
<tr>
<td>W</td>
<td>172</td>
<td>Quartz glass</td>
<td>1,34</td>
</tr>
<tr>
<td>Zn</td>
<td>117</td>
<td>Vycor glass</td>
<td>1,26</td>
</tr>
<tr>
<td>Zr</td>
<td>23</td>
<td>ZrO$_2$</td>
<td>5</td>
</tr>
<tr>
<td>Ag</td>
<td>428</td>
<td>Nylon-6,6</td>
<td>0,25</td>
</tr>
<tr>
<td>Cu-Ni(30%)</td>
<td>50</td>
<td>Polyethylene</td>
<td>0,33</td>
</tr>
<tr>
<td>Ferrite</td>
<td>75</td>
<td>Polyimide</td>
<td>0,21</td>
</tr>
<tr>
<td>Gold brass</td>
<td>222</td>
<td>Polystyrene foam</td>
<td>0,03</td>
</tr>
</tbody>
</table>
2.2 Thermal Properties

**Thermal Expansion**

Linear thermal extension coefficient $\alpha$

$$\alpha = \frac{1}{L_0} \cdot \left( \frac{\delta L}{\delta T} \right)_p$$

$$\Delta L = \alpha \cdot L_0 \cdot \Delta T$$

Volume-expansion coefficient $\gamma = 3\alpha$

$$\gamma = \frac{1}{V_0} \cdot \left( \frac{\delta V}{\delta T} \right)_p$$

$$\Delta V = \alpha \cdot V_0 \cdot \Delta T$$

Thermal expansion, explained utilizing the model of a diatomic anharmonic oscillator, described by the so-called Morse-potential.

The equilibrium distance increases with temperature, because evermore vibrational states are occupied.
2.2 Thermal Properties

Thermal Expansion Coefficient of Different Materials

**Ceramics**
Low expansion coefficient, due to highly ionic or covalent bonding
- $\text{Al}_2\text{O}_3$ $\alpha = 8.8$ ppm/K
- Quartz glass $\alpha = 0.5$ ppm/K

**Metals**
High expansion coefficient, since metallic bonds are weaker than covalent or ionic bonds
- Ag $\alpha = 19$ ppm/K
- Al $\alpha = 24$ ppm/K

**Polymers**
Very high expansion coefficients, due to only weak bonding interactions (van-der-Waals, H-bonds) between the individual polymer chains
- Teflon $\alpha = 150$ ppm/K
- Nylon-6,6 $\alpha = 80$ ppm/K
2.2 Thermal Properties

Thermal Expansion Coefficient and Melting Point

<table>
<thead>
<tr>
<th>Metal</th>
<th>$T_m$ [°C]</th>
<th>$\alpha$ [ppm/K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>3810</td>
<td>3.0</td>
</tr>
<tr>
<td>Ta</td>
<td>2996</td>
<td>6.5</td>
</tr>
<tr>
<td>Ir</td>
<td>2410</td>
<td>6.6</td>
</tr>
<tr>
<td>Pt</td>
<td>1772</td>
<td>9.0</td>
</tr>
<tr>
<td>Fe</td>
<td>1535</td>
<td>12.0</td>
</tr>
<tr>
<td>Ni</td>
<td>1495</td>
<td>13.0</td>
</tr>
<tr>
<td>Au</td>
<td>1064</td>
<td>14.3</td>
</tr>
<tr>
<td>Cu</td>
<td>1083</td>
<td>16.8</td>
</tr>
<tr>
<td>Ag</td>
<td>962</td>
<td>19.7</td>
</tr>
<tr>
<td>Al</td>
<td>660</td>
<td>25</td>
</tr>
<tr>
<td>Pb</td>
<td>327</td>
<td>29</td>
</tr>
<tr>
<td>Cd</td>
<td>321</td>
<td>30</td>
</tr>
<tr>
<td>Li</td>
<td>180</td>
<td>58</td>
</tr>
<tr>
<td>Na</td>
<td>98</td>
<td>71</td>
</tr>
<tr>
<td>K</td>
<td>64</td>
<td>84</td>
</tr>
<tr>
<td>Cs</td>
<td>29</td>
<td>97</td>
</tr>
</tbody>
</table>

![Graph showing the relationship between linear thermal expansion coefficient ($\alpha$) and melting point ($T_m$) for various metals.](image-url)
2.2 Thermal Properties

Thermal Expansion Coefficient – Challenges for Materials Sciences

Composites

- Expansion coefficients of the individual components must be adjusted properly, so that the material does not break upon temperature changes.

Development of materials with extremely low expansion coefficients

- Example: Zerodur made by Schott
  - Glass ceramics based on $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ (Zerodur):
    - Glass possess a positive expansion coefficient,
    - crystals exhibit negative expansion coefficients
  - $\Rightarrow \alpha(\text{Zerodur}) = 0.02 \text{ ppm/K}$
  - Application: Ceran hobs

Examples for substances with negative thermal expansion

- $\text{H}_2\text{O(l)} \ 0 – 4 ^\circ\text{C}$
- $\text{H}_2\text{O(s)} < 0 ^\circ\text{C}$
- Silicon
- Some zeolites
- Some tungstates and molybdates
2.2 Thermal Properties

Negative Thermal Expansion Occurs in Crystals with Highly Open Structure

**Cause**
Cooperative vibrational modes or so-called liberation movements of adjacent polyhedra

**Example:** ZrW$_2$O$_8$ discovered by A. Sleight in 1998 (Inorg. Chem. 37 (1998) 2854)
- negative thermal expansion from $T = 0$ K until decomposition at $1050$ K
- Liberation movements of ZrO$_6$-octahedra and WO$_4$-tetrahedra
- Liberation overcompensates normal thermal expansion
- Numerous technical applications, e.g. electronics, optics, fuel cells, oxygen sensors, shock absorbers, thermostats, dentures
2.3 Electrical and Dielectrical Properties

Relevance

1. Minimisation of thermal loss in power lines
   \[ \Rightarrow \text{as high electrical conductivity as possible of the cable materials} \]

2. Prevention of disruptive discharges or generation of light arcs
   \[ \Rightarrow \text{as low electrical conductivity as possible of the isolating materials} \]

3. Enhancement of the efficiency of solar cells as alternative energy sources
   \[ \Rightarrow \text{as high efficiency as possible of the formation of electron/hole pairs and their consecutive separation} \]

4. Miniaturisation in electronics
   \[ \Rightarrow \text{selective fine-tuning of electrical conductivity} \]
2.3 Electrical and Dielectrical Properties

Ohm’s Law and Electrical Conductivity

**Ohm’s law**

\[ R = \frac{U}{I} \]

- \( R \) = resistance [\( \Omega \)]
- \( U \) = voltage [V]
- \( I \) = current [A]

\( \rho \) = specific resistance [\( \Omega \cdot m \)]

Resistance \( R \) depends on

- Properties of conductive material
- Dimensions of conductor

\[ R = \rho \cdot \frac{1}{A} = \frac{1}{\sigma} \cdot \frac{1}{A} \]

According to the above equation, the dimensions of resistors can be adjusted for a particular application. Furthermore, the thermal loss should be as small as possible in order to minimize energy loss and unnecessary heating of the conductor.

**Thermal loss**

\[ P = U \cdot I = I^2 \cdot R \]
2.3 Electrical and Dielectrical Properties

Specific Resistance and Specific Conductivity

⇒ Specific material properties

Type of charge carrier

- Electrons
- Ions (cations > anions)

The specific conductivity/resistance of a material depends on charge, number density and the mobility of the charge carriers.

\[ \sigma = N_V \cdot q \cdot \mu \]

- \( N_V \) = number of charge carriers per volume \([m^{-3}]\)
- \( q \) = electrical charge \([C]\)
- \( \mu \) = electronic mobility \([m^2 \cdot V^{-1} \cdot s^{-1}]\)

Electrical conduction in

- Semi-conductors and insulators: number of charge carriers crucial
- Metals: mobility of charge carriers crucial
2.3 Electrical and Dielectrical Properties

Definition of Electrical mobility $\mu$

$\Rightarrow$ The electronic mobility $\mu$ is defined as the drift velocity of the charge carriers with regard to the applied electrical field strength

$$\mu = \frac{v}{E}$$

$v = \text{drift velocity} [\text{m/s}]$

$E = \text{electrical field strength} [\text{V/m}]$

The drift velocity $v = \Delta x/\Delta t$ is the average velocity of the charge carriers along the direction of the applied field.

Coincidental movements of charge carriers in a conductor due to scattering at atoms and lattice perturbations (impurities)
2.3 Electrical and Dielectrical Properties

Charge Carriers in Different Materials

a) Metals  
   mobile valence electrons

b) Semi-metals/insulators  
   promotion of electrons from valence into conduction band by breaking of covalent bonds

c) Ionic solids  
   Diffusion of ions

according to D.R. Askeland  
Materialwissenschaften  
Spektrum-Verlag 1996
### 2.3 Electrical and Dielectrical Properties

#### Band Gaps of Materials

<table>
<thead>
<tr>
<th>Metals</th>
<th>Semi-conductors</th>
<th>Insulators</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO</td>
<td>VO</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Si</td>
<td>GaAs</td>
</tr>
<tr>
<td>CdS</td>
<td>ZnS</td>
<td></td>
</tr>
<tr>
<td>C (diamond)</td>
<td>MgO</td>
<td></td>
</tr>
</tbody>
</table>

**Band gaps $E_g$ [eV]**

<table>
<thead>
<tr>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Metals** are black and intransparent, because visible light of each wavelength is absorbed.
- **Semi-conductors** are coloured, because light of a particular colour (energy) is absorbed (valence electrons are excited via band gap).
- **Insulators** are white (transparent), because the band gap is too high for visible light to excite the valence electrons. Thus, most insulators are colourless or transparent.
## Specific Electrical Conductivity of Selected Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Electronic configuration</th>
<th>Specific conductivity [$\Omega^{-1}\cdot m^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>[Ne]3s(^1)</td>
<td>2.13(\times)10(^5)</td>
</tr>
<tr>
<td>K</td>
<td>[Ar]4s(^1)</td>
<td>1.64(\times)10(^5)</td>
</tr>
<tr>
<td>Mg</td>
<td>[Ne]3s(^2)</td>
<td>2.25(\times)10(^5)</td>
</tr>
<tr>
<td>Ca</td>
<td>[Ar]4s(^2)</td>
<td>3.16(\times)10(^5)</td>
</tr>
<tr>
<td>Al</td>
<td>[Ne]3s(^2)3p(^1)</td>
<td>3.77(\times)10(^5)</td>
</tr>
<tr>
<td>Ga</td>
<td>[Ar]4s(^2)3d(^{10})4p(^1)</td>
<td>0.66(\times)10(^5)</td>
</tr>
<tr>
<td>Fe</td>
<td>[Ar]4s(^2)3d(^6)</td>
<td>1.00(\times)10(^5)</td>
</tr>
<tr>
<td>Ni</td>
<td>[Ar]4s(^2)3d(^8)</td>
<td>1.46(\times)10(^5)</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar]4s(^1)3d(^{10})</td>
<td>5.98(\times)10(^5)</td>
</tr>
<tr>
<td>Ag</td>
<td>[Kr]5s(^1)4d(^{10})</td>
<td>6.80(\times)10(^5)</td>
</tr>
<tr>
<td>Au</td>
<td>[Xe]6s(^1)5d(^{10})</td>
<td>4.26(\times)10(^5)</td>
</tr>
<tr>
<td>C(_{\text{cubic}}) (diamond)</td>
<td>[He]2s(^2)2p(^2)</td>
<td>&lt; 1(\times)10(^{-18})</td>
</tr>
<tr>
<td>Si</td>
<td>[Ne]3s(^2)3p(^2)</td>
<td>5.0(\times)10(^{-6})</td>
</tr>
<tr>
<td>Ge</td>
<td>[Ar]4s(^2)4p(^2)</td>
<td>0.02</td>
</tr>
<tr>
<td>Sn</td>
<td>[Kr]5s(^2)5p(^2)</td>
<td>0.9(\times)10(^{5})</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>-</td>
<td>1(\times)10(^{-15})</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>-</td>
<td>1(\times)10(^{-18})</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>-</td>
<td>1(\times)10(^{-14})</td>
</tr>
<tr>
<td>SiO(_2) (quartz glass)</td>
<td>-</td>
<td>1(\times)10(^{-17})</td>
</tr>
</tbody>
</table>
2.3 Electrical and Dielectrical Properties

Methods to Engineer Electrical Conductivity

In pure, defect-free metals, the conductivity depends solely on the mobility of the charge carriers:

- Mobility is proportional to drift velocity
- Which depends on the average free path length
- The higher the average free path length the higher is the mobility and thus the electrical conductivity
- The average free path length is defined as the average distance which can be covered by the electrons between two impacts ⇒ temperature-dependant resistance $\rho_T$

Influence of lattice perturbations (voids, interstitials, grain boundaries, alien atoms)

- By scattering of electrons at lattice perturbations the mobility and thus the conductivity is reduced
- Scattering at lattice vibrations yields a temperature-dependant term to the resistance $\rho_d = b \cdot (1-x) \cdot x$ with $x = 0.0 – 1.0 = \text{relative amount of alien atoms}$
- The total resistance $\rho$ is given by the addition of the temperature-dependant resistance and the resistance resulting from lattice perturbations $\rho = \rho_d + \rho_T$
2.3 Electrical and Dielectrical Properties

Methods to Engineer the Electrical Conductivity

Influence of fabrication and annealing

- Cold forming is an effective method to harden materials, whilst the electrical properties remain almost unchanged.
- Tempering leads to a reduction of defects and thus to a higher electrical conductivity (Exp.: Annealing of Cu)

Formation of mixed crystals + cold forming

Influence of alien atoms

according to D.R. Askeland Materialwissenschaften Spektrum-Verlag 1996
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Metals)

In metals, a high density of charge carriers is present, independent of the temperature. The movement of the conductive electrons accelerated by an applied voltage is hindered by impacts with the thermally excited lattice.

Electron movement in
ideal crystals (at rest)  Ideal crystals (thermally excited)  real crystals (thermally excited)

\[ \rho_T = \rho_r \cdot (1 + \alpha \Delta T) \]
\[ \rho = \rho_d + \rho_T \]
\[ \Rightarrow \rho = \rho_d + \rho_r \cdot (1 + \alpha \Delta T) \]

with \( \alpha = \) temperature coefficient [\( \Omega \text{cm/K} \)]
\( \rho_T = \) T-dependant resistance
\( \rho_d = \) defect-dependant resistance
## 2.3 Electrical and Dielectrical Properties

### Influence of Temperature (Metals)

Mobility and electrical conductivity are reduced by scattering, leading to a almost linear increase of the resistance with regard to the temperature (rule of Mathiesen)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Specific resistance $\rho_r$ at room temp. [$10^{-6} \ \Omega \text{cm}$]</th>
<th>Temperature coefficient $\alpha$ [K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>4.0</td>
<td>0.0250</td>
</tr>
<tr>
<td>Mg</td>
<td>4.45</td>
<td>0.0165</td>
</tr>
<tr>
<td>Ca</td>
<td>3.91</td>
<td>0.0042</td>
</tr>
<tr>
<td>Al</td>
<td>2.65</td>
<td>0.0043</td>
</tr>
<tr>
<td>Cr</td>
<td>12.90</td>
<td>0.0030</td>
</tr>
<tr>
<td>Fe</td>
<td>9.71</td>
<td>0.0065</td>
</tr>
<tr>
<td>Co</td>
<td>6.24</td>
<td>0.0060</td>
</tr>
<tr>
<td>Ni</td>
<td>6.84</td>
<td>0.0069</td>
</tr>
<tr>
<td>Cu</td>
<td>1.67</td>
<td>0.0068</td>
</tr>
<tr>
<td>Ag</td>
<td>1.59</td>
<td>0.0041</td>
</tr>
</tbody>
</table>
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Metals - Semi-Conductors - Insulators)

Metals: Electrical conductivity decreases with increasing temperature

Semi-conductors + insulators: Electrical conductivity increases with temperature
### 2.3 Electrical and Dielectrical Properties

#### Influence of the Temperature on Different Types of Electrical Conductors

<table>
<thead>
<tr>
<th>Type</th>
<th>charge carrier density ( N )</th>
<th>mobility ( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td>const.</td>
<td>( \sim T^{-1} )</td>
</tr>
<tr>
<td><strong>Intrinsic semi-conductors</strong></td>
<td>( \sim \exp(-\Delta E/kT) )</td>
<td>( \sim T^{-3/2} )</td>
</tr>
<tr>
<td><strong>Solid electrolytes</strong></td>
<td>const. (1) ( \sim \exp(-\Delta E/kT) ) (2) ( \sim \exp(-\Delta E/kT) )</td>
<td></td>
</tr>
<tr>
<td><strong>Liquid electrolytes</strong></td>
<td>const. (1) ( \sim \alpha_T ) (2) decreasing</td>
<td></td>
</tr>
</tbody>
</table>

*Graphs showing temperature dependence of charge carrier density \( N \) and mobility \( \mu \).*
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Intrinsic Semi-conductors)

Semi-conductors and intrinsic semi-conductors need electrons in the conduction band to become electrically conductive.

- The number of electrons and holes in intrinsic semi-conductors is equal
  \[ N_V = N_{V,e} = N_{V,h} \]
  ⇒ Formation of electron-hole pairs

- The number of electron-hole pairs limits the specific conductivity
  \[ \sigma = N_{V,e}q\mu_e + N_{V,h}q\mu_h \]
  \[ \Rightarrow \sigma = N_Vq(\mu_e + \mu_h) \]
2.3 Electrical and Dielectrical Properties

**Influence of Temperature (Intrinsic Semi-conductors)**

The number of electron-hole pairs $N_V$ (excitons) strongly depends on temperature!

