Fundamentals of Material Science

Content

1. Classification and Relevance
   - Classes of Materials
   - Interdisciplinary Connections to Other Science Branches

2. Structure of Solid State Materials
   - Principle Concepts and Classifications
   - Types of Bonding and Influences upon Structure
   - Ideal Crystals
   - Real Crystals
   - Phases and Phase Transitions
   - Phase Diagrams

Materials are like people – the imperfections make them interesting!

God created the solids, but evil the surfaces.
(Wolfgang Pauli)
Literature

**Solid State Chemistry**
- A.R. West, Grundlagen der Festkörperchemie, VCH Verlagsgesellschaft 1992
- L. Smart, E. Moore, Einführung in die Festkörperchemie, Vieweg 1995

**Structural Chemistry**
- U. Müller, Anorganische Strukturchemie, Teubner 1991
- R.C. Evans, Einführung in die Kristallchemie, deGruyter 1976

**Material Science**
- D.R. Askeland, Materialwissenschaften: Grundlagen, Übungen, Lösungen, Spektrum Akademischer Verlag 1996

**Materials**
- H. Briehl, Chemie der Werkstoffe, B.G. Teubner Verlagsgesellschaft 1995
Examples for Research on New Materials

(Ga,Al,In)N
- Blue and UV emitting diodes
- High-mobility-transistors
- Sensors

(Zn,Cd,Mg)O
- UV/blue emitting light sources
- Spintronic
- Polariton laser
- Nanoparticle as emulsion additive

Nitrides and oxynitrides, e.g.
TaO$_x$N$_y$ and (Ba,Sr,Ca)$_2$Si$_5$N$_8$:Eu
- Yellow and red pigments
- Phosphors for blue LEDs
1. Classification and Relevance

Examples for Research on New Materials

Starting point: Crystal structure and stability
- Inorganic Crystal Structure Database (ICSD): 187000 Entrees
- Minerals (Mineral Inspired Approach): About 4000 minerals
- Solid state chemistry: Search & description of new crystal structure

Protoypes
- About 9100 materials for engineering
- Further development by doping, solid solutions, process optimisation, Simulations and so on
- Alignment to novel application areas, e.g. TiO₂ (from colour pigments to catalysts and Graetzel cells)

Classification
- By the structure type: Garnet, Magnetoplumbite, Monazite, Olivine, Perovskite, Wurtzite
- By the chemical nature: Aluminatas, borates, carbonates, silicates, sulfates, sulphides
- By the function: Dielectrics, Electrics, Insulators, catalysts, magnetics, optics
# 1. Classification and Relevance

## Material Classes: “Electrics”

<table>
<thead>
<tr>
<th>Material class (property)</th>
<th>Compound</th>
<th>(Field of ) Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic conductors</td>
<td>Cu, Ag, Au</td>
<td>Electronics</td>
</tr>
<tr>
<td>Low-dimensional metallic conductors</td>
<td>K₂[Pt(CN)₄]₂, (SN)ₓ</td>
<td>Electronics</td>
</tr>
<tr>
<td></td>
<td>Hexagonal Cₓ (graphite)</td>
<td>Electrodes</td>
</tr>
<tr>
<td>Semi-conductors</td>
<td>Si, Ge, GaAs</td>
<td>Diodes, transistors, ICs</td>
</tr>
<tr>
<td></td>
<td>Si, CuInSe₂</td>
<td>Solar panels (photovoltaic)</td>
</tr>
<tr>
<td></td>
<td>GaAs, AlInGaP, AlInGaN, ZnTe</td>
<td>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-electric materials</td>
<td>Bi₂Te₃, PbTe</td>
<td>Thermo-electric cooler</td>
</tr>
<tr>
<td>Superconductors</td>
<td>Nb₃Sn</td>
<td>High-power magnets</td>
</tr>
<tr>
<td></td>
<td>YBaCu₃O₇</td>
<td>Electric transport without resistance</td>
</tr>
<tr>
<td>Ion conductors</td>
<td>NaAl₁₁O₁₇ (β-alumina), Li₃N</td>
<td>Long-life batteries, accumulator</td>
</tr>
<tr>
<td></td>
<td>ZrO₂:Y</td>
<td>O₂-sensors (Lambda-probe)</td>
</tr>
</tbody>
</table>
## 1. Classification and Relevance

### Materials Classes: “Dielectrics”, “Magnetics” and “Opticals”

<table>
<thead>
<tr>
<th>Material class (property)</th>
<th>Compound</th>
<th>(Field of) Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezo electric s</td>
<td>Pb(Ti&lt;sub&gt;1-x&lt;/sub&gt;Zr&lt;sub&gt;x&lt;/sub&gt;)O&lt;sub&gt;3&lt;/sub&gt; (PZT)</td>
<td>Electro acoustic: microphones, speaker</td>
</tr>
<tr>
<td>Pyro electric s</td>
<td>ZnO</td>
<td>IR-detectors</td>
</tr>
<tr>
<td>Ferro electric s</td>
<td>BaTiO&lt;sub&gt;3&lt;/sub&gt;, PbTiO&lt;sub&gt;3&lt;/sub&gt;, SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Compensators, sensors</td>
</tr>
<tr>
<td>Ferro and Ferri magnets</td>
<td>Nd&lt;sub&gt;2&lt;/sub&gt;Fe&lt;sub&gt;14&lt;/sub&gt;B, BaFe&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;19&lt;/sub&gt;, SmCo&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Permanent magnets</td>
</tr>
<tr>
<td></td>
<td>Fe, γ-Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, CrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Audio- and video tapes</td>
</tr>
<tr>
<td></td>
<td>MFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; (Ferrite), ZnFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Engines, transformers</td>
</tr>
<tr>
<td></td>
<td>Y&lt;sub&gt;3&lt;/sub&gt;Fe&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt; (YIG)</td>
<td>Information storage</td>
</tr>
<tr>
<td></td>
<td>FeBO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Magneto optics: modulation of light</td>
</tr>
<tr>
<td>Coloured pigments</td>
<td>CoAl&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, CdS, Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Colour filter, dispersion paint</td>
</tr>
<tr>
<td>Photoluminescence pigments – UV</td>
<td>BaMgAl&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;17&lt;/sub&gt;:Eu, Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;:Eu</td>
<td>Phosphorescence lamps</td>
</tr>
<tr>
<td></td>
<td>Y&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;:Ce, Sr&lt;sub&gt;2&lt;/sub&gt;Si&lt;sub&gt;5&lt;/sub&gt;N&lt;sub&gt;8&lt;/sub&gt;:Eu</td>
<td>White pcLEDs</td>
</tr>
<tr>
<td>Cathodoluminescence pigments</td>
<td>ZnS:Ag, ZnS:Cu, Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;S:Eu</td>
<td>Cathode ray tube</td>
</tr>
<tr>
<td>(Scintillators)</td>
<td>Bi&lt;sub&gt;4&lt;/sub&gt;Ge&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;, Lu&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;5&lt;/sub&gt;:Ce, Gd&lt;sub&gt;2&lt;/sub&gt;SiO&lt;sub&gt;5&lt;/sub&gt;:Ce, Gd&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;S:Pr, Ce,F</td>
<td>Positron emission tomography</td>
</tr>
<tr>
<td>Stimulated light emission</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;:Cr, Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;:Ti, Y&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;:Nd, Lu&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;:Nd, LiYF&lt;sub&gt;4&lt;/sub&gt;:Pr, YVO&lt;sub&gt;4&lt;/sub&gt;:Nd</td>
<td>Laser</td>
</tr>
</tbody>
</table>
1. Classification and Relevance