- **$T = 0 \text{ K}$**
  - all electrons in valence band

- **$T > 0 \text{ K}$**
  - probability for the transition of an electron into the conduction band increases with increasing temperature

$$N_V = 0 \quad N_V = N_{V,e} = N_{V,h} = N_{V,\infty} \cdot \exp\left(-E_G/2kT\right)$$

($k = 1.38 \cdot 10^{-23} \text{ J/K}$)

[Diagram showing electron energy levels and bands]

Functional Materials
Prof. Dr. T. Jüstel

Material Science
Slide 53
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Intrinsic Semi-conductors)

The electrical conductivity \( \sigma \) of a intrinsic semi-conductor is given by:

\[
\sigma = N_V \cdot q \cdot (\mu_e + \mu_h) \quad \text{and} \quad N_V = N_{V,e} = N_{V,h} = N_{V,\infty} \cdot \exp(-E_G/2kT) \quad \text{combined to:}
\]

\[
\sigma = q \cdot (\mu_e + \mu_h) \cdot N_{V,\infty} \cdot \exp(-E_G/2kT)
\]

<table>
<thead>
<tr>
<th>Material</th>
<th>Electronic mobility [cm(^2)/V\cdot s]</th>
<th>Mobility of holes [cm(^2)/V\cdot s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Csp(^3)</td>
<td>1800</td>
<td>1400</td>
</tr>
<tr>
<td>Si</td>
<td>1900</td>
<td>500</td>
</tr>
<tr>
<td>Ge</td>
<td>3800</td>
<td>1820</td>
</tr>
<tr>
<td>Sn</td>
<td>2500</td>
<td>2400</td>
</tr>
<tr>
<td>GaP</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>8800</td>
<td>400</td>
</tr>
</tbody>
</table>

- The mobility of the electrons and holes is proportional to \( T^{-3/2} \), thus decrease with increasing temperature
- But the temperature dependence of the number density is so dominating that the conductivity still increases with temperature
2.3 Electrical and Dielectrical Properties

The Size of the Band Gap $E_G$ Depends on the Chemical Composition, the Difference in Electronegativity and on the Structure

<table>
<thead>
<tr>
<th>Substance</th>
<th>Structure type</th>
<th>Band gap $E_G$ [eV]</th>
<th>EN-difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF$_2$</td>
<td>Rutile</td>
<td>12.0</td>
<td>2.9</td>
</tr>
<tr>
<td>MgO</td>
<td>Rock salt</td>
<td>7.8</td>
<td>2.3</td>
</tr>
<tr>
<td>AlN</td>
<td>Wurtzite</td>
<td>6.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Csp$^3$</td>
<td>Diamond</td>
<td>5.3</td>
<td>0.0</td>
</tr>
<tr>
<td>GaN</td>
<td>Wurtzite</td>
<td>3.5</td>
<td>1.2</td>
</tr>
<tr>
<td>AlP</td>
<td>Zinc blende</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>GaP</td>
<td>Zinc blende</td>
<td>2.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Si (crystalline)</td>
<td>Diamond</td>
<td>1.1</td>
<td>0.0</td>
</tr>
<tr>
<td>ZnSe</td>
<td>Zinc blende</td>
<td>2.3</td>
<td>0.9</td>
</tr>
<tr>
<td>GaAs</td>
<td>Zinc blende</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>InSb</td>
<td>Zinc blende</td>
<td>0.18</td>
<td>0.2</td>
</tr>
<tr>
<td>$\alpha$-Sn (grey)</td>
<td>Diamond</td>
<td>0.08</td>
<td>0.0</td>
</tr>
</tbody>
</table>
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Doped Semi-conductors)

- In doped semi-conductors (impurity semi-conductors) foreign atoms (dopants) are added
- The type of the atom is responsible for the type of conduction possible, the number of foreign atoms defines the conductivity

One differentiates between:

- n-semi-conductors, which are created by adding elements with more valence electrons (electronic conduction dominates: n-(negative)-semi-conductor)

and

- p-semi-conductor, which are created by the addition of elements with less valence electrons (conduction via holes dominates: p-(positive)-semi-conductors)
2.3 Electrical and Dielectrical Properties

Impurity Semi-conductors = Intrinsic Semi-conductors + Dopants

Example: Doping of Silicon
By doping pure silicon \((\sigma = 5 \times 10^{-6} \, \Omega^{-1} \text{cm}^{-1})\) its conductivity can be enhanced.

n-Si donors:
P, As, Sb “electron conductors”
1 ppm P \(\Rightarrow \sigma = 10 \, \Omega^{-1} \text{cm}^{-1}\)

p-Si acceptors:
B, Al, Ga, In „Lochleiter“
1 ppm B \(\Rightarrow \sigma = 4 \, \Omega^{-1} \text{cm}^{-1}\)

Typical concentration of dopants: \(10^{21} \, \text{m}^{-3}\) (lattice atoms \(\sim 10^{28} \, \text{m}^{-3}\) \(\Rightarrow \sim 10^{-5}\%\))
2.3 Electrical and Dielectrical Properties

 Silicon-based Semi-Conductor Materials

**n-semi-conductor**  Electron excess

- P, As, Sb  5 valence electrons
- Si  4 valence electrons

**p-semi-conductor**  Electron deficit

- B, Al, Ga, In  3 valence electrons
- Si  4 valence electrons

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Si</th>
<th>Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.045</td>
<td>0.0120</td>
</tr>
<tr>
<td>As</td>
<td>0.049</td>
<td>0.0127</td>
</tr>
<tr>
<td>Sb</td>
<td>0.039</td>
<td>0.0096</td>
</tr>
<tr>
<td>B</td>
<td>0.045</td>
<td>0.0104</td>
</tr>
<tr>
<td>Al</td>
<td>0.057</td>
<td>0.0102</td>
</tr>
<tr>
<td>Ga</td>
<td>0.065</td>
<td>0.0108</td>
</tr>
<tr>
<td>In</td>
<td>0.160</td>
<td>0.0112</td>
</tr>
</tbody>
</table>
2.3 Electrical and Dielectrical Properties

Excursion: p/n-Diode (Borderline between n- and p-doped Semi-conductor Crystal)

- **n**-semi-conductor
- **p**-semi-conductor

**Excess of holes (positive)**

- *- pole
- + pole
  - broadening of barrier layer $\Rightarrow$ no current

**Excess of electrons (negative)**

- + pole
- - pole
  - termination of barrier layer $\Rightarrow$ current

- 10^16 cm^-3
- 10^10 cm^-3

Electronen

Löcher

positive Raumladung
negative Raumladung

2.3 Electrical and Dielectrical Properties

Influence of Temperature (Doped Semi-conductor)

Besides impurities, i.e. the donor, there is intrinsic conductivity as well.

The total number density of charge carriers sums up to:

\[ N_{V,tot} = N_{V,e, \text{donor}} + N_{V,e, \text{intrinsic}} + N_{V,h, \text{intrinsic}} \quad \text{for n-semi-conductor} \]

\[ N_{V,tot} = N_{V,h, \text{acceptor}} + N_{V,e, \text{intrinsic}} + N_{V,h, \text{intrinsic}} \quad \text{for p-semi-conductor} \]

\[ N_{V,tot} = N_{V,\infty, \text{donor}} \cdot \exp\left(-\frac{E_d}{kT}\right) + 2N_{V,\infty, \text{intrinsic}} \cdot \exp\left(-\frac{E_G}{2kT}\right) \]

- At low temperatures, intrinsic conductivity is neglectable, but at high temperatures, becomes the dominating factor.
- In between, there is a plateau-like area, where conductivity is temperature-independant (donor-depletion).
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Doped Semi-conductor)

Si:P (n-semi-conductor)

Linear depiction

Arrhenius depiction (ln\(\sigma\) over 1/T)

Source: D.R. Askeland, Materialwissenschaften, Spektrum-Verlag 1996
2.3 Electrical and Dielectrical Properties

Influence of Temperature (Defect Semi-conductor)

Defect semi-conductors or non-stoichiometric semi-conductors are ionic compounds, which comprise either a excess of anions (p-conduction) or cations (n-conduction)

Fe$_{1-x}$O  
**p-defect-semi-conductors**

ZnO$_{1-x}$ (ZnO:Zn)  
**n-defect-semi-conductor**

- Exists for compounds, where the cation tends to interchange valences!
- Defects in optical materials lead to greying (phosphors, pigments)
2.3 Electrical and Dielectrical Properties

Defect-semi-conductors Show Luminescence

Example: ZnO:Zn,V\textsubscript{0}

\[
\begin{align*}
\text{ZnO} & \quad \text{ZnO} \\
\text{Zn}^x_{\text{Zn}} + \text{O}^x_{\text{O}} & \rightarrow \text{Zn}^x_{\text{i}} + 0.5 \text{O}_2 \quad \text{sowie} \quad \text{Zn}^x_{\text{Zn}} + \text{O}^x_{\text{O}} & \rightarrow \text{Zn}^x_{\text{Zn}} + \text{V}^\cdot_{\text{O}} + 0.5 \text{O}_2
\end{align*}
\]

Sauerstoffdefekte = Donatoren, n-Halbleiter

\[E_G \sim 3.3 \text{ eV} \quad \Delta E \sim 2.5 \text{ eV}\]

⇒ Application as an electroluminescence phosphor

\[
\begin{align*}
\text{E} & \quad \text{E}_G \\
\text{E}_d & \quad \Delta E
\end{align*}
\]
2.3 Electrical and Dielectrical Properties

**Influence of Temperature: Superconductor**

**Definition**
Superconductors are materials that lose any electrical resistance at a certain temperature (transition temperature), and then suppress subcritical magnetic fields from their inside (Meißner-Ochsenfeld-effect)

⇒ Already observed for more than 10000 materials

**Normal conductors**
Scattering of electrons at defects and interactions with lattice vibrations (electron-phonon-scattering) ⇒ fermions

**Superconductors**
Coupling of conduction electrons by electron-phonon interactions ⇒ bosons (spin: 0, 1ℏ, 2ℏ)
## History of Superconductor Research

<table>
<thead>
<tr>
<th>Year</th>
<th>Material</th>
<th>$T_c$ [K]</th>
<th>Autor/Literatur</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>Hg</td>
<td>4.2</td>
<td>H.K. Onnes</td>
</tr>
<tr>
<td>1930</td>
<td>Nb</td>
<td>9.3</td>
<td>W. Meißner, R. Ochsenfeld</td>
</tr>
<tr>
<td>1933</td>
<td>Meißner-Ochsenfeld-effect</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>Nb$_3$Sn</td>
<td>18.1</td>
<td>Bardeen, Cooper, Schrieffer</td>
</tr>
<tr>
<td>1957</td>
<td>BCS-theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1972</td>
<td>Nb$_3$Ge</td>
<td>23.3</td>
<td></td>
</tr>
<tr>
<td>1986</td>
<td>La$<em>{1.8}$Ba$</em>{0.2}$CuO$_4$</td>
<td>35</td>
<td>J.G. Bednorz, K.A. Müller</td>
</tr>
<tr>
<td>1987</td>
<td>YBa$_2$Cu$<em>3$O$</em>{7-x}$</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>1988</td>
<td>Bi$_2$Sr$<em>2$Ca$</em>{n-1}$Cu$_n$O$_x$</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>1988</td>
<td>Tl$_2$Ba$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>1993</td>
<td>HgBa$_2$Ca$_2$Cu$<em>3$O$</em>{8+x}$</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>1995</td>
<td>Pressure applications</td>
<td>164</td>
<td></td>
</tr>
<tr>
<td>2019</td>
<td>LaH$_{10}$ at 170 GPa</td>
<td>250</td>
<td>Nature 569 (2019) 528</td>
</tr>
</tbody>
</table>

Known superconductors, today: metals, alloys, cuprates, organic compounds, fullerenes
2.3 Electrical and Dielectrical Properties

BCS-Theory: Cooper-Pairs

Below $T_c$, electrons with anti-parallel spins form Cooper-pairs. A electron induces a elastic perturbation of the lattice in its surrounding, due to its charge, i.e. dislocation of the atomic torso. If a electron moves through the lattice, the perturbation follows straight. In Cooper-pairs, there is a 2nd electron coupled to the first electron via this perturbation.

Cooper-pairs exist only at very low temperatures. At high temperature, the interaction between the coupled electrons is cancelled and the electrons become Metallic in behaviour.

ev$\text{-}$distance: $0.1 - 1 \, \mu m$!
2.3 Electrical and Dielectrical Properties

High-temperature Superconductors

Prerequisites
- Strong coupling of electron movement with lattice vibrations
  ⇒ HT-superconductors should be poor conductors at room temp. (ceramic compounds)
  ⇒ Good metallic conductors (Cu, Ag) do not show transition into superconducting state
- Ready electrical polarisation of certain lattice elements
  ⇒ Small cations with high coordination number

La$_2$CuO$_4$ is anti-ferromagnetic and non-conducting, because Cu$^{2+}$ ([Ar]d$^9$) shows super exchange
La$_{1.8}$Sr$_{0.2}$CuO$_4$ comprises mixed-valent Cu$^{2+}$/3+, destroying the coupling of the electrons and supressing the anti-ferromagnetism.
2.3 Electrical and Dielectrical Properties

High-temperature Superconductors

Structure of YBa$_2$Cu$_3$O$_{7-x}$

Influence of the oxygen content $\delta$ on the transition temperature

Structure of TlBa$_2$Ca$_2$Cu$_3$O$_{8+x}$

CuO$_2$-layers mediate the superconductivity, Y$^{3+}$-cations act as “spacer”
2.3 Electrical and Dielectrical Properties

Organic High-temperature Superconductors

Organic compounds, e.g. polymers normally are insulators.
Even there formation of Cooper-pairs is possible (W.A. Little)

- Theoretical $T_{\text{trans.}}$ up to 300 K
- High potential due to versatile synthetic routes

$\Rightarrow$ Fulleride-superconductor: $\text{K}_3\text{C}_{60}$: $T_c = 19$ K, $\text{Rb}_3\text{C}_{60}$: $T_c = 27$ K, $\text{Cs}_3\text{C}_{60}$: $T_c = 40$ K
Complex-superconductors: $(\text{BEDT-TTF})_2\text{Cu(NCS)}_2$: $T_c = 11$ K

Bis-ethylenedi-thiotetra-thiafulvalene (BEDT-TTF)  \quad \text{C}_{60} \text{ fullerene}
2.3 Electrical and Dielectrical Properties

**Fermi-Dirac-Statistics**

**Bose-Einstein-Statistics**

**Fermions** are particles with half-integer spin, e.g. electrons, protons, neutrons, neutrinos, quarks

Pauli’s rule states that every energy state can be occupied by a maximum of two electrons with opposing spins

**Bosons** are particles with integer spin, e.g. photons, deuterium cores, gluons, gravitons

Cooper-pairs are formed by electrons with opposing spin, i.e. the total spin is zero. Cooper-pairs are bosons, too. Pauli’s rule does not apply anymore. All Cooper-pairs can occupy the same quantum-mechanical state of the same energy
Meißner-Ochsenfeld-Effect

Walther Meißner and Robert Ochsenfeld 1933

A external magnetic field is supressed from the inner of a superconductor, i.e. the superconductor becomes a ideal diamagnet (all electrons paired)

Explanation
Below the transition temperature, eddy currents are formed within the superconductor, which create a Magnetic field of their own

Both magnetic fields compensate each other
⇒ the magnet floats
2.3 Electrical and Dielectrical Properties

Applications for High-temperature Superconductors

- NMR-Spectroscopy
- Magnetic resonance tomography
- Propulsion technology for trains (Mag-lev Transrapid)
- Electrical engines and generators
- Fusion reactors
- Power lines for direct and alternating current
- Particle accelerator
- Measurement of extremely small magnetic fields
  (Superconducting Quantum Interference Device, SQUID)
2.3 Electrical and Dielectrical Properties

**Insulators (Dielectrics)**

⇒ A very high electrical resistance is caused by a high energy gap between valence and conduction band
⇒ Ceramics and polymers

Insulators can create (transmitter) or receive (antenna) information or they can store electrical charges in capacitors

The term “dielectrics” already implies that an external electrical field can penetrate the material.

In metals or semi-conductors it is $E' = 0$

In Insulators (dielectrics)

![Diagram showing electric field and polarization]

Free charge is rearranged until $E' = 0$

The external field is reduced by polarization

$E_0'$
2.3 Electrical and Dielectrical Properties

Dipoles and Polarisation

Electrical fields are capable to induce dipoles in materials or can align permanently existing dipoles along the field direction.

\[
\begin{array}{ccc}
-q & d & +q \\
\hline
\end{array}
\]

Elemental dipoles are atoms or groups of atoms, where positive and negative charges do not balance

\[\Rightarrow\text{Angled molecules: } H_2O, \text{NH}_3, \text{SO}_2, \text{CH}_2\text{Cl}_2, \text{.....}\]

The orientation of dipoles in an electrical field is called polarisation \( P \):

In molecules \( \text{in solids} \)

\[ P = q \cdot d \]
\[ P = z \cdot q \cdot d \]

\[ P = \varepsilon_0 \cdot (\varepsilon_r - 1) \cdot E_0 \]

\[ z = \text{number of shifted charge centres} \]
\[ q = \text{electrical charge} \]
\[ \varepsilon_r - 1 = \text{electrical susceptibility } \chi_e \]
\[ d = \text{distance between positive and negative charge} \]
\[ \varepsilon_0 = \text{Permittivity number of vacuum} = 8.854 \cdot 10^{-12} \text{ C}^2/\text{Jm} \]

\[ E_p = \frac{1}{(\varepsilon_0 \cdot \varepsilon_r)} \cdot P \]

\[ \varepsilon_r = \text{Permittivity number of the material} \]
2.3 Electrical and Dielectrical Properties

Types of Polarisation

a) Electron polarisation
In a electrical field, electrons are slightly shifted in positive field direction. This effect can be observed for all substances. The electron polarisation vanishes, when the field is switched off.

b) Ion polarisation
In a heteropolar-bound material a electrical field induces slight shifts of the charges. By these shifts the outer dimension of the material can be influenced. The ion polarisation vanishes, when the electrical field is switched off.