Interconnections to Other Sciences and Engineering

Mineralogy

Geology

Physics

Material Science

Biology

Chemistry

Pharmacy

Medicine

Electrical Engineering

Mechanical Engineering

Chemical Engineering
1. Classification and Relevance

Linkage to Chemistry

Atom / Ions
Electron configuration
Atomic and ionic radii
EN, EA, IE

⇒ Chemical bonding
Ionic charge density
Covalent part
Delocalisation of e⁻

Inorganic Chemistry
Solid State Chemistry

Atomic and electronic structure

Ideal crystals
Real crystals
Amorphous solids

Types of reactions
Diffusion
Ionic mobility + structure
Phase transitions

⇒ Preparation
Solid state reactions
Transport reactions
Crystal growth

Material Science

Properties
Isotropic - Anisotropic

Polarisation effects
Transport properties

Matter ⇄ Material
# 1. Classification and Relevance

## Comparison Between Molecular and Solid State Chemistry

<table>
<thead>
<tr>
<th></th>
<th>Molecular Chemistry</th>
<th>Solid State Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stoichiometry</strong></td>
<td>Daltonides: defined composition</td>
<td>Berthollides: non-stoichiometric, since defects, formation of solid solutions etc. are common</td>
</tr>
<tr>
<td><strong>Bonding</strong></td>
<td>Only covalent: directed, short range, localised electrons MO-description, structure prediction</td>
<td>Covalent, ionic, metallic: undirected, long range, band structure, complex structure prediction</td>
</tr>
<tr>
<td><strong>Isomerism</strong></td>
<td>Only topologically</td>
<td>Polymorphism, phase transitions</td>
</tr>
<tr>
<td><strong>Syntheses</strong></td>
<td>Endothermic chemistry: selective con- and destruction, kinetically controlled</td>
<td>Exothermic chemistry: diffusion, thermodynamically controlled</td>
</tr>
<tr>
<td><strong>Purification</strong></td>
<td>Volatility facilitates separation</td>
<td>Insoluble, no evaporation without decomposition</td>
</tr>
<tr>
<td><strong>Characterisation</strong></td>
<td>IR, MS, NMR</td>
<td>XRD, XRF</td>
</tr>
<tr>
<td><strong>Properties</strong></td>
<td>(No) cooperative interactions</td>
<td>Cooperative interactions</td>
</tr>
<tr>
<td></td>
<td>Structure-effect-correlations</td>
<td>Structure-properties-correlations</td>
</tr>
<tr>
<td></td>
<td>→ Biochemistry, medicine</td>
<td>→ Material science</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Classification – Crystalline vs. Amorphous Solids

**Crystalline Solids**
- Ideal crystals: Mathematical, spatial, periodical abstraction of real crystals
- Real crystals: Ideal crystal + defects + impurities (dopants)
- Single crystals: Crystal, that exhibits a homogenous and unified lattice

*In general: Elements (E) and compounds (AB, AB$_2$, etc...) in their solid state*

**Amorphous Solids**
- Only near-order, no long-range-order, i.e. no regular diffraction of X-rays

*Exp.: Glasses - inorganic (quartz glass)*
* - organic (perspex PMMA)*
# 2. Structure of Solid State Materials

**Classification – Crystal Lattice**

<table>
<thead>
<tr>
<th>Cation Types</th>
<th>Halides</th>
<th>Oxides</th>
<th>Nitrides</th>
<th>Sulphides</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary</strong></td>
<td>MX</td>
<td>M₂O</td>
<td>M₃N</td>
<td>M₂S</td>
</tr>
<tr>
<td></td>
<td>MX₂</td>
<td>MO₂</td>
<td>M₃N₂</td>
<td>MS</td>
</tr>
<tr>
<td></td>
<td>MX₃</td>
<td>MO₃</td>
<td>MN</td>
<td>M₂S₃</td>
</tr>
<tr>
<td></td>
<td>MX₄</td>
<td>MO₄</td>
<td>M₃N₄</td>
<td>MS₂</td>
</tr>
<tr>
<td><strong>Ternary</strong></td>
<td>M₁M₂X₃</td>
<td>M₁₂M₂O₂</td>
<td>M₁M₂N₂</td>
<td>M₁₂M₂S₂</td>
</tr>
<tr>
<td></td>
<td>M₁M₂X₄</td>
<td>M₁M₂O₃</td>
<td>M₁M₂N₅</td>
<td>M₁M₂S₃</td>
</tr>
<tr>
<td></td>
<td>M₁M₂X₅</td>
<td>M₁M₂O₄</td>
<td>M₁₂M₂₅N₈</td>
<td>M₁M₂S₄</td>
</tr>
<tr>
<td></td>
<td>M₁M₂X₆</td>
<td>M₁M₂O₇</td>
<td>M₁₃M₂₆N₁₁</td>
<td>M₁₂M₂₄S₆</td>
</tr>
<tr>
<td><strong>Quaternary</strong></td>
<td>M₁M₂M₃X₆</td>
<td>M₁M₂M₃₂O₆</td>
<td>M₁M₂M₃₃N₃</td>
<td>M₁₂M₂M₃S₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M₁M₂M₃₅O₁₀</td>
<td>M₁M₂M₃₄N₇</td>
<td>M₁₂M₂M₃S₅</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M₁M₂M₃₁₀O₁₇</td>
<td>M₁M₂M₃₆N₁₁</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>M₁M₂M₃₁₁O₁₉</td>
<td>M₁M₂M₃₁₁N₂₃</td>
<td></td>
</tr>
</tbody>
</table>