⇒ These two types are also called displacement polarisation!
Types of Polarisation

c) Molecular polarisation
Permanent dipoles align preferably along the external field. In some compounds, e.g. BaTiO$_3$ dipoles remain in their alignment after the electrical field is switched off (ഃ ferro electrics). BaTiO$_3$ crystallises in a tetragonal structure with permanent polarisation.

BaTiO$_3$ is a perowskit.

d) Polarisation by space charge
Alien atoms can cause accumulation of charges within inner phase boundaries of a material, which can migrate to the surface, if stimulated by an electrical field. For most dielectrics this kind of polarisation is of no importance.

⇒ These two types are also called orientation polarisation!
2.3 Electrical and Dielectrical Properties

Perowskit $ABX_3$

$X = \text{O}^2, \text{F}^-, \text{Cl}^-$

$A = \text{Alkali, alkaline earth and RE metals}$

$B = \text{Transition metals and Si, Al, Ge, Ga, Bi, Pb}$

$a = 2(r_B + r_O) = \frac{2(r_A + r_O)}{\sqrt{2}}$

$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \quad \text{"Tolerance - term"}$

$\Rightarrow \text{Jahn-Teller-Polarons (fermionic quasi particles)}$

Perowskit is the name of a Russian mineralogist: Count Lev Aleksevich of Perovski.

The mineral $\text{CaTiO}_3$ was discovered by Gustav Rose in 1839 at Ural, Russia.

$0.8 \quad \text{orthorhombic} \quad \text{(GdFeO}_3\text{)}$

$0.89 \quad \text{cubic} \quad \text{(SrTiO}_3\text{)}$

$1.0 \quad \text{hexagonal} \quad \text{(BaNiO}_3\text{)}$
2.3 Electrical and Dielectrical Properties

Matter as Mediator in Capacitors

Within dielectrics, a external field $E_0$ is reduced by the factor $\varepsilon_r$

Vacuum polarisation/fluctuation
- Lamb-shift
- Casimir-effect
- Spontaneous emission
- Van-der-Waals interactct.
- Hawking radiation
$\Rightarrow \varepsilon_0 = 8.854 \cdot 10^{-12} \text{ AsV}^{-1}\text{m}^{-1} \neq 0!$

If matter is introduced into the capacitor, $U$ is reduced by $\varepsilon_r$, since $E_0$ is also reduced by $\varepsilon_r$, and $U = E \cdot d$.

$Q$ remains unchanged, because the plates are not electrically connected!

Vacuum: $Q = C_0 \cdot U$ \hspace{1cm} $C_0 = \varepsilon_0 \cdot A/d$ \hspace{1cm} with $C = \text{capacity} \ [\text{C/V} = \text{F}]$

With matter: $Q = C_m \cdot U/\varepsilon_r$ \hspace{1cm} $C_m = \varepsilon_r \cdot \varepsilon_0 \cdot A/d$ \hspace{1cm} thus $C_m/C_0 = \varepsilon_r$

To obtain a high capacity capacitor, the area $A$ must be as large as possible, $d$ small and $\varepsilon_r$ of the filling as large as possible!
2.3 Electrical and Dielectrical Properties

**Capacitors**

Capacitors are used to:
- Store charge
- Smooth currents
- Couple frequency-dependant alternating and direct current circuits

**Criteria for the application of dielectric materials for capacitors**

1. High permittivity number $\varepsilon_r = \varepsilon/\varepsilon_0$
2. High dielectric strength: $E_{\text{max}} = (V/d)_{\text{max}}$
   - limits the maximal field strength a dielectric may be exposed to

High electrical resistance
- Prevents exchange of charges between the capacitor plates
- Polymers and ceramic materials

4. Low dielectric losses, thus a small loss factor = tan$\delta$
   - (Movement of dipoles leads to heating of the material and thus to a reduction of the offset angle of the current to $90^\circ - \delta$ with $\delta = \text{loss angle}$)
### Properties of Dielectric Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Permittivity number (at 10^6 Hz)</th>
<th>Dielectric strength (10^6 V/m)</th>
<th>tanδ (at 10^6 Hz)</th>
<th>Specific electrical resistance (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>2.3</td>
<td>20</td>
<td>0.0001</td>
<td>&gt; 10^{16}</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>2.1</td>
<td>20</td>
<td>0.00007</td>
<td>10^{18}</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>2.5</td>
<td>20</td>
<td>0.0002</td>
<td>10^{18}</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>3.5</td>
<td>40</td>
<td>0.05</td>
<td>10^{12}</td>
</tr>
<tr>
<td>Nylon</td>
<td>4.0</td>
<td>20</td>
<td>0.04</td>
<td>10^{15}</td>
</tr>
<tr>
<td>Rubber</td>
<td>4.0</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol resin</td>
<td>7.0</td>
<td>12</td>
<td>0.05</td>
<td>10^{12}</td>
</tr>
<tr>
<td>SiO₂ (quartz glass)</td>
<td>3.8</td>
<td>10</td>
<td>0.00004</td>
<td>10^{11} – 10^{12}</td>
</tr>
<tr>
<td>Sodium-lime glass</td>
<td>7.0</td>
<td>10</td>
<td>0.009</td>
<td>10^{15}</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.5</td>
<td>6</td>
<td>0.001</td>
<td>10^{11} – 10^{13}</td>
</tr>
<tr>
<td>TiO₂</td>
<td>14 – 110</td>
<td>8</td>
<td>0.0002</td>
<td>10^{13} – 10^{18}</td>
</tr>
<tr>
<td>Mica</td>
<td>7.0</td>
<td>40</td>
<td></td>
<td>10^{13}</td>
</tr>
<tr>
<td>Ba₁₋ₓCaₓTi₁₋ᵧZrᵧO₃</td>
<td>3000</td>
<td>12</td>
<td></td>
<td>10^{8} – 10^{15}</td>
</tr>
<tr>
<td>H₂O</td>
<td>78</td>
<td></td>
<td></td>
<td>10^{14}</td>
</tr>
</tbody>
</table>
2.3 Electrical and Dielectrical Properties

Properties of Dielectric Materials

High and highest permittivity numbers are observed for perowskites (BaTiO$_3$, PbTiO$_3$, LiNbO$_3$) and layered perowskites (Ba$_2$GdNbO$_6$)

BaTiO$_3$
- $\varepsilon_r = 7000$ close to Curie-temperature $T_c$
- But highly $T$-dependant, $\varepsilon_r$ decrease to 1000 – 2000 upon cooling

⇒ Dependence of capacity on temperature

Aim
Dielectrics with $\varepsilon_r =$ const. in the range of 218 K (-55 °C) till 398 K (+125 °C)
- Ceramics from (doped) mixed crystals
- Ba$_{1-x}$Ca$_x$Ti$_{1-y}$Zr$_y$O$_3$;Nb

In addition, particle size and particle size distribution influence the permittivity!

<table>
<thead>
<tr>
<th>Material T-dependence</th>
<th>$\varepsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP0</td>
<td>+/- zero</td>
</tr>
<tr>
<td>X7R</td>
<td>moderate</td>
</tr>
<tr>
<td>Z5U</td>
<td>strong</td>
</tr>
</tbody>
</table>

(Electronic Industries Association EIA)
2.3 Electrical and Dielectrical Properties

Designs of Capacitors

1. Disc capacitors

2. Multi-layer capacitors

3. Wound capacitor

4. Electrolyte capacitors
   Al-Elko: Al₂O₃ + electrolyte citric acid
   Ta-Elko: Ta₂O₅ + electrolyte sulphuric acid
2.3 Electrical and Dielectrical Properties

Piezoelectricity and Electrostriction

In a electrical field, the dimensions of a solid can change depending on the polarisation. This effect is called **electrostriction**

For certain **piezoelectric substances** a polarisation and the formation of a electrical voltage can be observed, if the dimensions of the material are changed by external forces

**Piezoelectric substances**

⇒ Unit cell without symmetry centre

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Piezo-modulus d [m/V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Quartz</td>
<td>SiO₂</td>
<td>2.3·10⁻¹²</td>
</tr>
<tr>
<td>Barium titanate</td>
<td>BaTiO₃</td>
<td>100·10⁻¹²</td>
</tr>
<tr>
<td>PZT</td>
<td>PbZrO₃-PbTiO₃</td>
<td>250·10⁻¹²</td>
</tr>
<tr>
<td>PLTZ</td>
<td>(Pb,La)(Ti,Zr)O₃</td>
<td>80·10⁻¹²</td>
</tr>
<tr>
<td></td>
<td>PbNb₂O₆</td>
<td></td>
</tr>
</tbody>
</table>

\[ E = \frac{1}{d} \cdot \frac{\Delta x}{x} = \frac{1}{d} \cdot \varepsilon \]
2.3 Electrical and Dielectrical Properties

The Piezoelectric Effect

By external compression the distances between the charges are reduced, so that a piezoelectric voltage is created.

Application of a external field results in a change in length (elongation) of the crystal.
2.3 Electrical and Dielectrical Properties

Application of the Piezoelectric Effect

1. Electroacoustic transducer
   Sound wave ↔ electrical signal
   ⇒ A impinging sound wave deforms the piezoelectric material by the frequency of the wave and creates a electrical alternating voltage
   (The alternating voltage can be retransformed into sound waves after sufficient amplification by a second transducer, e.g. in phono devices)

2. Temperature sensors
   ⇒ Changes in temperature can induce polarisation and electrical voltages in certain pyroelectric materials

3. Stabilisation of resonant circuits in watches and electronic devices
   ⇒ Quartz crystals are excited to vibrate by applying a external alternating field
   ⇒ As soon as the oscillation frequency of the quartz crystal coincides with the external electrical field resonance occurs and a stationary wave is created
2.3 Electrical and Dielectrical Properties

**Ferroelectricity**

In BaTiO$_3$ and several other materials a certain polarisation remains after switching off the electrical field!

Cause for the ferroelectric behaviour is the interaction between permanent dipoles (domains ~ 10 µm), which is favoured by their uniform orientation

At Curie-temperature $T_c$ ferroelectric behaviour vanishes

In BaTiO$_3$ at Curie-temperature, a Phase transition from tetragonal – cubic occurs!
The ability of ferroelectric materials to maintain a polarised state, offers the possibility to store information.

\[ P_r = \text{remanent polarisation} \]
\[ P_s = \text{saturation polarisation} \]
\[ E_c = \text{coercive field strength} \]
2.4 Magnetic Properties

The Magnetic Behaviour of Matter Is Determined by Mobile Charge Carriers

**History**

<table>
<thead>
<tr>
<th>Year</th>
<th>Person</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>Thales of Milet</td>
<td>λιθος μαγντίς = stone made of magnesia</td>
</tr>
<tr>
<td>100</td>
<td>Chinese</td>
<td>Compass</td>
</tr>
<tr>
<td>1820</td>
<td>Oersted</td>
<td>Electrical currents move a magnetic needle</td>
</tr>
<tr>
<td>1830</td>
<td>Faraday</td>
<td>Magnetic induction: generator, transformer, ...</td>
</tr>
<tr>
<td>1864</td>
<td>Maxwell</td>
<td>Electromagnetism (Maxwell-equations)</td>
</tr>
<tr>
<td>1896</td>
<td>Zeeman</td>
<td>Splitting of line spectra by magnetic field</td>
</tr>
<tr>
<td>1900</td>
<td>Curie</td>
<td>Temperature-dependence of magnetism</td>
</tr>
<tr>
<td>1907</td>
<td>Weiss</td>
<td>First quantum-mechanic interpretation of macroscopic magnetism</td>
</tr>
</tbody>
</table>

**Types of magnetism**

- **Diamagnetism**: Molecules without unpaired electrons
- **Paramagnetism**: Molecules with at least one unpaired electron
- **Ferromagnetism**: Cooperative effect
- **Ferrimagnetism**: Cooperative effect in solids only
- **Anti-ferromagnetism**: Cooperative effect
2.4 Magnetic Properties

Manifestations of Magnetism

1. Moving charge carriers in conductor
   ![Electrical conductor diagram]

2. Atomic magnetism, i.e. moving charge carriers (electrons) in atom
   ![Atomic magnetism diagram]

3. Molecular magnetism
   ![Molecular magnetism diagram]

4. Solid state magnetism
   - Haemoglobin
   - Magnetite Fe₃O₄ “a ferrimagnet“
# 2.4 Magnetic Properties

## Importance of Magnetism

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial magnetic field</td>
<td>Deflection of solar wind (→ aurora borealis)</td>
</tr>
<tr>
<td></td>
<td>Orientation of migrating birds, sharks, crayfish</td>
</tr>
<tr>
<td></td>
<td>$\Rightarrow \text{Fe}_3\text{O}_4$-nano-particles</td>
</tr>
<tr>
<td>Stellar magnetic field</td>
<td>Sunspots (magnetic tubes)</td>
</tr>
<tr>
<td></td>
<td>Form of planetary nebula</td>
</tr>
</tbody>
</table>

## Technical Area

<table>
<thead>
<tr>
<th>Area</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytics</td>
<td>NMR, EPR, optical spectroscopy</td>
</tr>
<tr>
<td>Data storage</td>
<td>Magnetic tapes, floppy drives, hard drives</td>
</tr>
<tr>
<td>Electronics</td>
<td>Coils, generators, transformers</td>
</tr>
<tr>
<td>High-energy physics</td>
<td>Ring accelerators</td>
</tr>
<tr>
<td>Medicine</td>
<td>MRTs, NMR-shift reagents</td>
</tr>
<tr>
<td>Optics</td>
<td>Magneto optic crystals</td>
</tr>
<tr>
<td>Navigation</td>
<td>Shipping</td>
</tr>
<tr>
<td>Sensors</td>
<td>Giant Magneto-Resistance (GMR)-sensors, Superconducting Quantum interference devices (SQUID)-sensors</td>
</tr>
</tbody>
</table>
2.4 Magnetic Properties

Magnetic Field Strength $H$, Magnetic flux density $B$, and Magnetisation $M$

A magnetic field induces, in vacuum, a magnetic flux, which strength and direction can be visualised by flux lines. The number of these lines per area unit is called magnetic flux density $B$ or magnetic induction and is proportional to the magnetic field strength $H$.

$$B = \mu_0 H$$

with $\mu_0 = \text{permeability of vacuum} \ [\text{Vs/Am}] = 4\pi \times 10^{-7} \ \text{Vs/Am}$

The flux density is changed upon penetration of the magnetic field into matter, which can be expressed by $\mu_r$ or $M$

$$B = \mu_0 \mu_r H$$

with $\mu_r = \text{relative permeability of the material}$

$M = \text{magnetisation}$

$$B = \mu H = \mu_0 H + \mu_0 M$$

$\mu = \mu_r \cdot \mu_0 = \text{absolute permeability}$
# 2.4 Magnetic Properties

## Typical magnetic Flux Densities $B$

<table>
<thead>
<tr>
<th>Example</th>
<th>Magnetic flux density $B$ [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colliding neutron stars</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>Neutron star</td>
<td>$10^8$</td>
</tr>
<tr>
<td>White dwarf</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Inner exchange fields in ferromagnets</td>
<td>$10^1 - 10^3$</td>
</tr>
<tr>
<td>Superconductive magnets</td>
<td>$10^1$ (world record: 30 T at HMI Berlin)</td>
</tr>
<tr>
<td>Coil with iron yoke</td>
<td>$10^0$</td>
</tr>
<tr>
<td>Surface of ferromagnets</td>
<td>$10^{-1} - 10^1$</td>
</tr>
<tr>
<td>Sunspots, planetary nebula</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>Terrestrial magnetic field</td>
<td>$10^{-4}$ (48 µT bei Frankfurt am Main)</td>
</tr>
<tr>
<td>Technical stray fields &quot;urban noise“</td>
<td>$10^{-12} - 10^{-5}$</td>
</tr>
<tr>
<td>Field in galaxies</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>Fields in galaxy clusters</td>
<td>$10^{-10} - 10^{-13}$</td>
</tr>
<tr>
<td>Intergalactic magnetic field</td>
<td>$10^{-13}$</td>
</tr>
</tbody>
</table>

$1 \text{T (Tesla) } = 1 \text{Vs/m}^2 = 10^4 \text{G (Gauß)}$
2.4 Magnetic Properties

**Magnetic Susceptibility** $\chi$

Is a degree for the field enforcement caused by a material:

$\chi_V = \frac{M}{H} = \frac{B_{\text{inside}} - B_{\text{outside}}}{B_{\text{outside}}}$

“Volume susceptibility”

Therefore, magnetic flux density can be expressed as:

$B = \mu H = \mu_0 H + \mu_0 M = \mu_0 (H + M) = \mu_0 (H + \chi H) = \mu_0 (1 + \chi) H$

Also:

$\mu_r = 1 + \chi$

with $\chi_V V_m = \chi_g M = \chi_{\text{mol}}$

$\chi_{\text{mol}}$ = molar susceptibility, $\chi_V$ = vol. suscept.

Of great technical importance are magnetic materials where $M$ is much higher than $H$

$\Rightarrow B \approx \mu_0 M$

| $\mu > 1$ and $\chi > 0$ | paramagnets |
| $\mu > > 1$ and $\chi >> 0$ | ferromagnets |
2.4 Magnetic Properties

Magnetic Dipoles and Magnetic Momentum $\mu$

Magnetisation $M$ is caused by orientation of induced or permanent magnetic dipoles in an external magnetic field with the field strength $H$.