No solid solutions!
## 2. Structure of Solid State Materials

### Classification – Survey of the Different Types of Compounds

<table>
<thead>
<tr>
<th>Group</th>
<th>Type of compound</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Elements</td>
<td>A1: Cu-Type c.c.p., A2: W-type b.c.c., A3: Mg-type h.c.p., A4: diamond-type</td>
</tr>
<tr>
<td>B</td>
<td>AB</td>
<td>B1: NaCl, B2: CsCl, B12: BN</td>
</tr>
<tr>
<td>C</td>
<td>AB₂</td>
<td>C4: TiO₂, C6: CdI₂</td>
</tr>
<tr>
<td>D</td>
<td>AₘBₙ</td>
<td>D1: NH₃</td>
</tr>
<tr>
<td>E</td>
<td>More than 2 types of atoms without connecting building units</td>
<td>PbFCl</td>
</tr>
<tr>
<td>F</td>
<td>Building units consisting of 2 or 3 atoms</td>
<td>F1: KCN</td>
</tr>
<tr>
<td>G</td>
<td>Building units consisting of 4 atoms</td>
<td>G1: MgCO₃</td>
</tr>
<tr>
<td>H</td>
<td>Building units consisting of 5 atoms</td>
<td>H2: BaSO₄</td>
</tr>
<tr>
<td>L</td>
<td>Alloys</td>
<td>CuAu</td>
</tr>
<tr>
<td>M</td>
<td>Mixed crystals</td>
<td>(Y,Eu)₂O₃</td>
</tr>
<tr>
<td>O</td>
<td>Organic compounds</td>
<td>O1: CH₄</td>
</tr>
<tr>
<td>S</td>
<td>Silicates</td>
<td>Mg₂SiO₄</td>
</tr>
</tbody>
</table>
Classification – Solid Solutions or Mixed Crystals

**Intercalation mixed crystals**
Compounds of at least two elements, whereas the smaller one - mostly a non-metallic component - occupies interstitial sites
Exp.: FeC, WC, Ti₂H, Fe₂N

**Substitutional mixed crystals**
Mixed crystal of at least two elements forming a joint lattice, where the second element occupies regular lattice positions of the first component. Driving force is entropy, overcompensating mixing enthalpy
Exp.: La₁₋ₓCeₓPO₄, Ca₁₋ₓSrₓS, K₁₋ₓRbₓ, Mo₁₋ₓWₓ

Formation of complete solid solutions only, if
1. Both elements/compounds crystallise in the same type of lattice (isotypic)
   \[ a_{AB} = a_A(1-x_B) + a_Bx_B \] with \( a = \) lattice constant
2. The difference in atom/ionic radii is smaller than 15% (room temperature) or 20% (high temperatures)
3. Both atoms/ions possess a similar valence and electronegativity

\[ \text{Fundamentals of Material Science} \]
\[ \text{Prof. Dr. T. Jüstel, FH Münster} \]
2. Structure of Solid State Materials

Classification – Substitutional Mixed Crystals

Consequences

• Formation of mixed crystals is more likely to occur, if cations and not anions are substituted

• If the two borderline cases crystallise in different structures, mixed crystals will occur only to a certain extent

\[
\begin{align*}
\text{Mg}_2\text{SiO}_4 & \quad \text{Forsterite} \\
\text{Zn}_2\text{SiO}_4 & \quad \text{Willemite}
\end{align*}
\]

\[
\begin{align*}
\text{Mg}_{2-x}\text{Zn}_x\text{SiO}_4 & \quad x < 0.4 \\
\text{Zn}_{2-x}\text{Mg}_x\text{SiO}_4 & \quad x < 0.4
\end{align*}
\]

• If there are different valences, the resulting charge must be compensated

\[
\begin{align*}
\text{Ca}^{II}_3\text{Al}_2\text{Si}^{IV}_3\text{O}_{12} & \rightarrow (\text{Ca}^{II}_{1-a}\text{Y}^{III}_a)_3\text{Al}_2(\text{Si}^{IV}_{1-a}\text{Al}^{III}_a)_3\text{O}_{12} & \rightarrow \text{Y}^{III}_3\text{Al}_2\text{Al}^{III}_3\text{O}_{12}
\end{align*}
\]

• Compounds forming complete solid solutions are difficult to gain in their pure borderline stoichiometry

\[\Rightarrow \text{compounds of lanthanides, such as LnPO}_4 \text{ (monazite, xenotim) or Ln}_2\text{O}_3 \text{ (bixbyite)}\]

Notation

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Material sci.</th>
<th>Laser physics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn\text{\textsubscript{2-x}}Mn\text{\textsubscript{x}}\text{SiO}\text{4}</td>
<td>Zn\text{\textsubscript{2}}SiO\text{4}:Mn</td>
<td>Mn:Zn\text{\textsubscript{2}}SiO\text{4}</td>
</tr>
<tr>
<td>La\text{\textsubscript{1-x-y}}Ce\text{\textsubscript{x}}Tb\text{\textsubscript{y}}PO\text{4}</td>
<td>LaPO\text{4}:Ce,Tb</td>
<td>Ce,Tb:LaPO\text{4}</td>
</tr>
<tr>
<td>Y\text{\textsubscript{3-x}}Nd\text{\textsubscript{x}}Al\text{\textsubscript{5}}O\text{12}</td>
<td>Y\text{\textsubscript{3}}Al\text{\textsubscript{5}}O\text{12}:Nd</td>
<td>Nd:Y\text{\textsubscript{3}}Al\text{\textsubscript{5}}O\text{12}</td>
</tr>
</tbody>
</table>
### 2. Structure of Solid State Materials

#### Types of Bonding and Structure Defining Parameters

<table>
<thead>
<tr>
<th>Bonding character</th>
<th>Covalent</th>
<th>Ionic</th>
<th>Metallic</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΣEN</td>
<td>Large</td>
<td>Medium</td>
<td>Small</td>
</tr>
<tr>
<td>ΔEN</td>
<td>Small</td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td>Energy gain</td>
<td>LCAO (per 2 AOs)</td>
<td>IE, EA, coulomb</td>
<td>LCAO (all AOs)</td>
</tr>
<tr>
<td>Nature of bond</td>
<td>Directed</td>
<td>Undirected</td>
<td>Undirected</td>
</tr>
<tr>
<td>Reach of bond</td>
<td>Short</td>
<td>Medium</td>
<td>Far</td>
</tr>
<tr>
<td>Coordination number</td>
<td>1 - 4</td>
<td>4 - 8</td>
<td>8 – 24</td>
</tr>
<tr>
<td>Radii</td>
<td>Covalent single bond radii</td>
<td>Ionic radii</td>
<td>Metallic radii</td>
</tr>
<tr>
<td>Structural concept</td>
<td>VSEPR</td>
<td>Close packing of anions with distinct voids</td>
<td>Close packing</td>
</tr>
<tr>
<td>Properties of the 3-dim. material</td>
<td>Very hard insulators/ semi-conductors</td>
<td>Hard, brittle insulators</td>
<td>Ductile conductors</td>
</tr>
</tbody>
</table>
Ideal Crystals – Metallic Structures

Closely packed layer

Hexagonal close packing (h.c.p.)

Cubic close packing (c.c.p.)
2. Structure of Solid State Materials

Ideal Crystals – Metallic Structures

Hexagonal close packing
(h.c.p.)

Cubic close packing
(c.c.p.)
## 2. Structure of Solid State Materials

### Ideal Crystals – Metallic Structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>Spatial occupation</th>
<th>Coordination number</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.c.P. (cubic body centred)</td>
<td>74%</td>
<td>12</td>
<td>Ca, Sr, Al, Ni, Cu, Rh, Pd, Ag</td>
</tr>
<tr>
<td>h.c.P. (cubic primitive)</td>
<td>74%</td>
<td>12</td>
<td>Be, Mg, Sc, Ti, Co, Zn, Y, Zr</td>
</tr>
<tr>
<td>cubic body centred</td>
<td>68%</td>
<td>8 + 6</td>
<td>Alkali metals, V, Cr, Fe, Nb, Mo, Ta, W</td>
</tr>
<tr>
<td>cubic primitive</td>
<td>52%</td>
<td>6</td>
<td>Po</td>
</tr>
<tr>
<td>diamond</td>
<td>34%</td>
<td>4</td>
<td>C, Si, Ge</td>
</tr>
</tbody>
</table>

### Spatial occupation

\[
SO = \frac{4}{3} \pi r^3 \cdot \left(\frac{Z}{V}\right)
\]

- \( r \): radius of the spheres
- \( Z \): number of spheres per volume

---

**Fundamentals of Material Science**

Prof. Dr. T. Jüstel, FH Münster
2. Structure of Solid State Materials

**Ideal Crystals – Metallic Structures**

<table>
<thead>
<tr>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
<td>La</td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
</tr>
</tbody>
</table>

Hexagonal close packing
Cubic close packing
Other stacking variations of close packings

Cubic body centred packing
(*high pressure modification)
Structure type in its own right
## 2. Structure of Solid State Materials

### Ideal Crystals – Symmetry

Macroscopic crystals can be classified by symmetry elements

<table>
<thead>
<tr>
<th>Symmetry element</th>
<th>Symbol (Hermann-Mauguin)</th>
<th>Symmetry operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>E</td>
<td>x, y, z → x, y, z</td>
</tr>
<tr>
<td>Rotation axis</td>
<td>X</td>
<td>Rotation by 360°</td>
</tr>
<tr>
<td>one-fold</td>
<td>1</td>
<td>360°</td>
</tr>
<tr>
<td>two-fold</td>
<td>2</td>
<td>180°</td>
</tr>
<tr>
<td>three-fold</td>
<td>3</td>
<td>120°</td>
</tr>
<tr>
<td>four-fold</td>
<td>4</td>
<td>90°</td>
</tr>
<tr>
<td>six-fold</td>
<td>6</td>
<td>60°</td>
</tr>
<tr>
<td>Inversion centre</td>
<td>-1 (= i)</td>
<td>Mirroring through a point</td>
</tr>
<tr>
<td>Mirror plane</td>
<td>-2 (= m)</td>
<td>Mirroring along mirror plane</td>
</tr>
<tr>
<td>Rotation inversion axis</td>
<td>-X</td>
<td></td>
</tr>
<tr>
<td>Three-, four-, six-fold axis</td>
<td>-3, -4, -6</td>
<td>Rotation by 360/n° and inversion</td>
</tr>
</tbody>
</table>

The possible combinations of these symmetry operations results in 32 crystal classes (crystallographic point groups), which can be categorized into 7 crystal systems.
2. Structure of Solid State Materials

Ideal Crystals – Symmetry

Symmetry element: Rotation axis
Symmetry operation: Rotation

Examples (molecules)
• $\text{H}_2\text{O}$ exhibits a two-fold axis
  $360^\circ/2 = 180^\circ$
  After rotation by $180^\circ$ the atoms appear at the same position as before

• $\text{NH}_3$ exhibits a three-fold axis
  $360^\circ/3 = 120^\circ$
  Atoms appear at their given position after rotation by $120^\circ$ and $240^\circ$

• $\text{XeF}_4$ exhibits a four-fold axis
  $360^\circ/4 = 90^\circ$
  Atoms appear at their given position after rotation by $90^\circ$, $180^\circ$ and $270^\circ$
Ideal Crystals – Symmetry

Symmetry element: Mirror plane
Symmetry operation: Mirroring

Examples
- $\text{H}_2\text{O}$
  2 mirror planes, perpendicular to one another:
  $\sigma_v$ and $\sigma_v'$
  including main rotation axis ($C_2$-axis in this case)
- Tetrachloro platinum anion $[\text{PtCl}_4]^{2-}$
  1 mirror plane $\sigma_h$ perpendicular to main rotation axis ($C_4$-axis in this case)
2. Structure of Solid State Materials

Ideal Crystals – Symmetry

Symmetry element: Point
Symmetry operation: Inversion (mirroring through a point)

Examples
a) Octahedra possess a inversion centre
   e.g. $[\text{CoF}_6]^{3-}$

b) Tetrahedra possess no inversion centre
   e.g. $[\text{BF}_4]^{-}$
2. Structure of Solid State Materials

Ideal Crystal – Symmetry (Basic Object with Arbitrary Symmetry)

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Crystal classes</th>
<th>Point groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hermann-Mauguin</td>
<td>Schoenflies</td>
</tr>
<tr>
<td>Triclinic</td>
<td>1, -1</td>
<td>C₁, Cᵢ</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2, m, 2/m</td>
<td>C₂, Cₛ, C₂h</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>2 2 2, m m 2, m m m</td>
<td>D₂, C₂ᵥ, D₂h</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4, -4, 4/m, 4 2 2</td>
<td>C₄, S₄, C₄h, D₄</td>
</tr>
<tr>
<td></td>
<td>4 m m, 4 m, 4/m m m</td>
<td>C₄ᵥ, D₂d, D₄h</td>
</tr>
<tr>
<td>Trigonal</td>
<td>3, -3, 3 2, 3 m, -3 m</td>
<td>C₃, C₃ᵢ, D₃, C₃ᵥ, D₃d</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>6, -6, 6/m, 6 2 2</td>
<td>C₆, C₆h, C₆h</td>
</tr>
<tr>
<td></td>
<td>6 m m, -6 m 2, 6/m m m</td>
<td>D₆, C₆ᵥ, D₃h, D₆h</td>
</tr>
<tr>
<td>Cubic</td>
<td>2 3, m 3, 4 3 2, -4 3 m, m 3 m</td>
<td>T, Tₕ, O, Tₜ, Oₕ</td>
</tr>
</tbody>
</table>