The strength of the magnetic field induced by the dipole is its magnetic momentum $\mu$

Every electron in an atom causes a magnetic moment comprising of components:

a. Spin momentum: Angular momentum (spin) of an electron: $\mu_S = -g_s \mu_B S$ with $g_s = 2$

b. Orbital momentum: Results from movement of an electron: $\mu_l = -g_l \mu_B n$ with $g_l = 1$

c. Total momentum: Due to spin orbit coupling: $\mu_J = -g_j \mu_B J$ with $g_l < g_j < g_s$

Additionally, a nuclear spin momentum exists, which can be neglected for the macroscopically observable magnetism due to its small value ($m_{\text{proton}} \sim 1836 \, m_e$).
2.4 Magnetic Properties

Bohr’s Magneton $\mu_B$

The elemental magnetic moments can be expressed as multiples of Bohr’s magneton $\mu_B$, which is the base unit of the magnetic momentum

$$\mu_B = \frac{e \cdot h}{4\pi \cdot m_e} = 9.27 \cdot 10^{-24} \text{ Am}^2$$

- $e = 1.602 \cdot 10^{-19} \text{ C}$ unit charge
- $h = 6.626 \cdot 10^{-34} \text{ Js}$ Planck’s constant
- $m_e = 0.9109 \cdot 10^{-30} \text{ kg}$ rest mass of electron

It equals a magnetic moment which is induced by an electron on a circular path with Bohr’s radius (53 pm) around a proton

For light elements with $n$ unpaired electrons the magnetic moment $\mu$ equals the “spin-only” value

$$\mu_{\text{ber}} = \sqrt{n(n+2)} \cdot \mu_B$$

total spin $S = \Sigma s$
with $s = \frac{1}{2}$ d. h. $S = n/2$
and $n = 2S$
### 2.4 Magnetic Properties

#### Magnetic Behaviour of 3d-Transition Metal Ions

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Ion</th>
<th>Ground state</th>
<th>Number of unpaired electrons</th>
<th>$\mu_{\text{calc.}}$ [µ$_B$]</th>
<th>$\mu_{\text{exp.}}$ [µ$_B$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ar]3d$^0$</td>
<td>Sc$^{3+}$</td>
<td>$^1S_0$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[Ar]3d$^1$</td>
<td>Ti$^{3+}$</td>
<td>$^2D_{3/2}$</td>
<td>1</td>
<td>1.73</td>
<td>1.7 – 1.8</td>
</tr>
<tr>
<td>[Ar]3d$^2$</td>
<td>V$^{3+}$</td>
<td>$^3F_2$</td>
<td>2</td>
<td>2.83</td>
<td>2.7 – 2.9</td>
</tr>
<tr>
<td>[Ar]3d$^3$</td>
<td>V$^{2+}$, Cr$^{3+}$, Mn$^{4+}$</td>
<td>$^4F_{3/2}$</td>
<td>3</td>
<td>3.87</td>
<td>3.7 – 3.9</td>
</tr>
<tr>
<td>[Ar]3d$^4$</td>
<td>Cr$^{2+}$, Mn$^{3+}$</td>
<td>$^5D_0$</td>
<td>4</td>
<td>4.90</td>
<td>4.8 – 4.9</td>
</tr>
<tr>
<td>[Ar]3d$^5$</td>
<td>Mn$^{2+}$, Fe$^{3+}$</td>
<td>$^6S_{5/2}$</td>
<td>5</td>
<td>5.92</td>
<td>5.7 – 6.0</td>
</tr>
<tr>
<td>[Ar]3d$^6$</td>
<td>Fe$^{2+}$, Co$^{3+}$</td>
<td>$^5D_4$</td>
<td>4</td>
<td>4.90</td>
<td>5.0 – 5.6</td>
</tr>
<tr>
<td>[Ar]3d$^7$</td>
<td>Co$^{2+}$, Ni$^{3+}$</td>
<td>$^4F_{9/2}$</td>
<td>3</td>
<td>3.87</td>
<td>4.3 – 5.2</td>
</tr>
<tr>
<td>[Ar]3d$^8$</td>
<td>Ni$^{2+}$</td>
<td>$^3F_4$</td>
<td>2</td>
<td>2.83</td>
<td>2.9 – 3.9</td>
</tr>
<tr>
<td>[Ar]3d$^9$</td>
<td>Cu$^{2+}$</td>
<td>$^2D_{5/2}$</td>
<td>1</td>
<td>1.73</td>
<td>1.9 – 2.1</td>
</tr>
<tr>
<td>[Ar]3d$^{10}$</td>
<td>Cu$^+$, Zn$^{2+}$</td>
<td>$^1S_0$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The electron spin is almost exclusively responsible for the magnetic behaviour of 3d-transition metal ions.
## 2.4 Magnetic Properties

### Excursion: Units of Electromagnetism

<table>
<thead>
<tr>
<th>Electricity</th>
<th>Magnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical field strength E</td>
<td>Magnetic field strength H</td>
</tr>
<tr>
<td>[V/m]</td>
<td>[A/m]</td>
</tr>
<tr>
<td>Electrical flux density D</td>
<td>Magnetic flux density B</td>
</tr>
<tr>
<td>[As/m²]</td>
<td>[Vs/m²]</td>
</tr>
<tr>
<td>Permittivity of vacuum ε₀</td>
<td>Permeability of vacuum μ₀</td>
</tr>
<tr>
<td>(electrical field constant)</td>
<td>(magnetic field constant)</td>
</tr>
<tr>
<td>[As/Vm]</td>
<td>[Vs/Am]</td>
</tr>
<tr>
<td>Electrical resistance R</td>
<td>Magnetic resistance Rm</td>
</tr>
<tr>
<td>[V/A]</td>
<td>[A/V]</td>
</tr>
</tbody>
</table>

If electrical units shall be compared to analogous magnetics units, A and V have to be interchanged.
2.4 Magnetic Properties

Classification of Magnetic Materials

Magnetic materials

Weakly magnetic

- Dia-magnets

- Paramagnets

Strongly magnetic

- Antiferromagnets

- Ferromagnets

- Ferri-magnets

Ferromagnetismus
2.4 Magnetic Properties

Diamagnetism

Diamagnetism is caused by the magnetic orbital momentums of the electrons and occurs in every material. If a magnetic field is switched on, it induces circular currents which according to Lenz’s rule weaken the external magnetic field:

\[ \mu_r < 1 \text{ and } \chi < 0 \]

- Diamagnetism is weak and is superimposed by other types of magnetism
- Diamagnetism is independent of the field strength and almost temperature-independent
- Atoms, ions and molecules with filled shells or solids comprising such are diamagnetic
- Superconductors in not to strong fields are ideal diamagnets!

<table>
<thead>
<tr>
<th>Material</th>
<th>Susceptibility ( \chi ) ( [10^{-6}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 )</td>
<td>-0.0003</td>
</tr>
<tr>
<td>( Cu )</td>
<td>-1.1</td>
</tr>
<tr>
<td>( Pb )</td>
<td>-1.8</td>
</tr>
<tr>
<td>( C_{sp}^3 )</td>
<td>-2.1</td>
</tr>
<tr>
<td>( Ag )</td>
<td>-2.4</td>
</tr>
<tr>
<td>( Hg )</td>
<td>-2.9</td>
</tr>
<tr>
<td>( C_{sp}^2 )</td>
<td>-2.1, -260</td>
</tr>
<tr>
<td>( C_6H_6 )</td>
<td>-7.2</td>
</tr>
<tr>
<td>( NaCl )</td>
<td>-13.9</td>
</tr>
<tr>
<td>( Bi )</td>
<td>-16.6</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>-90</td>
</tr>
</tbody>
</table>
2.4 Magnetic Properties

**Paramagnetism**

Paramagnetism occurs, if a permanent magnetic momentum exists, for which unpaired electrons (spin magnetism) or unfilled electron shells (orbital magnetism) can be responsible.

Without a magnetic field the momentums are statistically distributed.
In a magnetic field, they are oriented in such a way that they enforce the external field, i.e. $\mu_r > 1$ and $\chi > 0$

**Temperature-dependence of paramagnetic materials**

**Curie-Weiß-law**

$$\chi = \frac{C}{T - \Theta}$$

with $\Theta = \text{paramagnetic Curie-temperature}$

$C = \text{Curie-constant}$

The paramagnetic susceptibility decreases with increasing temperature, because thermal movement contradicts magnetic ordering.

$1/\chi$ vs. $T$
2.4 Magnetic Properties

Cooperative Magnetism (Bi-nuclear Metal Complexes as a Example)

**Ferromagnetism**
Parallel orientation of spins at low temperatures with high total spin
⇒ \( \text{Cr}^{4+}(d^2)-\text{O}-\text{Cr}^{4+}(d^2) \) \( S = 4/2 \)

**Anti-ferromagnetism**
Antiparallel orientation of spins at low temperatures, total spin is zero
⇒ \( \text{Mn}^{2+}(d^5)-\text{O}-\text{Mn}^{2+}(d^5) \) \( S = 0 \)

**Ferrimagnetism**
Antiparallel orientation of spins at low temperatures, but total spin is not zero
⇒ \( \text{Fe}^{2+}(d^6)-\text{O}-\text{Fe}^{3+}(d^5) \) \( S = 1/2 \)

![Diagram of magnetic orientations](https://example.com/diagram23-16.jpg)

*Aus "Allgemeine und Anorganische Chemie" (Binningweis, Jackel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg, © 2004 Elsevier GmbH München, Abbildung23-16.jpg*
2.4 Magnetic Properties

Distance-dependence of Exchange Interactions

Positive (ferromagnetic) exchange interactions (+)
Delocalised s- and d-electrons (band magnetism)

Examples: Fe, Co, Ni, Gd

Negative (antiferromagnetic) exchange interactions (−)
Overlap of 3d-orbitals (super-exchange)

Examples: Cr, Mn, MnO
2.4 Magnetic Properties

Ferromagnetism

Below a certain temperature $T_C$ a spontaneous orientation of elemental magnets is observed
⇒ Even without external field domains exist (Weiβ areas), where neighbouring magnetic momentums are oriented in parallel
⇒ These domains have a length of about 50 µm and are separated by about 100 nm thick Bloch walls →

Properties of prominent ferromagnetic materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_C$ (K)</th>
<th>Magnetic momentum $[\mu_B]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>1394</td>
<td>1.715</td>
</tr>
<tr>
<td>Fe</td>
<td>1043</td>
<td>2.22</td>
</tr>
<tr>
<td>Ni</td>
<td>631</td>
<td>0.605</td>
</tr>
<tr>
<td>MnSb</td>
<td>587</td>
<td>3.5</td>
</tr>
<tr>
<td>CrO$_2$</td>
<td>386</td>
<td>2.03</td>
</tr>
<tr>
<td>Gd</td>
<td>289</td>
<td>7.5</td>
</tr>
<tr>
<td>Dy</td>
<td>88</td>
<td>10.2 → Spin-Bahn-Kopplung → J</td>
</tr>
<tr>
<td>EuO</td>
<td>70</td>
<td>6.9</td>
</tr>
</tbody>
</table>
2.4 Magnetic Properties

Ferromagnetism

Upon application of an external magnetic field, the domains that are oriented parallel to the external field expand. The other domains shrink.

Above Curie-temperature $T_C$ ferromagnets become paramagnetic

$H = 0, M = 0$ $H > 0, M < M_s$

Magnetic remanence $M_R$
Saturation magnetisation $M_s$
Coercive field strength $H_c$
Antiferromagnetism

Below a certain temperature $T_N$ (Néel-temperature) neighbouring magnetic momentums are oriented in anti-parallel and compensate each other.

Then, the following is valid: $\mu_r = 1$ und $\chi = 0$

Example: MnO
Magnetic momentums of Mn$^{2+}$-ions in different levels compensate each other.

Above Néel-temperature $T_N$ anti-ferromagnets become paramagnetic.

Further examples
EuTe, Rb$_2$MnCl$_4$
2.4 Magnetic Properties

**Ferrimagnetism**

Adjacent magnetic momentums are oriented in anti-parallel but do not compensate each other totally. Ferrimagnetism occurs in materials where different types of ion exhibit strongly deviating magnetic momentums:

- **Ferrites**
  - \( \text{MFe}_2\text{O}_4 \) with \( 
  \text{M} = \text{Zn}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}
  \)

- **Garnets**
  - \( \text{M}_3\text{Fe}_2\text{Fe}_3\text{O}_{12} \) with \( \text{M} = \text{Ln}^{3+} \)

In a magnetic field, the magnetic momentums of the different types of ions are oriented in anti-parallel, resulting in a net magnetisation.

**Remark**

Anti-ferromagnetism is, strictly speaking, a special case of the more general ferrimagnetism, where both sub-layers can be regarded as equivalent.
2.4 Magnetic Properties

Ferrimagnetism in Inverse Iron Oxide Spinels Fe₃O₄ (Magnetite), cubic

Natural magnets are crystalline materials frozen in the terrestrial magnetic field ⇒ permanent magnetisation

\[ Fe_3O_4 = FeFe_2O_4 = [Fe^{3+}]^{\text{tet}}[Fe^{2+}Fe^{3+}]^{\text{oct}}O_4 \]

\[ \begin{array}{cccccc}
[Fe^{3+}]^{\text{tet}} & [Ar]3d^5 \text{ h.s.} & \uparrow\uparrow\uparrow\uparrow\uparrow\uparrow \\
[Fe^{3+}]^{\text{oct}} & [Ar]3d^5 \text{ h.s.} & \downarrow\downarrow\downarrow\downarrow\downarrow \\
[Fe^{2+}]^{\text{oct}} & [Ar]3d^6 \text{ h.s.} & \uparrow\uparrow\uparrow\uparrow\uparrow \\
\end{array} \]

\[ S = 0 \quad [Fe^{3+}]^{\text{tet}}-O-[Fe^{3+}]^{\text{oct}} \]

\[ S = 4/2 \rightarrow \text{Magnetisation!} \]

For \( T < T_c \): Parallel orientation of spins in single domain
2.4 Magnetic Properties

Behaviour of Matter in a Magnetic Field: Summary and Examples

Types of magnetisation

- **Diamagnetism**  
  Bi, Cu, Ag, Au, Al₂O₃

- **Paramagnetism**  
  Al, Ti, Cu alloys

- **Ferromagnetism**  
  Fe, Co, Ni, Gd, γ-Fe₂O₃

- **Antiferromagnetism**  
  Mn, Cr, MnO, NiO, α-Fe₂O₃

- **Ferrimagnetism**  
  Ferrites, garnets, Fe₃O₄
2.4 Magnetic Properties

Application of Magnetisation Curve

Size and shape of the hysteresis loop determine the behaviour of materials in a magnetic field and thus their range of application.

Hard magnets: Energy storage, power source

Soft magnets: sensors, transformer sheets
2.4 Magnetic Properties

Application and Properties of Soft-magnetic Materials

⇒ Coil slugs of electromagnets, electric engines, transformers, generators, ...

The hysteresis loop must be run repeatedly, because, here, alternating current is used
⇒ Soft-magnetic materials are preferably used

Soft-magnetic materials exhibit the following properties
• High saturation magnetisation
  ⇒ Magnets show high flux densities
• High permeability
  ⇒ weak magnetic fields suffice to achieve saturation
• Small coercive field strength
  ⇒ Re-orientation of domains happens for small field strengths
• Small remanence
  ⇒ without external field, only small residual magnetisation remains
• Rapid reaction to high-frequency alternating fields
  ⇒ small energy losses due to friction of dipoles
• Small electric conductivity (ceramics with high resistance)
  ⇒ small Joule loss due to eddy currents
2.4 Magnetic Properties

Magnetic Storage Materials for Data Storage in Magnetic and Audio Tapes and Floppy Disks or Disk Storages

Operation scheme of magnetic storage materials
- Magnetisation remains even without magnetic field
- The opposing magnetisation directions correspond to the binary values 0 and 1
- Write and erase of information is achieved by ready re-magnetisation

Which conditions must be met by magnetic pigments?
1. High remanence
   ⇒ residual magnetisation after switching off the magnetic field
2. Needle-shaped particles
   ⇒ ready orientation in magnetic field
3. No loss of magnetisation $M$ through heating of magnetic band
   ⇒ High Curie- or Néel-temperatures
4. High signal/noise-ratio (dynamic)
   ⇒ Pigments with as small particles as possible (uniform domains/particle)
5. Possibility to fully erase magnetisation
   ⇒ Intermediate coercive field strength $H_c$ (needed field strength to de-magnetise)
### 2.4 Magnetic Properties

#### Magnetic Pigments for Magnetic Tapes

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Application</th>
<th>Particle Size [µm]</th>
<th>Specific surface [m²/g]</th>
<th>Coercive field strength [kA/m]</th>
<th>Saturation magnetisation MS/δ [µTm³/kg]</th>
<th>Mᵣ/Mₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Fe₂O₃</td>
<td>Studio radio tapes</td>
<td>0.40</td>
<td>17 – 20</td>
<td>23 – 27</td>
<td>85 – 92</td>
<td>0.80 – 0.85</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>Cassettes IEC I</td>
<td>0.35</td>
<td>20 – 25</td>
<td>27 – 30</td>
<td>87 - 92</td>
<td>0.80 – 0.90</td>
</tr>
<tr>
<td>γ-Fe₂O₃ (Co-coated)</td>
<td>Cassettes IEC II</td>
<td>0.30</td>
<td>30 – 40</td>
<td>52 – 57</td>
<td>94 - 98</td>
<td>0.85 – 0.92</td>
</tr>
<tr>
<td>Fe (metallic)</td>
<td>8 mm video</td>
<td>0.25</td>
<td>50 - 60</td>
<td>115 - 127</td>
<td>130 - 160</td>
<td>0.85 – 0.90</td>
</tr>
</tbody>
</table>
2.4 Magnetic Properties

Audio Tape

Functional principle: presented by Valdemar Poulsen during world exhibition in Paris (1900)

AEG Magnetophon (1936)

Compact cassette (around 1960)
2.4 Magnetic Properties

Floppy Disks

Construction of a storage medium
A Al-plate carrying a polymer film with magnetic pigments was used for floppy disks as well as for disk storages.