All macroscopic crystals (convex polyhedra) can be subdivided into 32 crystal classes or point groups, respectively
2. Structure of Solid State Materials

Ideal Crystals – Unit Cell

The unit cell is unambiguously defined by
- Side lengths \(a, b, c\)
- Angles between planes \(\alpha, \beta, \gamma\)

By definition
- \(\alpha = \text{angle between } b \text{ and } c\)
- \(\beta = \text{angle between } a \text{ and } c\)
- \(\gamma = \text{angle between } a \text{ and } b\)

Direction of axes describes a right-handed coordinate system

Determination of unit cell
- As small as possible
- Short lengths of axes (repeating element)
- All angles as close to 90° as possible
2. Structure of Solid State Materials

Ideal Crystals – Unit Cell

Characteristics of the unit cell

- Imaginary representation, since the crystal consists of atoms, ions or molecules
- Serves as a simplified description of the periodical building blocks in a crystal

Advantages

- Splits complicated systems into small identical units
- For the description of the structure only a small number of parameters is needed
- Structure determination is limited to the content of the unit cell

Number of unit cells in a crystal of the volume of 1 mm$^3$ ($10^{21}$ Å$^3$)

- NaCl  $10^{19}$ unit cells
- D-xylose-isomerase  $10^{15}$ unit cells
## 2. Structure of Solid State Materials

### Ideal Crystals – Crystal Systems (Basic Object with Spherical Symmetry: Balls)

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Unit Cell</th>
<th>Minimal Symmetry Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$\alpha \neq \beta \neq \gamma$</td>
<td>None</td>
</tr>
<tr>
<td></td>
<td>$a \neq b \neq c$</td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$</td>
<td>Two-fold axis or a symmetry plane</td>
</tr>
<tr>
<td></td>
<td>$a \neq b \neq c$</td>
<td></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Combination of three perpendicular two-fold axes or symmetry planes</td>
</tr>
<tr>
<td></td>
<td>$a \neq b \neq c$</td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Four-fold rotation axis or a four-fold inversion axis</td>
</tr>
<tr>
<td></td>
<td>$a = b \neq c$</td>
<td></td>
</tr>
<tr>
<td>Trigonal</td>
<td>$\alpha = \beta = \gamma \neq 90^\circ$</td>
<td>One three-fold axis</td>
</tr>
<tr>
<td></td>
<td>$a = b = c$</td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\alpha = \beta = 90^\circ$</td>
<td>Six-fold rotation axis or a six-fold inversion axis</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 120^\circ$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = b \neq c$</td>
<td></td>
</tr>
<tr>
<td>Cubic</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>Four three-fold axes, intersecting under 109.5$^\circ$</td>
</tr>
<tr>
<td></td>
<td>$a = b = c$</td>
<td></td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Ideal Crystals – Crystal Systems (Primitive Unit Cell)

- **Triklin**
- **Monoklin**
- **Orthorhombisch**
- **Tetragonal**
- **rhomboedrisch / trigonal**
- **Kubisch**
- **Hexagonal**
2. Structure of Solid State Materials

Ideal Crystals – Primitive and Centred Unit (2D: Elementary Knots)
⇒ Complete Occupation of the Space (2D: Area) without Overlapping
2. Structure of Solid State Materials

Ideal Crystals – Primitive and Centred Unit Cell

monoklin

orthorhombisch

c-flächenzentriert  c-flächenzentriert  innenzentriert  flächenzentriert

tetragonal

tetragonal

tetragonal

inennzentriert  innenzentriert  flächenzentriert
2. Structure of Solid State Materials

Ideal Crystals – Translational Lattices

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Allowed lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>P</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>P, C</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>P, F, I, A or B or C</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>P, I</td>
</tr>
<tr>
<td>Trigonal</td>
<td>P or R</td>
</tr>
<tr>
<td>(Rhombohedral)</td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>P</td>
</tr>
<tr>
<td>Cubic</td>
<td>P, I, F</td>
</tr>
</tbody>
</table>

⇒ 14 Translational or Bravais lattices
2. Structure of Solid State Materials

Ideal Crystals – Translational Lattices (Bravais lattices)

The Bravais lattices represent the 14 possibilities to construct a space by a 3-dimensional periodical arrangement of points.

These translational lattices can be
- primitive (1 lattice point per unit cell) or
- centred (>1 lattice point per unit cell)

There are 7 primitive and 7 centred Bravais lattices

<table>
<thead>
<tr>
<th>Lattice type</th>
<th>Symbol</th>
<th>Lattice points per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primitive</td>
<td>P</td>
<td>1</td>
</tr>
<tr>
<td>Body-centred</td>
<td>I</td>
<td>2</td>
</tr>
<tr>
<td>Basis face-centred</td>
<td>A, B, C</td>
<td>2</td>
</tr>
<tr>
<td>Face-centred</td>
<td>F</td>
<td>4</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Ideal Crystals – Symmetry of the Discontinuum

The basic objects of a real crystal are atoms, ions or molecules. These objects are arranged within the crystal lattice. The basis is made up from at least one atom, but can also easily include thousands of atoms, as in a protein crystal.

The crystal lattice is a three dimensional arrangement of (mathematical) points. The smallest unit of the lattice is the unit cell.

Thus, the lattice is created by the translation of the unit cell in all three spatial dimensions.
⇒ Translational lattices (Bravais lattices) consist of one sort of particles (points).

Introduction of a basis (more complex as simple balls or points)
⇒ Further symmetry elements (8): 1 glide plane, 7 screw axes.
2. Structure of Solid State Materials

Ideal Crystal - 3-Dimensional Translational Arrangement of Building Blocks

Can be visualized by transmission electron microscopy

Cu-phthalocyanine | Hepadna virus (duck virus) | CdSe quantum dots (5 nm)

⇒ Depiction of the electron density distribution
## 2. Structure of Solid State Materials

### Ideal Crystal – Space Groups

The combination of all symmetry elements existing in a crystal, i.e. X, m, i, -X, with all translational symmetry elements leads to 230 combinations in total, and are called space groups.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Symmetry Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centrosymmetric</td>
<td>Translation, screw-axes, mirror planes, inversion centres</td>
</tr>
<tr>
<td>Non-centrosymmetric</td>
<td>Translation, screw-axes, mirror planes</td>
</tr>
<tr>
<td>Chiral</td>
<td>Translation, screw-axes (→ chiral molecules)</td>
</tr>
</tbody>
</table>

**General notation**
1234 (usually)

**Example**

Fmmm  
- lattice type F-centred  
- mirror plane perpendicular to a, b and c axis  

(La$_2$NiO$_4$)
2. Structure of Solid State Materials

Ideal Crystal – Space Groups

10 Symmetry operations: 1, 2, 3, 4, 6, -1 (= i), -2 (= m), -3, -4, -6

32 crystal classes

Universell translational vectors

14 Translational lattices (Bravais lattices)

230 Space groups

individuel translational vectors

glide planes & screw axes
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

Packing: c.c.p. or h.c.p.
usually of the anions

Voids: Tetrahedral or octahedral voids
usually of the cations

For N packed particles

\[
\text{c.c.p.:} \quad \begin{align*}
(N) \text{ Octahedral sites} \\
(2N) \text{ Tetrahedral sites}
\end{align*}
\]

\[
\text{h.c.p.:} \quad \begin{align*}
(N) \text{ Octahedral sites} \\
(2N) \text{ Tetrahedral sites}
\end{align*}
\]
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

Usually, octahedral and tetrahedral sites are only partially occupied. Nonetheless, the level of occupancy determines the structure type.
2. Structure of Solid State Materials

### Ideal Crystals – Ionic Structures

<table>
<thead>
<tr>
<th>Anions - Arrangement</th>
<th>$\text{T}_+$</th>
<th>$\text{T}_-$</th>
<th>O</th>
<th>Structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.c.p. (ABCABC...)</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>NaCl (common salt)</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ZnS (zinc blende)</td>
</tr>
<tr>
<td>1/8</td>
<td>1/8</td>
<td>1/2</td>
<td></td>
<td>MgAl$_2$O$_4$ (spinel)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td></td>
<td>CdCl$_2$</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td></td>
<td>CuFeS$_2$ (chalcopyrite)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1/3</td>
<td></td>
<td>CrCl$_3$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>-</td>
<td></td>
<td>K$_2$O (antifluorite)</td>
</tr>
<tr>
<td>h.c.p. (ABAB...)</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>NiAs</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ZnS (wurtzite)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td></td>
<td>CdI$_2$</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1/2</td>
<td></td>
<td>TiO$_2$ (rutile)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1/3</td>
<td></td>
<td>Al$_2$O$_3$ (corundum)</td>
</tr>
<tr>
<td>1/8</td>
<td>1/8</td>
<td>1/2</td>
<td></td>
<td>Mg$_2$SiO$_4$ (olivin)</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td></td>
<td>$\beta$-Li$_3$PO$_4$</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>-</td>
<td></td>
<td>$\gamma$-Li$_3$PO$_4$</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB-Structures – NaCl (kitchen salt)

Cubic close packing of anions

Coordination 6 : 6
N = 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Na⁺</td>
</tr>
<tr>
<td>T⁺</td>
<td>empty</td>
</tr>
<tr>
<td>T⁻</td>
<td>empty</td>
</tr>
</tbody>
</table>

Examples
- MgO, CaO, SrO, BaO
- TiO, MnO, FeO, CoO, NiO
- LiF, LiCl, LiBr, LiI
- NaF, NaCl, NaBr, NaI
- KF, KCl, KBr, KI
- RbF, RCl, RbBr, RbI
- AgF, AgCl, AgBr
Ideal Crystals – Ionic Structures

AB-Structures – CsCl (caesium chloride)

Cubic primitive packing of anions

Coordination 8 : 8
N = 1

Examples
- CsCl, CsBr, CsI, CsCN
- TlCl, TlBr, TlI
- NH₄Cl, NH₄Br
Ideal Crystals – Ionic Structures

AB-Structures – ZnS (zinc blende or sphalerite)

Cubic close packing of anions

Coordination 4 : 4
N = 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>empty</td>
</tr>
<tr>
<td>T+</td>
<td>Zn$^{2+}$</td>
</tr>
<tr>
<td>T-</td>
<td>leer</td>
</tr>
</tbody>
</table>

Examples
- CdS, CdSe, CdTe
- HgS, HgSe, HgTe
- BN, BP, BAs
- AlP, AlAs, AlSb
- GaP, GaAs, GaSb
- Csp$^3$ (diamond), all positions occupied by C

$S^{2-}$ $Zn^{2+}$
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB-Structures – ZnS (wurtzite)

Hexagonal close packing of anions

Coordination 4 : 4
N = 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>empty</td>
</tr>
<tr>
<td>T+</td>
<td>Zn$^{2+}$</td>
</tr>
<tr>
<td>T-</td>
<td>empty</td>
</tr>
</tbody>
</table>

Examples
- ZnO, ZnS, ZnSe, ZnTe
- BeO, SiC
- CdS, CdSe
- MnS
- AlN, GaN, InN
2. Structure of Solid State Materials

Ideal Crystals – Influence of the Ionic Radii

The highest possible coordination number depends on the ratio of the ionic radii $r_{\text{Cation}}/r_{\text{Anion}}$ (comparable to coordination chemistry)

<table>
<thead>
<tr>
<th>Ratio</th>
<th>CN</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>Cubeoctahedron</td>
</tr>
<tr>
<td>0.732 - 0.999</td>
<td>8</td>
<td>Cube</td>
</tr>
<tr>
<td>0.414 - 0.732</td>
<td>6</td>
<td>Octahedron</td>
</tr>
<tr>
<td>0.225 - 0.414</td>
<td>4</td>
<td>Tetrahedron</td>
</tr>
</tbody>
</table>

$r_{\text{Cation}}/r_{\text{Anion}} = 1$ is found in many metallic crystals and in some ionic crystals with extremely large cations, i.e. Cs$^+$
2. Structure of Solid State Materials

Ideal Crystals – For $r_C/r_A > 0.732$ Caesium Chloride Structure Occurs

- Anions do not have contact
  
  $r_C/r_A = 1$

- Anions do have contact
  
  $r_C/r_A = \sqrt{3}/1$
  
  $(r_C + r_A)/r_A = \sqrt{3}/1$

- Anions can not get closer to the cation
  
  $r_C/r_A < 0.732$

Example $r_C/r_A$

<table>
<thead>
<tr>
<th>Example</th>
<th>$r_C/r_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsCl</td>
<td>0.94</td>
</tr>
<tr>
<td>CsBr</td>
<td>0.87</td>
</tr>
<tr>
<td>TlCl</td>
<td>0.83</td>
</tr>
<tr>
<td>CsI</td>
<td>0.79</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Ideal Crystals – For $0.414 < \frac{r_C}{r_A} < 0.732$ Cations Are Coordinated Octahedrally