Working scheme
During “writing”, the current circulating through Coil of the head creates a magnetisation pattern within the magnetic layer.

During “reading”, the magnetisation pattern induces a current in the coil of the head.

For the writing head a soft magnet is used, e.g. a Fe/Ni-alloys (Permalloy)

According to D.R. Askeland, Materialwissenschaften, Spektrum-Verlag 1996
2.4 Magnetic Properties

Application and Properties of Hard-magnetic Materials

Hard-magnetic materials are used for permanent magnets and must possess the following properties:

- High remanence
- High permeability
- High coercive field strength
- Broad hysteresis loop ⇒ high energy density

Energy density \((BH)_{\text{max}} = B \cdot H\) [VAs/m³ = J/m³]

\(B =\) magnetic flux density [T = Vs/m²]
\(H =\) magnetic field strength [A/m]

Meaning that the strength of a permanent magnet increases with the size of the hysteresis loop and thus with the maximal energy density
2.4 Magnetic Properties

Materials for Permanent Magnets

- The structure of cutting-edge permanent magnets is extremely fine
  ⇒ every crystallite contains only one domain, with grain boundaries and not Bloch walls separating them
- The orientation of these domains by rotation needs more energy than growth of domains in combination with a shift of Bloch walls
  ⇒ Magnets are difficult to demagnetize

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Coercive field strength $H_c$ [kA/m]</th>
<th>Typical energy density $(BH)_{\text{max}}$ [kJ/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel (0.9% C, 1.0% Mn)</td>
<td>4</td>
<td>1.6</td>
</tr>
<tr>
<td>Martensitic steel (9% Co)</td>
<td>11</td>
<td>3.3</td>
</tr>
<tr>
<td>AlNiCo (21% Ni, 12% Al, 5% Co, Fe)</td>
<td>35</td>
<td>11</td>
</tr>
<tr>
<td>CuNiFe (60% Cu, 20% Fe, 20% Ni)</td>
<td>44</td>
<td>12</td>
</tr>
<tr>
<td>SrFe$<em>{12}$O$</em>{19}$</td>
<td>260</td>
<td>29</td>
</tr>
<tr>
<td>SmCo$_5$</td>
<td>760</td>
<td>200</td>
</tr>
<tr>
<td>Sm$<em>2$Co$</em>{17}$</td>
<td>720</td>
<td>250</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{14}$B:Dy,Pr</td>
<td>880</td>
<td>360</td>
</tr>
</tbody>
</table>
### 2.4 Magnetic Properties

**Electronic Configuration of Lanthanides and their Cations**

**Metals**

| [Xe] | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 6s   | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  | 2  |
| 5d   | 1  | 1  | 0  | 0  | 0  | 0  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 1  |
| 4f   | 0  | 1  | 3  | 4  | 5  | 6  | 7  | 7  | 9  | 10 | 11 | 12 | 13 | 14 |

**Cations**

| [Xe] | La$^{3+}$ | Ce$^{3+}$ | Pr$^{3+}$ | Nd$^{3+}$ | Pm$^{3+}$ | Sm$^{3+}$ | Eu$^{3+}$ | Gd$^{3+}$ | Tb$^{3+}$ | Dy$^{3+}$ | Ho$^{3+}$ | Er$^{3+}$ | Tm$^{3+}$ | Yb$^{3+}$ | Lu$^{3+}$ |
|------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 4f   | 0         | 1         | 2         | 3         | 4         | 5         | 6         | 7         | 8         | 9         | 10        | 11        | 12        | 13        |

**Electronic configuration**

<table>
<thead>
<tr>
<th>$m_l$</th>
<th>-3</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>0</th>
<th>-1</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
</table>

- e.g. Gd$^{3+}$/Eu$^{2+}$/Tb$^{4+}$
  - [Xe] $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$
  - 4f
  - 5d
  - 6s
  - 6p

- Ce$^{3+}$, Yb$^{3+}$, Pr$^{4+}$, Nd$^{4+}$, Tb$^{4+}$, Dy$^{4+}$, Sm$^{2+}$, Eu$^{2+}$, Tm$^{2+}$ → paramagnetic ions
- Gd$^{0}$, Tb$^{0}$, Dy$^{0}$ → ferromagnetic ordering ($T_C < RT$)
2.4 Magnetic Properties

Materials for Permanent Magnets – Advantages of Lanthanides

Highly paramagnetic as cations
- Gd$^{3+}$ ⇒ magnetic contrast agent [Gd$^{3+}$(dota)]
- Dy$^{3+}$/Ho$^{3+}$ ⇒ maximal magnetic moment of all elemental cations ~ 10.6 $\mu_B$
- For comparison: Fe$^{3+}$/Mn$^{2+}$ $\mu_{\text{eff}} = 5.9$ $\mu_B$

Ferromagnetic as metal or alloy
- Gd/Tb/Dy
- Nd$_2$Fe$_{14}$B
- SmCo$_5$ and Sm$_2$Co$_{17}$

As building block in ferromagnetic materials
- Y$_3$Fe$_5$O$_{12}$ „YIG“
- Gd$_3$Fe$_5$O$_{12}$ „GdIG“
2.4 Magnetic Properties

Application Areas of Nd$_2$Fe$_{14}$B, SmCo$_5$, and Sm$_2$Co$_{17}$

- Application in electric engines in automotive industry
  > 25 actuating motors per car
  electric drive & brake

- Hard drives (HDDs)
  Magnets: 2 wt-% of HDD
  Rare earths: 0.6 wt-% of HDD

- Wind power stations
  Off-shore: 650 kg Nd/station
  ~ 100 kg/MW power output
Alternatives for Nd$_2$Fe$_{14}$B, SmCo$_5$ and Sm$_2$Co$_{17}$

- Permanent magnets on basis of iron oxide with addition of other oxides
  Problem: energy product $(BH)_{\text{max}}$ is by a factor of ten smaller than for rare earth magnets
  $\Rightarrow$ Not-applicable in many engines and generators!

- Nano-scale Fe/Co-compounds
  Nano-rods that order magnetically and can be stabilized as ferromagnetic domains in a matrix
  $\Rightarrow$ Technologically demanding

- Novel molecular magnets
  Exp.: $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]\cdot2\text{CH}_3\text{COOH}\cdot4\text{H}_2\text{O}$
  “Mn$_{12}$ac“
  $\Rightarrow$ long-term research goal
2.5 Optical Properties

Wave Theory of Light: Huygens, Fresnel, Hertz, Maxwell

→ The light field consists of an electric and a magnetic field component

But: The light field can take up or transfer energy only in packages (light quantums = photons)

→ “Wave-particle-dualism”

Proof for above hypothesis:

• Photons liberate electrons from an electrode, if their frequency
  \( \nu > \frac{E}{h} \) (critical frequency)

• Derivation of Planck's radiation law for cavity radiation is based on the quantization of the energy of the light field (Planck, 1900)

→ Electromagnetic radiation consists of wave packages (photons) with discrete energy \( E \) and momentum \( p \).
2.5 Optical Properties

**Photoelectric Effect: Einstein 1905 → Nobel Price 1912**

Light is quantized into photons of the energy $h\nu$. This quantization is fundamental and does not correlate with the quantization of harmonic oscillators as in Planck’s explanation of the cavitation radiation.

$$\phi = \nu h \quad \text{Einstein-eqation}$$

$$\nu = \frac{\phi}{h} \quad \text{Critical frequency:}$$

$$\lambda = \frac{hc}{\phi} \quad \text{Critical wavelength:}$$

$E_{\gamma} = h\nu$

$E_{e^{-\text{(kin)}}} = h\nu - \phi$

Vacuum potential

$\phi = \text{Work function}$

Conduction electrons

Fermi edge

$
\begin{align*}
E_F & \quad 0 \\
E & \quad E_{\gamma} = h\nu \\
E_{\text{kin}} & = h\nu - \phi \\
\phi & = \text{Work function}
\end{align*}
$
2.5 Optical Properties

The Optical Properties of a Substance Are Defined by its Interaction with Electromagnetic Radiation

Macroscopic phenomena

- Absorption → Luminescence, heat, charge separation or storage
- Transmission including refraction
- Reflection diffuse and specular
- Spontaneous emission by virtual photons
- Stimulated emission by irradiated photons

Solid (n > 1.0)

- Refraction
- Absorption
- Energy-transfer
- Transmission
- Heat
- Emission (spontaneous or stimulated)

Electrons Vibrations
2.5 Optical Properties

Interactions between Electromagnetic Radiation and Matter

Absorption A
Uptake of electromagnetic energy by a medium

Reflection (refraction) R
Incident radiation is reflected, obeying the law of refraction

Transmission T
Passage of radiation
$A + T + R = 1$

Degree of absorption $A$: ratio of absorbed to total received radiation
Degree of transmission $T$: part of the radiation that passes an object
Degree of reflection $R$: ratio of reflected radiation (diffuse and specular) to total received radiation
## 2.5 Optical Properties

### Interaction between Electromagnetic Radiation and Matter

#### Physical processes and types of radiation

<table>
<thead>
<tr>
<th>Process</th>
<th>Radiation</th>
<th>Phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core excitation</td>
<td>Gamma-rays</td>
<td>Mößbauer effect</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fission, fusion</td>
</tr>
<tr>
<td>Excitation of inner electrons</td>
<td>X-rays</td>
<td>X-ray fluorescence (XRF)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>X-ray diffraction (XRD)</td>
</tr>
<tr>
<td>Excitation of outer electrons</td>
<td>UV/Vis-radiation</td>
<td>Luminescence processes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Refraction, diffraction</td>
</tr>
<tr>
<td>Excitation of vibrations</td>
<td>IR-radiation</td>
<td>Vibrations of molecules</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid state phonons</td>
</tr>
<tr>
<td>Excitation of rotations</td>
<td>Micro waves</td>
<td>Rotation of molecules</td>
</tr>
<tr>
<td>Excitation of core spin</td>
<td>Radio waves</td>
<td>EPR and NMR</td>
</tr>
</tbody>
</table>
2.5 Optical Properties

Types of Radiation and Physical Processes

Radiation

Optical radiation
(10 nm – 1 mm)

Visible Light
(380 – 780 nm)
2.5 Optical Properties

Mikroskopische Wechselwirkungen zwischen elektromagnetischer Strahlung und Materie

Absorption (induced)

\[ E_2, N_2 \]

\[ E_1, N_1 \]

\[ \text{hv} \]

\[ \frac{dN_1}{dt}_{\text{ind.}} = -B_{12} \cdot N_1 \cdot u(\nu) \]

Spontaneous Emission

\[ \text{hv} \]

\[ \frac{dN_2}{dt}_{\text{spont.}} = -A_{21} \cdot N_2 \cdot u(\nu) \]

Stimulated Emission

\[ \text{hv} \]

\[ \frac{dN_2}{dt}_{\text{ind.}} = -B_{21} \cdot N_2 \cdot u(\nu) \]

mit \( A_{21}, B_{12}, B_{21} = \text{Einstein-Koeffizienten} \) und \( u(\nu) = \text{energy} \)

\[ g_1 B_{12} = g_2 B_{21} \text{ mit } g_1, g_2 = \text{degeneration} \]

\[ B_{21} = A_{21} \cdot \lambda^3/8\pi h \text{ d.h. Abklingzeit } \tau \sim \lambda^3 \]

Erhaltungssätze

1. Energieerhaltung: \( \text{hv} = E_2 - E_1 = \Delta E \)
2. Impulserhaltung: \( h/\lambda = \pm 1 = \Delta l \)

\( n_s \rightarrow n_p \) sowie \( n_f \rightarrow (n+1)d \) Übergänge sind erlaubt
\( n_d \rightarrow n_d \) sowie \( n_f \rightarrow n_f \) Übergänge sind verboten
2.5 Optical Properties

Absorption: Electronic Transitions

Example: PrPO₄ (powder)
1. 4f² - 4f² transitions (450 and 580 nm)
2. [Xe]4f² – [Xe]4f¹5d¹ transitions (210 nm)
3. VB - CB transition (~150 nm)
2.5 Optical Properties

Absorption: Vibronic Transitions

Example: Absorption of light by atmosphere (absorbing gases: CO$_2$, H$_2$O, O$_3$)

IR-Spectrum

Normal vibrations of H$_2$O

Dipol transitions for various vibrational modes.
## 2.5 Optical Properties

### Conversion of the absorbed energy

<table>
<thead>
<tr>
<th>Process</th>
<th>Radiation → Energy Type</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar thermal</td>
<td>Thermal energy</td>
<td>Colour pigments, Solar panels</td>
</tr>
<tr>
<td>Luminescence</td>
<td>Light</td>
<td>Light sources, Laser, Scintillators, Diagnostics</td>
</tr>
<tr>
<td>Photo voltaics</td>
<td>Electric energy</td>
<td>Solar cells</td>
</tr>
<tr>
<td>Photo synthesis</td>
<td>Chemical energy</td>
<td>Autotrophes organisms, Photochemistry</td>
</tr>
<tr>
<td>Storage</td>
<td>Charge carrier</td>
<td>Afterglow pigments, Detectors, Optical Storage</td>
</tr>
</tbody>
</table>
2.5 Optical Properties

Transmission: Classification of Materials

1. Transparent (plain) materials
   - high transmission
   - negligible reflection and absorption
   - Single crystals, transparent ceramic

2. Translucent (dull) materials
   - high transmission, but strong refraction
   - Light is transmitted hazily
   - Frosted glass, nano-powder layers

3. Opaque (intransparent) materials
   - high reflection and absorption
   - Negligible transmission
   - Ceramic, thick powder layers

Degree of transmission $T = \frac{I}{I_0}$ with $I = I_0 \cdot e^{-\mu \cdot d}$

Extinction $E = -\log(I/I_0) = \log(I_0/I) = \log O$

with $O = $ Opacity
2.5 Optical Properties

Reflection: Specular (Regular)

Reflection at polished surface in one direction (reflective surface)

1. Case: Non-absorbing materials

\[
R_{\text{reg}} = \frac{(n_1 - n_0)^2}{(n_1 + n_0)^2}
\]

2. Case: Absorbing materials

\[
R_{\text{reg}} = \frac{(n_1 - n_0)^2 + (n_1 k_1)^2}{(n_1 + n_0)^2 + (n_1 k_1)^2}
\]

with \(n = \) refractive index \(k = \) absorption index

Result

Based on a (specular) reflection spectrum, a absorption spectrum can be calculated, if the reflection spectrum is known over the whole range of the electromagnetic spectrum (Kramers-Kronig-Transformation)

<table>
<thead>
<tr>
<th>Substance</th>
<th>refractive index (n_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>1,000</td>
</tr>
<tr>
<td>Air</td>
<td>1,0003</td>
</tr>
<tr>
<td>H(_2)O(s)</td>
<td>1,309</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>1,333</td>
</tr>
<tr>
<td>CaF(_2) (Flussspat)</td>
<td>1,434</td>
</tr>
<tr>
<td>SiO(_2) (Glass)</td>
<td>1,46</td>
</tr>
<tr>
<td>SiO(_2) (Quartz)</td>
<td>1,55</td>
</tr>
<tr>
<td>Al(_2)O(_3) (Sapphire)</td>
<td>1,76</td>
</tr>
<tr>
<td>Y(_3)Al(<em>5)O(</em>{12}) (YAG)</td>
<td>1,83</td>
</tr>
<tr>
<td>Y(_2)O(_3) (Bixbyite)</td>
<td>1,90</td>
</tr>
<tr>
<td>ZrSiO(_4) (Zirconia)</td>
<td>1,923</td>
</tr>
<tr>
<td>Diamond</td>
<td>2,417</td>
</tr>
<tr>
<td>Lead glass</td>
<td>2,50</td>
</tr>
</tbody>
</table>
### 2.5 Optical Properties

**Reflection: Diffuse (Irregular)**

Reflection at a non-polished surface in all directions of the half space (dull surface)

**Description by Kubelka-Munk-Theory**
- requires optically infinitely thick powder
- holds for diffuse irradiation and diffuse remission, i.e. directional reflection must be eliminated
- Assumption: The sample consists of infinitesimal thin layers that are irradiated above and from below and weaken the light through absorption

\[
 f(R) = \frac{(1 - R)^2}{2R} = \frac{1}{s} \epsilon c
\]

with
- \( R = \) degree of diffuse reflection
- \( s = \) refractive coefficient
- \( c = \) concentration of absorber
- \( \epsilon = \) absorption coefficient
2.5 Optical Properties

Frequency-dependence of Optical Properties

The tendency to refract, transmit and reflect in a material is to a greater or lesser extent dependent on the frequency.