The structure type depends on the packing of the anions

<table>
<thead>
<tr>
<th>Anion packing</th>
<th>hexagonal close</th>
<th>cubic close</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer sequence</td>
<td>ABABAB</td>
<td>ABCABCABC</td>
</tr>
<tr>
<td>Structure type</td>
<td>NiAs-type</td>
<td>NaCl-type</td>
</tr>
</tbody>
</table>

Example $\frac{r_C}{r_A}$

- KBr: 0.71
- KI: 0.64
- NaCl: 0.56
- NaBr: 0.52
- NaI: 0.47

[Diagram showing crystal structures]
2. Structure of Solid State Materials

Ideal Crystals – For $r_C/r_A < 0.414$ Cations Are Coordinated Tetrahedrally

Again, the structure type depends on the packing of the anions

<table>
<thead>
<tr>
<th>Anion packing</th>
<th>cubic close</th>
<th>hexagonal close</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer sequence</td>
<td>ABCABCABC</td>
<td>ABABAB</td>
</tr>
<tr>
<td>Structure type</td>
<td>Zinc blende-type</td>
<td>Wurtzite-type</td>
</tr>
</tbody>
</table>

Example $r_C/r_A$

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>0.25</td>
</tr>
<tr>
<td>BeS</td>
<td>0.19</td>
</tr>
</tbody>
</table>

[Diagram showing crystal structures for BeO and BeS]
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB$_2$-Structures – CaF$_2$ (Flussspat or fluorite)

Cubic close packing of cations

Coordination 8 : 4
N = 4

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>empty</td>
</tr>
<tr>
<td>T$_+$</td>
<td>F$^-$</td>
</tr>
<tr>
<td>T$_-$</td>
<td>F$^-$</td>
</tr>
</tbody>
</table>

Example
- CaF$_2$, SrF$_2$, BaF$_2$
- CrCl$_2$, BaCl$_2$, SrBr$_2$
- Li$_2$O, Li$_2$S, Li$_2$Se, Li$_2$Te

2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

Properties of CaF$_2$ (Flussspat or fluorite)

• Extremely wide band gap ~ 11.0 eV (115 nm) and low phonon frequencies
  ⇒ broad optical window ⇒ material for optical lenses (spectroscopy)

• Fluorides are prone to the formation of point defects (colour centres + luminescence)
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB$_2$-Structures – TiO$_2$ (rutile)

Distorted hexagonal close packing of anions

Coordination 6 : 3
N = 2

Site    Occupancy
O       ½ Ti$^{4+}$
T$_+$    empty
T$_-$    empty

Examples
- GeO$_2$, SnO$_2$, PbO$_2$
- MgF$_2$, MnF$_2$, FeF$_2$, CoF$_2$, NiF$_2$, ZnF$_2$, PdF$_2$
- TiO$_2$, CrO$_2$, β-MnO$_2$, NbO$_2$, TaO$_2$, MoO$_2$, WO$_2$
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

Polymorphism of TiO$_2$ (anatase and brookite are metastable)

Anatase (tetragonal)  
Rutile (tetragonal)  
Brookite (orthorhombic)

4 mutual edges  
2 mutual edges  
3 mutual edges
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

Properties of TiO$_2$ (rutile and anatase)

Low band gap ~ 3.2 eV (390 nm, rutile) and 3.5 eV (360 nm, anatase), highly covalent character and strong interactions with light

⇒ UV-absorber
⇒ Photo-catalytically active
⇒ High refractive index (2.5 – 2.8)

Applications of rutile and anatase
⇒ White pigment
⇒ Solar cells (Grätzel)
⇒ UV-protection additives
⇒ Photo reactors (purification of water)
⇒ Polymer additives

![Graph showing reflection vs. wavelength for rutile and anatase](image-url)
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB$_2$-Structures – CdI$_2$ (cadmium iodide)

Hexagonal close packing of anions, layer structure

Coordination 6 : 3
N = 3

Layer | Occupancy
--- | ---
A | I$^-$
B | Cd$^{2+}$
C | I$^-$

Examples
- CdI$_2$, MgI$_2$, CaI$_2$, TiI$_2$, VI$_2$, MnI$_2$, FeI$_2$, ZnI$_2$
- TiBr$_2$, VBr$_2$, MnBr$_2$, FeBr$_2$, CoBr$_2$
- Mg(OH)$_2$, Ca(OH)$_2$, Fe(OH)$_2$, Co(OH)$_2$, Ni(OH)$_2$

Source: Orci – own work with diamond 3
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB₂-Structures – SiO₂ (β-cristobalite)

Can be derived formally from cubic close packing (Si occupies Zn²⁺ and S²⁻ positions of zinc blende structure)

Coordination 4 : 2
N = 8

Examples
• BeF₂
• SiO₂

β-cristobalite is a modification of SiO₂ as α-quartz, β-quartz and β-tridymite
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

$A_2B_3$-Structures – $\alpha$-$Al_2O_3$ (corundum)

Distorted hexagonal close packing of anions

Coordination 6 : 4
N = 4
$Al^{3+}$ is distorted octahedrally coordinate!

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2/3 $Al^{3+}$</td>
</tr>
<tr>
<td>$T_+$</td>
<td>empty</td>
</tr>
<tr>
<td>$T_-$</td>
<td>empty</td>
</tr>
</tbody>
</table>

Examples
- $\alpha$-$Al_2O_3$, $\alpha$-$Ga_2O_3$
- $Ti_2O_3$, $V_2O_3$, $Cr_2O_3$, $\alpha$-$Fe_2O_3$
- $Rh_2O_3$
2. Structure of Solid State Materials

Ideal Crystals - Ionic Structures

A$_2$B$_3$-Structures – polymorphism of Fe$_2$O$_3$

α-Fe$_2$O$_3$ (trigonal, corundum)  γ -Fe$_2$O$_3$ (cubic, metastable)

Anti-ferromagnetic  Ferromagnetic
2. Structure of Solid State Materials

Ideal Crystals - Ionic Structures

ABX₃-Structures – CaTiO₃ (perowskit)

Cubic close packing of A- and X-ions with the ratio of 1:3 and B-ions occupying one fourth of the octahedra sites. Alternative description: corner-connected TiO₆-octahedra, where Me²⁺ is twelve-fold coordinate

Coordination 12 : 6 : 2
N = 1

Example
• CaTiO₃, SrTiO₃, BaTiO₃, PbTiO₃
• KIO₃
• LaVO₃, LaCrO₃, LaFeO₃, LaCoO₃
2. Structure of Solid State Materials