This is macroscopically described by the refractive index \( n(\nu) \) (index 0 = vacuum):

\[
n(\nu) = \frac{c_0}{c_1(\nu)} = \frac{\lambda_1(\nu)}{\lambda_0}
\]

In a medium, electromagnetic waves spread with lower velocity than in vacuum due to polarisation of electrons:

\[
c_1(\nu) = \frac{1}{\sqrt{\mu(\nu)\varepsilon(\nu)}}
\]

thus, for non-magnetic materials:

\[
c_1(\nu) = \frac{1}{\sqrt{\varepsilon(\nu)}}
\]

The correlation between permittivity and refractive index is given by:

\[
n(\nu) = \frac{c_0}{c_1(\nu)} = \sqrt{\frac{\mu(\nu)\varepsilon(\nu)}{\mu_0(\nu)\varepsilon_0(\nu)}} = \mu_r(\nu)\varepsilon_r(\nu)
\]

and for non-magnetic materials:

\[
n(\nu) = \sqrt{\varepsilon_r(\nu)}
\]
2.5 Optical Properties

Frequency-dependence of Optical Properties

Thus, the refractive index of a material must always be given for a certain frequency
⇒ often, the frequency of sodium-D-line is chosen (589 nm)

The electromagnetic wave polarises the electrons of the medium
⇒ electronic polarisation
(Example: Silicon nitride Si$_3$N$_4$)

The strength of the interaction between photons and electrons thus depends on the polarizability of the electrons
⇒ Materials with high (electron)density have a high refractive index (lead glass)
⇒ Materials with a low band gap have a high refractive index (TiO$_2$, ZnS)
2.5 Optical Properties

**Frequency-dependence of Optical Properties**

At low frequencies (IR-region) ionic polarisation (vibrations) dominates the interaction between solids and photons.

At very high frequencies the interaction between photons and electrons becomes weaker and weaker, so that the refractive index approaches 1.

\[ n = 1 \] for x-ray and gamma radiation.
2.5 Optical Properties

Frequency-dependence of Optical Properties

Microwave region (radar radiation)
- Absorption: Materials with the possibility for orientation polarisation or easily polarizable electrons
  - Conducting polymers
  - Ferrimagnets
- Transmission and reflection
  - Ceramics
  - Polymers

Infrared region (thermal radiation)
- Absorption: Molecular vibrations or ionic polarisation
- Transmission and reflection
  - Materials with low phonon frequencies, e.g. halides

Visible spectral region (optical radiation)
- Absorption: Electronic polarisation and electronic transitions
2.5 Optical Properties

Anisotropy of Refractive Index

The refractive index, $n$, can be dependent on spatial direction, thus being anisotropic

⇒ Crystals with low symmetry ($\text{CaCO}_3$, calcite)

By variation of $n$ depending on the direction of the polarisation of the electrical field, birefringence can occur

Optical Properties of substances with anisotropic refractive indices can be influenced by applying (high) voltages

Applications

• In Pockels cell: electro-optical modulator, which changes the polarisation of light during passage, if voltage is applied (optical switches) $\text{LiNbO}_3$, $\text{KH}_2\text{PO}_4$, $\beta\text{-BaB}_2\text{O}_4$

• LCD panels: control of light flux through polarisation via liquid crystals

Calcite-crystal (above)
Demonstration of birefringence (below)
2.5 Optical Properties

Absorption and Emission

Light interacts with electrons of the atoms. Through interaction of a light quantum with an electron the quantum can be absorbed or reinforced. Crucial is the energy state of the electron.

Absorption

spontaneous emission (luminescence)

stimulated emission (reinforced luminescence)

Transformation of radiation or other forms of energy into visible light or UV-radiation is called luminescence.
2.5 Optical Properties

Light Amplification by Stimulated Emission of Radiation (Laser)

Short introduction into history of Laser technology
1917  theoretical foundation (A. Einstein, D)
1954  first microwave Laser demonstrated: Maser
1960  first pulsed lasing processes in ruby-solid-state Laser demonstrated
       (Theodore H. Maiman, CA, USA)
1961  first Nd-glass-Laser
1964  first cw CO₂-Laser
1965  first application of a Laser to process diamond (Herziger, D)
1966  first tunable dye laser pumped by a ruby laser
1969  first factory to drill watch stones (Herziger, D)
1978  first Laser cutting system in a company
1995  first high-power diode-Laser for hardening
2002  first high-power fibre-Laser for welding
2016  13.5 nm (EUV) radiation generated by a CO₂-Laser irradiated molten Sn droplet

Laser radiation is the form of energy with the highest possible degree of order or minimal entropy and highest coherence
2.5 Optical Properties

Materials for Solid-State Laser

1. Active medium
   - Single crystals or transparent ceramics
     Oxides: $\text{Al}_2\text{O}_3$, $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Lu}_3\text{Al}_5\text{O}_{12}$, $\text{BeAl}_2\text{O}_4$, $\text{YAlO}_3$, $\text{CaWO}_4$, $\text{YVO}_4$, $\text{GdVO}_4$, $\text{KYW}_2\text{O}_8$
     Fluorides: $\text{MgF}_2$, $\text{CaF}_2$, $\text{BaY}_2\text{F}_8$, $\text{LiCaAlF}_6$, $\text{LiYF}_4$, $\text{KY}_3\text{F}_{10}$
   - Glasses: phosphates and silicates
   - The host material must possess extremely good optical, mechanical and thermal properties

2. Dopants
   - Transition metal ions
     $\text{Cr}^{3+}$ (e.g. in ruby-Laser), $\text{Ti}^{3+}$ (e.g. in sapphire Laser), $\text{U}^{3+}$
   - Ions of rare earth elements (lanthanide ions)
     $\text{Pr}^{3+}$, $\text{Nd}^{3+}$, $\text{Sm}^{3+}$, $\text{Gd}^{3+}$, $\text{Ho}^{3+}$, $\text{Er}^{3+}$, $\text{Tm}^{3+}$, $\text{Yb}^{3+}$
   - Density of Laser-active dopants: $10^{19}$ cm$^{-3}$ (higher as for gas-Laser: $10^{15} – 10^{17}$ cm$^{-3}$)
2.5 Optical Properties

Ruby-Laser (Al₂O₃:Cr)

Excitation by a flash lamp in the blue and green spectral region leads to excitation of Cr³⁺ [Ar]3d³ (pumping)

The lifetime of the ⁴F₁ states is very short and relaxation into metastable E-levels occurs (ISC)

Population of the E-levels increases until so-called population inversion is reached

Further irradiation by photons leads to stimulated emission and total depletion of the E-level

3-level-Laser: More than 50% of the atoms must be excited to achieve population inversion and light amplification
2.5 Optical Properties

**YAG:Nd Laser (Y$_3$Al$_5$O$_{12}$:Nd)**

Most important commercial solid-state Laser

Excitation by diodes or flash lamps

4-level-Laser

Splitting of $^2S+^1L_J$ multiplets into Stark-Levels by strong crystal field in YAG

But the splitting is relatively small, because the 4f-electrons are shielded by the outer completely occupied shells ($5s^2$ and $5p^6$)

$\sim 200 - 240$ cm$^{-1}$

---

Energy [cm$^{-1}$]

1064 nm
2.5 Optical Properties

**YAG:Nd Laser (Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Nd)**

Strong splitting of $^4F_{3/2} \to ^4I_{11/2}$ transition of Nd\textsuperscript{3+} in garnets of the LnAG-type. Tuneable by type of occupation of the dodecahedral site

<table>
<thead>
<tr>
<th>Material</th>
<th>Laser Type</th>
<th>Wellenlänge [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LuAG:Ce,Nd</td>
<td>YAG:Nd</td>
<td>203 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>YAG:Nd</td>
<td>YAG:Ce,Nd</td>
<td>230 cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>235 cm\textsuperscript{-1}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Physical effect**

Crystal field splitting

$\Delta E = f($coordination number, symmetry, ionic charge density, ...$)$

Lu\textsuperscript{3+} < Y\textsuperscript{3+} < Nd\textsuperscript{3+} < Ce\textsuperscript{3+}
2.5 Optical Properties

Light Emitting Diodes (LEDs)

LEDs are opto-electronic components with pn-transitions, composed of materials with band gap energies equivalent to visible radiation ⇒ III/V-semiconductors

Al, Ga, In + N, P, As, Sb
(Al,Ga)N
(Ga,In)N
(Al,Ga)P
(In,Ga)N/(Al,Ga)N multi quantum well structure
(Al,Ga,In)P
(Al,Ga)As
GaAs

Applications
Signal lamps
Designer lamps
Back lighting
General lighting
Street lighting

~100 µm

p-electrode
transparent metal (Au/Ni)
p-GaN contact layer
(In,Ga)N/(Al,Ga)N multi quantum well structure
n-electrode
n-GaN contact layer
buffer layer to adapt to the host layer

transparent substrate:
Al₂O₃ (sapphire), SiC, Si, or GaN
2.5 Optical Properties

Light Emitting Diodes (LEDs)

Standard 5 mm LED

High-performance-LED

![Diagram of LED structures](image)
2.5 Optical Properties

Light Emitting Diodes (LEDs)

Thin Film Flip Chip  Flip Chip  Vertical Thin Film Chip

2.5 Optical Properties

White emitting LEDs (Phosphor Converted Light Emitting Diodes pc LEDs)

- **Red + Green + Blue LEDs**
- **Blue LED + yellow phosphor**
- **Blue LED + RG phosphor blend**
- **UV LED + RGB phosphor blend**
2.5 Optical Properties

**Semi-conductor Laser or Laser Diodes**

1. Promotion of electrons from valence into conduction band by applying voltage

2. Electron $e_1$ recombines with hole $h_1$ and emits a photon which triggers the recombination of $e_2$ with hole $h_2$ under emission of a second photon

3. Continuous stimulation of further emission by reflected photons within the diode

4. At the semi-transparent mirror some photons are coupled out from the active area and leave the diode as laser beam

→ Resonator results in spectral focusing
2.5 Optical Properties

LEDs and Laser diodes

<table>
<thead>
<tr>
<th>Wellenlänge (nm)</th>
<th>Emissionsintensität (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>375</td>
<td>400</td>
</tr>
<tr>
<td>400</td>
<td>425</td>
</tr>
<tr>
<td>425</td>
<td>450</td>
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<tr>
<td>450</td>
<td>465</td>
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<tr>
<td>465</td>
<td>480</td>
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<td>480</td>
<td>500</td>
</tr>
<tr>
<td>500</td>
<td>525</td>
</tr>
<tr>
<td>525</td>
<td>550</td>
</tr>
</tbody>
</table>

„LED platform“
- **465 nm LEDs** Illumination
- **410 nm LEDs** Full conversion
- **365 nm LEDs** Black light
- **265 nm LEDs** Disinfection

„Laser diode platform“
- **940 nm** Remote controls
- **785 nm** CD
- **655 nm** DVD
- **405 nm** Blue ray DVD

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2.5 Optical Properties

LEDs and Laser diodes

At high current density one observes saturation of the electroluminescence due to the Auger effect

Due to stimulated emission in Laser diodes saturation will only observed for much higher current densities: Wall plug efficiency (WPE) up to 70%!

2.5 Optical Properties

Fibre Optics for Transfer of Information

Signal generation
A Laser beam is loaded with information by modulating the beam intensity via the applied voltage.
The modulated Laser beam is guided to the receiver through a fibre optic.

Signal reception
Working principle is based on the photoelectric effect. During applied voltage, electrical current is measurable proportional to the incident beam intensity

nach D.R. Askeland, Materialwissenschaften, Spektrum-Verlag 1996
2.5 Optical Properties

Fibre Optics for Transfer of Information

Light guidance in glasses is based on total reflection of light. A effect that is described by Snellius’ equation:

\[ n_0 \cdot \sin \alpha_0 = n_1 \cdot \sin \alpha_1 \]

Total reflection occurs upon transition from a optically more dense into a optically less dense medium, if the critical angle \( \alpha_T \) is exceeded

Critical angle: \( \alpha_1 = \arcsin(n_0/n_1) \quad n_0 \sim 1.0 \text{ for air} \quad n_1 \sim 1.5 \text{ for normal glass} \)

Air/glass: \( \alpha_T = \arcsin(1/n_1) = \arcsin(1/1.5) = 41.8^\circ \)

Maximal entrance angle into fibre = 90° - \( \alpha_T = 48.2^\circ \)

90° - \( \alpha_T \) increases with increasing refractive index of the fibre material!
2.5 Optical Properties

Materials for Fibre Optics

1. Efficient light guidance over great distances requires little damping of the optical signals:
   - no loss of intensity by lateral irradiation
   - as high transparency as possible of the fibre material for the used wavelength
2. Small signal distortion is achieved by gradient fibres:
   - fibre which refractive index continuously decreases from core to mantle

Sodium silicate glass ($\text{Na}_2\text{O-}\text{SiO}_2$) is highly transparent for wavelengths important for optical transmissions, i.e. 0.8 and 1.8 µm but absorption due to impurities (ppm-range)
   - Fe, Co, Cr, Ni, V, Cu
   - $\text{H}_2\text{O}$ as OH-groups
and refraction by defects
   - gas bubbles
   - crystallites
leads to damping of the optical signal

**Reduction of refractive index by**
addition of $\text{B}_2\text{O}_3$ or fluorides

**Elevation of refractive index by**
addition of $\text{P}_2\text{O}_5$, GeO$_2$ or PbO
Interference Layers

- Anti-reflection layers to enhance light in- and out-coupling
- Sequence of layers from highly refractive to low refractive materials, e.g. SiO₂ + TiO₂

“Moth-eye-effect”

(Ca,Sr)S:Eu coated by SiO₂
n(SrS) ~ 2,1, n(SiO₂) ~ 1,5
2.5 Optical Properties

Interference Layers

⇒ Moth-eye-coating to enhance light in-coupling
⇒ Solar cells with higher efficiency

Periodic surface structure
(Spektrum der Wissenschaft, August 1997, 20)
2.6 Catalytic Properties

Homogeneous and Heterogeneous Catalysis

Homogeneous catalysis: reagents and catalysts are in the same phase

Heterogeneous catalysis: reagents and catalysts are in different phases

⇒ Interaction at surfaces, e.g. reaction in gas phase or in solution
   Physisorption: 20 – 50 kJ/mol
   Chemisorption: some 100 kJ/mol

Application areas for heterogeneous catalytic materials
Selective synthesis of organic and inorganic compounds

- Exhaust gas treatment
- Water treatment (waster, process, drinking water)
- Solar cells (Grätzel-cell)
2.6 Catalytic Properties

Materials for Heterogeneous Catalysis

Effect
1. Decrease of activation energy
2. Localisation of reagents (educts) by absorption on surface

Prerequisites
- High selectivity, e.g. zeolites
- High reactivity, e.g. transition metals → Pt-group metals
- High specific surface area
  - Single-phase catalysts
    - Nano particles
    - Zeolites and clay minerals
  - Multi-phase catalysts
    - Pt on γ-Al₂O₃ or MgO: electron donators
    - Pt on silica gel SiO₂ or ZrO₂: electron acceptors
- Sufficient stability and lifetime (catalytic cycles) ⇒ protection from catalyst poison, e.g. sulphur
2.6 Catalytic Properties

Synthesis of Organic and Inorganic Compounds

1. (Stereo selective) hydrations
   \[ \text{CH}_3\text{-C≡C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 + \text{H}_2 \rightarrow \text{cis-2-Hexen} + \text{trans-2-Hexen} \]
   (2-Hexin)

2. Oxidation reactions
   \[ 2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2 \]
2.6 Catalytic Properties

Synthesis of Organic and Inorganic Compounds

3. Methanol-synthesis
   \[ CO_2 + 3 \, \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]
   \[ \Rightarrow \text{reduction of C} \Rightarrow \text{electropositive catalysts} \Rightarrow \text{NiO, CuO, ZnO} \]

4. Liquefaction of coal: Fischer-Tropsch-Synthesis (1923)
   \[ \text{C} + 3 \, \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \text{ (synthetic gas)} \]
   \[ n \, \text{CO} + (2n+1) \, \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n \, \text{H}_2\text{O} \]
   \[ \Rightarrow \text{reduction of C} \Rightarrow \text{highly electropositive catalysts} \Rightarrow \text{Fe, Co} \]
   \[ \Rightarrow \text{sulphur- and nitrogen-free carbohydrates} \]

5. NH₃-Synthesis: Haber-Bosch-process (1913)
   \[ \text{N}_2 + 3 \, \text{H}_2 \Leftrightarrow 2 \, \text{NH}_3 \]
   \[ \Rightarrow \text{reduction of N}_2 \Rightarrow \text{highly electropositive} \]
   \[ \text{Catalysts} \Rightarrow \text{Fe with K}_2\text{O (electronegative promoter)} \]
   \[ \text{Formation of iron nitride Fe≡N at surface} \]
2.6 Catalytic Properties

Synthesis of Organic and Inorganic Compounds

6. Chlorination of alkenes
   \[ \text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl} \]
   Activation of Cl₂ molecule by polarisation ⇒ electron-rich catalysts ⇒ MgO-catalysts

   \[
   \text{MgO} \quad \overset{+ \text{Cl}_2}{\rightarrow} \quad \text{Cl} \quad \text{Cl} \quad \overset{+ \text{R}-\text{H}}{\rightarrow} \quad \text{R} \quad \text{Cl} \quad \overset{- \text{R}-\text{Cl}}{\rightarrow} \quad \text{MgO}
   \]

   \[ \text{MgO} + \text{HCl} \rightarrow \text{Mg(OH)}\text{Cl} \]

7. De-chlorination of organic compounds
   Activation of R-Cl bond ⇒ MgO-catalyst
   \[ \text{R-CH}_2\text{-CH}_2\text{Cl} \rightarrow \text{R-CH}═\text{CH}_2 + \text{HCl} \]
   \[ \text{MgO} + 2 \text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} \]
2.6 Catalytic Properties

Exhaust Treatment

Autocatalyst Pd/Pt-pigment
On ceramic substrate
2 CO + O₂ → 2 CO₂
CₓHᵧ + (x + y/4) O₂ → x CO₂ + y/2 H₂O
2 NO + 2 CO → N₂ + 2 CO₂
CₓHᵧ + (2x + y/2) NO →
x CO₂ + (x + y/4) N₂ + y/2 H₂O

Oxygen regulation through Ce⁴⁺O₂
2 Ce⁴⁺O₂ ⇌ Ce³⁺₂O₃ + ½ O₂

Selective Catalytic Reduction (SCR)-catalysts (FeVO₄ on ceramic substrate)
6 NO + 4 NH₃ → 5 N₂ + 6 H₂O and 6 NO₂ + 8 NH₃ → 7 N₂ + 12 H₂O

Reduction of soot in diesel exhaust (regenerative additives)
1. Particle filter
2. Optimal engine management ⇒ application of regenerative additives, such as CeO₂ (or Fe₂O₃): C + 2 CeO₂ → CO + Ce₃O₃
2.6 Catalytic Properties

Water Treatment

Germ-free water ⇒ Cl₂, Cl₂O, O₃, UV-A + cat., UV-C (240 - 280 nm)
- Waste water
- Process water
- Drinking water

Ultra-pure water ⇒ VUV (180 - 190 nm) ~ “band edge“ of H₂O
- Semi-conductor industry

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Drinking water</td>
<td>37</td>
<td>63.5</td>
<td>72</td>
</tr>
<tr>
<td>Waste water</td>
<td>90.5</td>
<td>122.5</td>
<td>35</td>
</tr>
<tr>
<td>Process water</td>
<td>5.5</td>
<td>9.5</td>
<td>72</td>
</tr>
<tr>
<td>Other applications</td>
<td>15</td>
<td>23.5</td>
<td>57</td>
</tr>
<tr>
<td>Total market</td>
<td>148</td>
<td>219</td>
<td>48</td>
</tr>
</tbody>
</table>
2.6 Catalytic Properties

Water Treatment with UV-A Radiation and Catalyst

⇒ Pigments with low band gap: TiO₂, ZnO, ZnS, In₂O₃, Ba₂In₂O₅, WO₃, MoO₃, Fe₂O₃, CaTiO₃, Nb₂O₅, SiC, SnO₂, Nb₂O₅, Ta₂O₅

<table>
<thead>
<tr>
<th>Modification</th>
<th>E₉ [eV]</th>
<th>E₉ [nm]</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>3.5</td>
<td>360</td>
<td>2.55</td>
</tr>
<tr>
<td>Rutile</td>
<td>3.2</td>
<td>390</td>
<td>2.79</td>
</tr>
</tbody>
</table>

1. UV-absorption (protective pigment)
⇒ Application of rutile or ZnO
sunscreen, polymers, fronts

2. Photochemistry
⇒ Application of anatase

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2^* (h_{\text{VB}}^+ + e_{\text{CB}}^-)
\]
\[
h_{\text{VB}}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^{-}
\]
\[
e_{\text{CB}}^- + \text{O}_2 \rightarrow \text{O}_2^- \text{ (superoxide anion)} \Rightarrow \text{oxidative decomposition of organic substances in water or air as well as on surfaces} \]
2.6 Catalytic Properties

Water Treatment with UV-A Radiation and Catalyst

\[ \text{TiO}_2 \text{Nano particles (anatase)} \]

\[ \text{hv} (<380 \text{ nm}) \]

1. Absorption

\[ \text{O}_2 + \text{H}^+ \rightarrow \text{HOO}^- \]

2. Diffusion

\[ \text{OH}^- \rightarrow \frac{1}{2} \text{H}_2\text{O}_2 \]

\[ \text{TiO}_2^* + \text{O}_2 \rightarrow \text{TiO}_2^+ + \text{O}_2^- \]

\[ \text{TiO}_2^* + \text{OH}^- \rightarrow \text{TiO}_2^- + \text{OH}^- \]

\[ \text{O}_2^- + \text{H}^+ \rightarrow \text{HOO}^- \]

\[ 2 \text{OH}^- \rightarrow \text{H}_2\text{O}_2 \]

\[ 3n \text{H}_2\text{O}_2 + \text{C}_n\text{H}_{2n+2} \rightarrow n \text{CO}_2 + (4n+1) \text{H}_2\text{O} \]

photoreactors, working with sunlight

⇒ recent research: doping for sensitisation of optical spectrum
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

TiO$_2$ is the catalyst for the charge separation!

Glass substrate with SnO$_2$:F (0.5 µm) and Pt-coating (2 µm)

TiO$_2$-nano particle membrane (5 - 10 µm)

Electrolyte solution with redox mediator

Incidence of light
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

1. Photosensibilisation by dyes

High efficiency requires strong absorption of light of a wavelength < 1100 nm (> 1.1 eV) $\Rightarrow$ excitation of allowed electronic transitions:

- **Organic compounds**
  - $\pi \rightarrow \pi^*$ -transitions
  - anthocyanins, carotenoids, chlorophylls
  - (extended $\pi$ -electron system)

- **Coordination compounds**
  - **Charge-transfer (CT)-transitions**
  - 
    - **Ligand-metal (LMCT)**
      - $\text{WO}_4^{2-}$ $\rightarrow$ $5d^0$ $\text{O}^2- \rightarrow W^{6+}$
    - **Metal-ligand (MLCT)**
      - $\text{L}_6\text{Ru}^{2+}$ $\rightarrow$ $4d^6$ $\text{Ru}^{2+} \rightarrow \text{L}$

Diagram:

$\text{L}$ $\text{Ru}$ $\text{N}$ $\text{H}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$ $\text{L}$

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### 2.6 Catalytic Properties

**Solar Cells (Grätzel-Cell)**

1. Photosensibilisation by dyes

<table>
<thead>
<tr>
<th>Complex</th>
<th>MLCT [nm]</th>
<th>$E^0_{Ru^{2+}/Ru^{3+}}$ [V vs NHE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{RuL}_2\text{Cl}_2]$</td>
<td>534</td>
<td>+0.80</td>
</tr>
<tr>
<td>$[\text{RuL}_2(\text{NCS})_2]$</td>
<td>534*</td>
<td>+1.09</td>
</tr>
<tr>
<td>$[\text{RuL}_2(\text{CN})_2]$</td>
<td>493</td>
<td>+1.40</td>
</tr>
</tbody>
</table>

*the absorption edge is located at 800 nm (1.6 eV)*

vs NHE = against normal hydrogen electrode:

$$2 \text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g)$$

$L = 2,2'\text{-bipyridine}-4,4'\text{-dicarboxonic acid}$
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

1. Photosensibilisation by dyes

Advantages of Ru^{2+}-chelating complexes
- Reversible Ru^{2+}/Ru^{3+} redox pair
- Electronic low-spin configuration (anti-bonding orbitals are unoccupied)
- Chelating effect (entropic effect) ⇒ kinetically very stable (slow ligand exchange reaction)
- Allowed MLCT transitions at relative low energies ⇒ intense absorption bands in the visible range of the spectrum
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

2. Charge injection into TiO$_2$

Photoreduction of TiO$_2$

$[\text{Ru}^{2+}L_2(\text{NCS})_2] \xrightarrow{\text{hv}} [\text{Ru}^{2+}L_2(\text{NCS})_2]^*$

$[\text{Ru}^{2+}L_2(\text{NCS})_2]^* + \text{Ti}^{4+}\text{O}_2 \xrightarrow{\text{hv}} [\text{Ru}^{3+}L_2(\text{NCS})_2]^+ + \text{Ti}^{3+}\text{O}_2^-$
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

2. Charge injection into TiO$_2$

Efficiency of charge injection

\[ \phi_{\text{inj}} = \frac{k_{\text{inj}}}{(\tau^{-1} + k_{\text{inj}})} \]

with

\[ k_{\text{inj}} = \text{rate of charge injection} \]
\[ > 1.4 \times 10^{11} \text{ s}^{-1} \]
\[ \tau = \text{lifetime of MLCT-state} \]
\[ = 50 \text{ ns (fluorescence)} \]

\[ \Rightarrow \phi_{\text{inj}} > 99.9\% \]

\[ \frac{k_{\text{inj}}}{k_{\text{back}}} > 10^3 \]
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

3. Charge separation

A mobile redox system dissolved in an electrolyte is responsible for the charge separation.

**Counter electrode**

\[ I_3^- + 2e^- \rightleftharpoons 3I^- \]  
(0.3 M LiI and 0.03 M I₂ in CH₃CN)

\( E^0 = +0.536 \) V vs NHE

**Reaction at negative electrode**

\[ [\text{Ru}^3+\text{L}_2(\text{NCS})_2]^+ + \text{I}^- \rightarrow 2[\text{Ru}^2+\text{L}_2(\text{NCS})_2] + \text{I} \]

2 \( \text{I} \rightarrow \text{I}_2 \)

\( \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \)

**Reaction at positive electrode**

\( \text{I}_3^- + 2e^- \rightarrow 3\text{I}^- \)
2.6 Catalytic Properties

Solar Cells (Grätzel-Cell)

3. Charge separation - global electron flow

\[ (S^+/S)^* \]

\[ \text{CB} \]

\[ \text{TiO}_2 \]

\[ \text{VB} \]

\[ \text{Load} \]

\[ \text{Electrolyte} \]

\[ \text{hv} \]

\[ U \sim 0.7 \text{ V} \]

\[ e^- \]

\[ I_3^- + 2 e^- \rightleftharpoons 3 I^- \]

\[ E^0 [\text{V vs NHE}] \]

-0.5

0.0

+0.5

+1.0

+1.5

+3.0

+3.5
3.1 Ceramic Materials

Definition and Classification

Ceramics are solids, neither metallic nor inter-metallic nor organic, made of a single structure of one or more phases (crystalline, glassy).

Glass ceramics
Fine-grained microstructure made of a ceramic and a glass phase

Clay ceramics (silicate ceramics)
Most important component: layered silicates ⇒ Kaolinite $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$, Montmorillonite

1. Pottery (porous)
   a. Earthenware: pottery
   b. Stoneware: crockery, sanitary ware

2. Pottery (dense)
   a. Stoneware: tiles, sanitary ware
   b. Porcelain: crockery ⇒ hard porcelain:
3.1 Ceramic Materials

Definition and Classification

High-performance ceramics (high-temperature and functional ceramics)
Chemically produced, highly pure oxides, borides, carbides, nitrides, and silicides of a certain composition and particle size (5 nm – 50 µm), which are processed by pressing and sintering to give compact bodies

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Borides</th>
<th>Carbides</th>
<th>Nitrides</th>
<th>Silicides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>TiB$_2$</td>
<td>SiC</td>
<td>Si$_3$N$_4$</td>
<td>MoSi$_2$</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>ZrB$_2$</td>
<td>B$_4$C</td>
<td>BN</td>
<td>WSi$_2$</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>LaB$_6$</td>
<td>WC</td>
<td>AlN</td>
<td></td>
</tr>
<tr>
<td>MO·Fe$_2$O$_3$ (ferrite)</td>
<td>TiC</td>
<td>TiN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MTiO$_3$ (titanate)</td>
<td>HfC</td>
<td>ZrN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>3$O$</em>{7-x}$ (cuprate)</td>
<td>TaC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M$_2$O·nX$_2$O$_3$ (β-aluminate)</td>
<td>NbC</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.1 Ceramic Materials

Structure

In general, ceramics consist of, more or less, randomly oriented crystalline grains (crystallites), amorphous areas and defects.

Coherent defects possess the same structure as the host but leads to elastic distortion thereof.

Incoherent defects possess a different structure than the host but does not lead to distortions.


### 3.1 Ceramic Materials

#### Properties

Because of their ionic or covalent bonds, ceramic compounds often exhibit the following properties:

- Small thermal and electrical conductivity
- Great hardness and brittleness
- High melting point (> 1500 °C)
- High chemical and thermal stability
- Low density

Ceramics where the focus is laid on function and not on mechanical properties may show different behaviour, such as:

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [g/cm³]</th>
<th>Tensile strength [N/mm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>4.0</td>
<td>210</td>
</tr>
<tr>
<td>SiC</td>
<td>3.1</td>
<td>175</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>3.2</td>
<td>560</td>
</tr>
<tr>
<td>SiAlON</td>
<td>3.2</td>
<td>420</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>5.8</td>
<td>455</td>
</tr>
</tbody>
</table>

SiAlON = Si₃₋ₓAlₓN₄₋ₓOₓ

FeO, ZnO: Semiconductor
YBa₂Cu₃O₇₋ₓ: Superconductor
β-NaAl₁₁O₁₇: Ionic conductor
CrO₂, Y₃Fe₅O₁₂: Magnetics
(Pb,La)(Zr,Ti)O₃: Pressure sensors
MoSi₂: Heating elements
3.1 Ceramic Materials

Applications

Hardness: $\text{Al}_2\text{O}_3$, $\text{Si}_3\text{N}_4$, $\text{SiAlON}$

⇒ Tools for milling and cutting

High melting point: $\text{Al}_2\text{O}_3$, $\text{Si}_3\text{N}_4$, $\text{SiC}$

⇒ Crucible, furnaces, engines, turbines

Chemical stability: $\text{Al}_2\text{O}_3$, $\text{Y}_3\text{Al}_5\text{O}_{12}$

⇒ Ceramic lamps (CDM), Laser

Biological compatibility: $\text{TiO}_2$, $\text{ZrO}_2$

⇒ Dental and bone implants

Optical transparency: $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{Gd}_2\text{SiO}_5$, $\text{Lu}_2\text{SiO}_5$

⇒ LEDs, scintillators
3.1 Ceramic Materials

Oxidic Ceramics: $\text{Al}_2\text{O}_3$ Corundum-Structure-Type (Oxygen hcp)

Fire resistant materials, transparent ceramics $\Rightarrow$ polycrystalline aluminium oxide (PCA)

Translucency: no pores

Transparency: nano-crystallites

Glass or transparent ceramic

Intensity (log)

Intensity (log)

PCA grain size = 20 μm

Glass or transparent ceramic

1200 °C

5 mm
3.1 Ceramic Materials

Oxidic Ceramic: $\text{MO} \cdot n \text{X}_2 \text{O}_3 \beta$-Alumina-Structure-Type

$M = \text{alkali}^+, \text{Cu}^+, \text{Ag}^+, \text{Ga}^+, \text{In}^+, \text{Ti}^+, \text{NH}_4^+, \text{H}_3\text{O}^+; X = \text{Al}^{3+}, \text{Ga}^{3+}, \text{Fe}^{3+}; 5 < n < 11$

⇒ Layered structure comprising spinel blocks ($n \text{X}_2 \text{O}_3$) and intermediate layers (MO)

β-alumina phase is formed only with big cations

High ionic conductivity of the intermediate layers

⇒ Solid electrolytes in fuel cells
3.1 Ceramic Materials

Oxidic Ceramics: ZrO₂ Cubic Fluorite-Structure-Type (Oxygen ccp)

\[
\begin{align*}
1100^\circ & \text{C} & \quad & 2350^\circ & \text{C} & \quad & 2680^\circ & \text{C} \\
\text{ZrO}_2 \text{ (monoclinic)} & \rightleftharpoons & \text{ZrO}_2 \text{ (tetragonal)} & \rightleftharpoons & \text{ZrO}_2 \text{ (cubic)} & \rightleftharpoons & \text{melt}
\end{align*}
\]

To prevent phase transitions during cooling at 1100°C, cubic ZrO₂ is stabilised by the addition of CaO, MgO or Y₂O₃, e.g.

\[
\text{CaO} + \text{Zr}_\text{Zr} + \text{O}_\text{O} \rightleftharpoons \text{Ca}^{\prime\prime}_\text{Zr} + \text{V}^{\text{V}}_\text{O} + \text{ZrO}_2
\]

Due to the created anion vacancies, doped ZrO₂ is a solid electrolyte (anion conductor)

⇒ Solid electrolyte in fuel cells
⇒ Galvanic chain in O₂-sensors (Lambda-probe)
3.1 Ceramic Materials

Oxidic Ceramic: Gd$_2$O$_2$S:Pr, Ce, F (GOS)

Scintillator in computed tomographs (CTs) $\Rightarrow$ transparent ceramics

Production of ceramics is almost always more cost efficient than growing single crystals
3.1 Ceramic Materials

Oxidic Ceramics: $Y_3Al_5O_{12}$:Ce and $Y_3Al_5O_{12}$:Pr (Garnets)

- e.g. as scintillators in positron emission tomographs (PETs) ⇒ transparent ceramics

Scintillator
511 keV photon → visible photons → signal

Materials with cubic crystal structure
⇒ $Y_2O_3$, $Y_3Al_5O_{12}$, ...

Preparation of ceramic precursors (nano particles)
Addition of binder/flux + formation of green bodies
Thermal treatment: combustion of binder + sintering (vacuum)

511 keV photon
Visible photons
Signal

Normalised emission intensity
Wavelength [nm]

Cutting
Polishing
3.1 Ceramic Materials

Oxidic Ceramics: Garnets and Sesquioxides

e.g. as optical components solid state Lasers (SSL) \(\Rightarrow\) transparent ceramics

\[
\begin{align*}
\text{Y}_3\text{Al}_5\text{O}_{12} & \quad \text{Optic to form beam} \\
(Y,\text{Lu})_3\text{Al}_5\text{O}_{12}:\text{Nd} & \quad \text{Laser with high pulse repetition rate} \\
(Y,\text{Lu,Gd})_3\text{Al}_5\text{O}_{12}:\text{Yb} & \quad \text{Disk Laser + other SSL} \\
\text{Sc}_2\text{O}_3:\text{Yb} & \quad \text{Disk Laser + other SSL} \\
(Y,\text{Lu})_2\text{O}_3:\text{Yb} & \quad \text{Disk Laser + other SSL} \\
\text{Gd}_2\text{O}_3:\text{Yb} & \quad \text{Disk Laser + other SSL}
\end{align*}
\]

Processes that reduce transmission (aim: \(T > 99\%\))

a) Refraction at grain boundaries
b) Refraction at pores or impurities
c) Refraction at secondary phases (glassy phase)
d) Reflection or birefringence at boundary layers
e) Refraction at surface roughness
3.1 Ceramic Materials

Translucent Ceramic Lu$_3$Al$_5$O$_{12}$ (LuAG)

LuAG:Pr Scintillator
LuAG:Nd NIR Laser

Crystal system: cubic (garnet)

Melting point $T_m$: 1987 °C

Density: 6.72 g/cm$^3$

Optical band gap $E_g = 7.3$ eV

Max. phonon frequency: ~ 600 cm$^{-1}$

Refractive index: $n = 1.825$ @ 1014 nm

$T = 1 - R_{\text{total}}$ ($R_{\text{total}} = 2 \cdot R_{\text{reg}}$), if $A = 0$

→ max. pure transmission = 82.9% @ 1014 nm

$$R_{\text{reg}} = \frac{(n_1 - n_0)^2}{(n_1 + n_0)^2}$$
3.1 Ceramic Materials

Translucent Ceramic $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG)

Transmission

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>81.1%</td>
<td>0.24 mm</td>
<td>TD-K44</td>
<td></td>
</tr>
<tr>
<td>94.9%</td>
<td>0.14 mm</td>
<td>NW-K88</td>
<td></td>
</tr>
<tr>
<td>97.6%</td>
<td>0.24 mm</td>
<td>NW-K88</td>
<td></td>
</tr>
<tr>
<td>95.3%</td>
<td>1.2 mm</td>
<td>NW-K90</td>
<td></td>
</tr>
<tr>
<td>94.8%</td>
<td>0.43 mm</td>
<td>NW-K91</td>
<td></td>
</tr>
<tr>
<td>95.6%</td>
<td>0.53 mm</td>
<td>NW-K95</td>
<td></td>
</tr>
<tr>
<td>92.2%</td>
<td>0.40 mm</td>
<td>NW-K100</td>
<td></td>
</tr>
<tr>
<td>95.7%</td>
<td>0.25 mm</td>
<td>NW-K148</td>
<td></td>
</tr>
<tr>
<td>95.5%</td>
<td>0.34 mm</td>
<td>NW-K158</td>
<td></td>
</tr>
</tbody>
</table>

Pores

- $0.15 \text{ mm}$
- $0.30 \text{ mm}$
3.2 Glasses and Glass Ceramics

Glasses Are Amorphous Solids, Solidifying from Melts during Cooling or Formed by Quenching without Visible Crystallisation

Properties

- Wide optical window
- Small electrical and thermal conductivity
- Good corrosion resistance
- Highly brittle

Classification according to linear thermal Expansion coefficient $\alpha$

- Soft glasses $\alpha > 6 \times 10^{-6} \text{ K}^{-1}$
- Hard glasses $\alpha < 6 \times 10^{-6} \text{ K}^{-1}$
3.2 Glasses and Glass Ceramics

Analogous to Liquids, Glasses Possess Near-range Order (< 0.5 nm) but no Long-range Order, thereby Behaving like Thermoplastics

Building blocks of glasses (network creators) are similar to those of crystals but the arrangement in glasses is more irregular than in crystals

Si-O-distance in SiO$_4$-tetrahedron: 1.61 Å in $\alpha$-quartz, 1.62 Å in amorphous SiO$_2$

Crystalline solids

Amorphous solids
3.2 Glasses and Glass Ceramics

Glasses Can Easily Be Discriminated from Crystalline Solids by X-Ray Diffraction

In terms of order, glasses resemble liquids, with the lacking long-range order being the reason for optical transparency and low quantum efficiencies of dissolved activator ions.

Doped glasses are useful as colour filters, e.g. in LCDs but not as efficient phosphors.
### 3.2 Glasses and Glass Ceramics

**Building Blocks (Network or Glass Creators)**

<table>
<thead>
<tr>
<th>Type</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>C (glassy), S, Se, P ⇒ allotropy</td>
</tr>
<tr>
<td>Oxides</td>
<td>B$_2$O$_3$, SiO$_2$, P$_2$O$_5$, V$_2$O$_5$, GeO$_2$, As$_2$O$_3$, Sb$_2$O$_3$</td>
</tr>
<tr>
<td>(acidic)</td>
<td></td>
</tr>
<tr>
<td>Sulphides</td>
<td>As$_2$S$_3$, Sb$_2$S$_3$, various compounds with Tl, Sn, Pb, As, Sb, Bi, Si, P</td>
</tr>
<tr>
<td>Selenides/Tellurides</td>
<td>various compounds with Tl, Sn, Pb, As, Sb, Bi</td>
</tr>
<tr>
<td>Halides</td>
<td>BeF$_2$, AlF$_3$, ZnCl$_2$, ZrF$_4$-BaF$_2$-AlF$_3$, ScF$_3$-BaF$_2$-YF$_3$</td>
</tr>
<tr>
<td>Polymers</td>
<td>Polycarbonate (PC), Polyethylene PE), Polymethylmethacrylate (PMMA), Polystyrene (PS)</td>
</tr>
</tbody>
</table>
3.2 Glasses and Glass Ceramics

Glasses Based on Silicates Are Most Common

Quartz or silica glass (pure SiO$_2$) possess high melting points ($T_m = 1723$ °C), high thermal stability ($T_g = 1500$ °C), and very small linear thermal expansion coefficients ($\alpha = 5.4 \cdot 10^{-7}$ K$^{-1}$).

Quartz glass shows excellent stability upon temperature changes!
3.2 Glasses and Glass Ceramics

Normally, Glasses Are Synthesised by Mixing Network Creators like SiO\(_2\) with Other (Alkaline) Oxides as Interstitial Ions and Network Modifiers

- Decrease in glass transition temperature
- Modification of mechanical properties
- Modification of physical properties

**Interstitial ions**
- MgO, PbO, Al\(_2\)O\(_3\), Y\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\), SnO\(_2\), ZnO, BeO

**Network Modifiers**
**Inorganic glasses**
- Na\(_2\)O, K\(_2\)O, CaO, SrO, BaO

**Polymeric glasses**
- Softener, e.g. phthalate acid ester
# 3.2 Glasses and Glass Ceramics

## Composition of Technical (Silicate) Glasses (All Numbers Given in wt-%)

<table>
<thead>
<tr>
<th>Type of Glass</th>
<th>SiO₂</th>
<th>B₂O₃</th>
<th>Al₂O₃</th>
<th>PbO</th>
<th>CaO</th>
<th>MgO</th>
<th>BaO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Container</td>
<td>72</td>
<td>2</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Flat</td>
<td>72</td>
<td>1.5</td>
<td>8.5</td>
<td></td>
<td>3.5</td>
<td></td>
<td></td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>Laboratory</td>
<td>80</td>
<td>10</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Cathode-ray tubes</td>
<td>60</td>
<td>4</td>
<td>11</td>
<td>1.7</td>
<td>1.2</td>
<td>1.3</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Lead crystal</td>
<td>60.5</td>
<td>8</td>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>Crystal</td>
<td>76.5</td>
<td>0.3</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>6</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Optical</td>
<td>28</td>
<td></td>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Crone</td>
<td>72</td>
<td>8.2</td>
<td>1.6</td>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
<td>7.2</td>
<td>10.5</td>
</tr>
<tr>
<td>Quartz</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 3.2 Glasses and Glass Ceramics

#### Composition and Applications of Special Glasses

<table>
<thead>
<tr>
<th>Type of Glass</th>
<th>Composition</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz glass (silica glass)</td>
<td>SiO₂</td>
<td>Optical fibres</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UV-transparent optics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Crucibles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Semi-conductor technology</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UV-lamps</td>
</tr>
<tr>
<td>Fluoride glasses</td>
<td>ZrF₄-BaF₂-AlF₃, ZrF₄-BaF₂-LaF₃</td>
<td>Optical fibre for infrared light</td>
</tr>
<tr>
<td>Chalkogenide glasses</td>
<td>AsTe₃, As₂S₃, GeSe₂, GeS₂</td>
<td>IR-transparent optics</td>
</tr>
<tr>
<td>Glass fibre</td>
<td>SiO₂, Al₂O₃, CaO, MgO, Na₂O, K₂O</td>
<td>Admixture of metals, ceramics and glasses</td>
</tr>
<tr>
<td>Glass solder</td>
<td>Lead-borate-glass</td>
<td>Reinforcement of polymers</td>
</tr>
<tr>
<td>Glass finish</td>
<td>Glass coating</td>
<td>Thermal insulation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UV-protection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mirror</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Filter</td>
</tr>
</tbody>
</table>

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**Functional Materials**  
Prof. Dr. T. Jüstel  
Material Science  
Slide 194
3.2 Glasses and Glass Ceramics

Modification of physical properties

- Enhancement of thermal changing behaviour \( \Rightarrow \) \( \text{B}_2\text{O}_3 \)-addition

- Increased UV-transparency \( \Rightarrow \) \( \Rightarrow \) higher silicate content

- Increased refractive index \( \Rightarrow \) \( \text{PbO}/\text{GeO}_2 \)-addition

- Increased absorption of X-rays \( \Rightarrow \) \( \text{BaO}/\text{SrO}/\text{PbO} \)-addition

- Colourisation \( \Rightarrow \) coloured ions or metal clusters (e.g. Au)

- Dull finish \( \Rightarrow \) \( \text{ZrSiO}_4/\text{Ca}_3(\text{PO}_4)_2 \)-addition

- Anti-reflection coating \( \Rightarrow \) coating with \( \text{SiO}_2 \)-nano particles

Transparency of sodium silicate glasses
3.2 Glasses and Glass Ceramics

Bleaching of Glasses

Flat glass and other technical glasses (glass for lamps etc.) often contain small amounts of Fe$^{2+}$ which gives the glasses a bluish-greenish colour.

Addition of oxidising agents, such as MnO$_2$

$$\Rightarrow 2 \text{Fe}^{2+} + \text{Mn}^{4+} \rightarrow 2 \text{Fe}^{3+} + \text{Mn}^{2+}$$

Problem: solarisation of these glasses by UV-light (sun light or plasma radiation)

$$\Rightarrow \text{Mn}^{2+} \xrightarrow{hv} \text{Mn}^{3+} \text{(violet)} + e^- \text{(colour centre)}$$

Alternative oxidising agent is As$_2$O$_5$ which decomposes upon heating

$$\Rightarrow \text{As}_2\text{O}_5 \xrightarrow{\Delta T} \text{As}_2\text{O}_3 + \text{O}_2$$
$$\Rightarrow 4 \text{FeO} + \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3$$
3.2 Glasses and Glass Ceramics

Colourisation of Glasses

1. Addition of transition metal ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Coordination number</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>6</td>
<td>violet</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>6</td>
<td>transparent</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>6</td>
<td>green</td>
</tr>
<tr>
<td>V$^{5+}$</td>
<td>4</td>
<td>transparent</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>6</td>
<td>green</td>
</tr>
<tr>
<td>Cr$^{6+}$</td>
<td>4</td>
<td>yellow</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>6</td>
<td>transparent</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>6</td>
<td>violet</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>4</td>
<td>bluish-green</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>4, 6</td>
<td>light yellow</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>4, 6</td>
<td>blue, violet</td>
</tr>
<tr>
<td>Co$^{3+}$</td>
<td>4</td>
<td>green</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>4, 6</td>
<td>blue, yellow</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>6</td>
<td>blue</td>
</tr>
</tbody>
</table>

Absorption spectrum of $[\text{Ti(H}_2\text{O)}_6]^{3+}$
3.2 Glasses and Glass Ceramics

Colourisation of Glasses

2. Addition of lanthanide or actinide ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Coordination number</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(^{3+})</td>
<td>6</td>
<td>transparent</td>
</tr>
<tr>
<td>Ce(^{4+})</td>
<td>6</td>
<td>transparent to yellow</td>
</tr>
<tr>
<td>Pr(^{3+})</td>
<td>6</td>
<td>green</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>6</td>
<td>violet</td>
</tr>
<tr>
<td>UO(_2^{2+})</td>
<td>6</td>
<td>yellow-green (fluorescent)</td>
</tr>
</tbody>
</table>

- Ce\(^{3+}\) is used as UV-A filter in halide- and Hg-high-pressure lamp glass
- Nd\(^{3+}\) is used in glasses for spectacles and displays to increase contrast

3. Formation of metal colloids (10 – 50 nm)
   raw materials: CuCl\(_2\), AgNO\(_3\), AuCl\(_3\)
   + reducing agent: SnCl\(_2\), As\(_2\)O\(_3\)
3.2 Glasses and Glass Ceramics

Organic Glasses – Properties, Applications and Structure

Polymethacrylatemethylester. (PMMA) Polycarbonate (PC)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Polymethacrylatemethylester (PMMA)</th>
<th>Polycarbonate (PC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>high (UV-)transparency</td>
<td>high (UV-)transparency (E_g ~4.4 eV)</td>
<td>high transparency</td>
</tr>
<tr>
<td>high resistance to light</td>
<td>high resistance to light</td>
<td>high tensile strength and viscosity</td>
</tr>
<tr>
<td>Solubility in non-polar solvents</td>
<td>Solubility in non-polar solvents</td>
<td>high impact and ultimate strength</td>
</tr>
</tbody>
</table>

Applications

-plexiglas panels
-spectacle glasses, (contact)lenses
-storage medium (CDs and DVDs)
-visor

Chemical structures of PMMA and PC
3.2 Glasses and Glass Ceramics

**Organic Glasses - Dopants**

With organic luminophores
- Perylene derivatives (Lumogen™)
- Coumarin derivatives (Laser-dyes)
- Rhodamines, e.g. rhodamine B or 6G
- Fluorescein

**Application**
- Design elements
- Traffic signs
- (Light sources)

*Source: BASF AG*
3.2 Glasses and Glass Ceramics

Glass Technology

Glasses are processed at temperatures, where their viscosity allows deformation without breaking.

The viscosity of a glass-forming melt can be described by the Vogel-Fulcher-Tammann-equation:

\[ \eta = C \cdot \exp \left( \frac{E_\eta}{k_B(T - T_0)} \right) \]

With
- \( C \) = pre exponential factor [Nm\(^{-2}\)s]
- \( k_B \) = Boltzmann constant [J/K]
- \( E_\eta \) = Activation energy [J]
- \( T \) = Temperature [K]

- Glass at room temperature
- Transformation area
- Processing area: glass blowing
- Processing area: pressing, blowing, pulling, floating
- Melting and refinement area
3.2 Glasses and Glass Ceramics

Glass Technology – Melting Area $\eta = 5 - 50 \text{ Nm}^{-2}\text{s}$

- Disks and sheet glass is produced from a melt. Processes are waltzing between water-cooled rolls and floating on tin

- Glass fibres are pulled from a melt using Pt-nozzles

- For the production of optical lenses glass melts are poured into moulds that are cooled slowly to prevent cracks and tensions

Heating by gas burner

Reducing atmosphere

Melting & refinement

Homogenisation

Liquid tin

Addition of raw materials

Heating by gas burner

Reducing atmosphere

Melting & refinement

Homogenisation

Liquid tin

Addition of raw materials
**3.2 Glasses and Glass Ceramics**

*Glass Technology – Melting Area $\eta = 10^3 - 10^6$ Nm$^{-2}$s*

Glass vessels or glass bulbs for incandescent and halogen lamps are produced by pressing, pulling or blowing.

The glass is in a temperature range where it can be formed but does not “run away”.

**Glass transformation processes**

a) Pressing-process

b) Pressing-blowing-process

*D.R. Askeland, Materialwissenschaften, Spektrum Verlag GmbH Heidelberg, Berlin, Oxford, 1996*
3.2 Glasses and Glass Ceramics

Glass Technology – Relaxation Areas $\eta = 10^6 - 10^{12}$ Nm$^{-2}$s

Some glasses must be relaxed (annealed) to get rid of tensions which occurred during deformation.

Some glasses are thermally treated to precipitate crystalline areas within the glass
$\Rightarrow$ glass ceramics

**Pre-stressed glass** can be produced by quenching of sheet glass in air. Thereby, the surface layer is cooling off rapidly and contracts. The inner layers are cooling down more. The as produced glass exhibits higher thermal resistance against tensile stress and impacts.
3.2 Glasses and Glass Ceramics

Glass Ceramic – Definition and Properties

Glass amorphous solid
Ceramic polycrystalline solid
Glass ceramic crystallites in glass matrix mostly Li$_2$O-SiO$_2$-Al$_2$O$_3$ based

⇒ Complex production process
⇒ Ultrapure raw materials needed
⇒ Colourisation is complex

Properties

• Small or even negative thermal expansion
• High resistance against temperature changes
• Some types can be processed by machines
Seed formation can be achieved by the addition of seed formation centres, such as TiO\textsubscript{2}, or thermal treatment.
3.2 Glasses and Glass Ceramics

Glass Ceramic - Structure
3.2 Glasses and Glass Ceramics

Glass Ceramic - Applications

- Scaffolds for huge reflecting telescopes VLT, ELT)
- Stove tops (Ceran™)
- Heat shield for aerospace technology
- Temperature-resistant front panels for fireplaces
- LED Converter
  
  Ce$^{3+}$-doped Garnets \((Y,Gd,Tb)_3Al_5O_{12}::{Ce}\)
  
  Eu$^{2+}$ doped Silicates \((Ca,Sr,Ba)_2SiO_4::{Eu}, (Ca,Sr,Ba)_3SiO_5::{Eu}\)
  
  Eu$^{2+}$ doped Nitrides \(Ba_2Si_5N_8::{Eu}, CaAlSiN_3::{Eu}\)
  
  Eu$^{3+}$ doped Metallates \(Ln_x(Mo,W)_yO_z\)
- Resonators for solid state lasers
  
  Sesquioxides \(Y_2O_3::{Yb}\)
  
  Garnets \(Y_3Al_5O_{12}::{Nd}, Y_3Al_5O_{12}::{Yb}\)