Ideal Crystals - Ionic Structures

Properties of CaTiO$_3$

Small band gap und high polarizability of the octahedrally coordinate B-ions

⇒ External electrical fields induce a dipole moment by shifting the cations
⇒ Ferroelectric ceramics made from Ba$_{1-x}$Ca$_x$Ti$_{1-y}$Zr$_y$O$_3$ show the highest permittivity values ($\varepsilon_r$ up to 7000), for comparison: H$_2$O $\varepsilon_r = 78$

Applications in
⇒ Capacitors
⇒ Membranes (Speakers)
⇒ Sensors (microphones)
⇒ Micro nozzles (inkjet printer)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

$AB_2X_4$-Structures – $\text{MgAl}_2\text{O}_4$ (spinel)

Cubic close packing of anions

Coordination 4 : 6 : 4
$N = 8$

<table>
<thead>
<tr>
<th>Site</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>$1/2$</td>
</tr>
<tr>
<td>$T_+$</td>
<td>$1/8$</td>
</tr>
<tr>
<td>$T_-$</td>
<td>$1/8$</td>
</tr>
</tbody>
</table>

Examples

$\text{MgAl}_2\text{O}_4$, $\text{MnAl}_2\text{O}_4$, $\text{FeAl}_2\text{O}_4$, $\text{CoAl}_2\text{O}_4$

$\text{CuCr}_2\text{S}_4$, $\text{CuCr}_2\text{Se}_4$, $\text{CuCr}_2\text{Te}_4$

$\text{MgIn}_2\text{O}_4$, $\text{MgIn}_2\text{S}_4$
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

AB$_2$X$_4$–Structures – MgAl$_2$O$_4$ (spinel)

<table>
<thead>
<tr>
<th>Ordinary spinels</th>
<th>Inverse spinels</th>
<th>Mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A]$^{tet}$[B]$_2$$^{oct}$O$_4$</td>
<td>[B]$^{tet}$[A,B]$^{oct}$O$_4$</td>
<td>[B$<em>x$A$</em>{1-x}$]$^{tet}$[A$<em>x$B$</em>{1-x}$]$^{oct}$O$_4$</td>
</tr>
<tr>
<td>$\gamma = 0.0$</td>
<td>$\gamma = 1.0$</td>
<td>$\gamma = x$ with $0.0 &lt; x &lt; 1.0$</td>
</tr>
</tbody>
</table>

Examples:

- MgAl$_2$O$_4$
- CoAl$_2$O$_4$
- FeAl$_2$O$_4$
- CoCo$_2$O$_4$ (= Co$_3$O$_4$)
- MnMn$_2$O$_4$ (= Mn$_3$O$_4$)
- MgFe$_2$O$_4$
- FeFe$_2$O$_4$ (= Fe$_3$O$_4$)
- NiFe$_2$O$_4$
- CoFe$_2$O$_4$
- NiAl$_2$O$_4$
- MnFe$_2$O$_4$
- NiFe$_2$O$_4$
- CuFe$_2$O$_4$

Influence upon $\gamma$ (occupancy parameters of B$^{3+}$-ions on tetrahedral sites)

- Ionic radius
- Coulomb energy
- Covalent character
- Crystal field stabilisation energy
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Properties of spinels

Spinels are extremely hard (high lattice energy!), exhibit isotropic physical properties (cubic structure), and show - analogous to many transition metals - distinct ferroelectricity (unpaired electrons) and ferro-, ferri- or anti-ferromagnetism

Ferrimagnetics: $\text{Fe}_3\text{O}_4$ magnetite
Ferroelectrics: $\text{M}^{2+}\text{Fe}_2\text{O}_4$ ferrite

Prerequisites for good ferroelectrics
As high permeability as possible in combination with low coercivity = max. induction by min. magnetic field strength, e.g. write/read head in audio and video recorders or transformer and coil cores.
Are met by cubic soft ferrites, because they are electrically isolating (suppression of eddy currents), ferrimagnetic with low saturation magnetisations but low crystallographic anisotropy (cubic symmetry) at the same time.
Typical composition: Fe-Mn-Zn-oxide comprising 70% Fe, 25% Mn, 5% Zn
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Garnet $\text{C}^{II}_3\text{A}^{III}_2\text{(Si}^{IV}\text{O}_4)_3$

Isle silicates (neso silicates) with
$[\text{SiO}_4]^{4-}$ or $[\text{TO}_4]^{4-}$-groups
Cubic structure type – space group Ia3d (#230)

Coordination of cations
C = 8  Dodecahedral site
A = 6  Octahedral site
T = 4  Tetrahedral site
Z = 8  160 atoms in unit cell!

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrop</td>
<td>$\text{Mg}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}$</td>
</tr>
<tr>
<td>Grossular</td>
<td>$\text{Ca}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}$</td>
</tr>
<tr>
<td>Almandine</td>
<td>$\text{Fe}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}$</td>
</tr>
<tr>
<td>Spessartinn</td>
<td>$\text{Mn}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}$</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Garnet variations $C_{\text{II}}^{\text{III}}A_{\text{IV}}^{\text{III}}_2(Si_{\text{IV}}O_{\text{IV}})_3$

- **Ca$_3$Al$_2$Si$_3$O$_{12}$** (Grossular) → $(Ca_{1-a}Y_a)_3Al_2(Si_{1-a}Al_a)_3O_{12}$ → $Y_3Al_2Al_3O_{12}$ (YAG)
- **Ca$_3$Fe$_2$Si$_3$O$_{12}$** (Andradite) → $(Ca_{1-a}Y_a)_3Fe_2(Si_{1-a}Fe_a)_3O_{12}$ → $Y_3Fe_2Fe_3O_{12}$ (YIG)
- **Ca$_3$Cr$_2$Si$_3$O$_{12}$** (Uwarowit)

- **Y$_3$Al$_5$O$_{12}$** (YAG) → $(Y_{1-x}M^a_x)_3Al_5O_{12}$ $M^a = Ce, Pr, Nd, Sm, Eu$ (limited) $M^a = Gd – Lu$ (unlimited)
  → $Y_3(Al_{1-x}M^b_x)_5O_{12}$ $M^b = Ga, Sc$
  → $(Y_{1-x}M^a_x)_3(Al_{1-x}M^b_x)_5O_{12}$
  → $Y_3(Al_{1-x}M^c_{x/2}M^d_{x/2})_5O_{12}$ $M^c = Si, M^d = Mg$
  → Ca$_2$Lu$M^e_{2}Al_3$O$_{12}$ $M^e = Zr, Hf$
  → $Y_3(Al_{1-x}M^f_{x})_5O_{12-x}N_x$ $M^f = Si$
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Physical properties of $Y_3Al_5O_{12}$ (YAG: Yttrium Aluminium Garnet)

- **Density** \( \rho = 4.55 \text{ g/cm}^3 \)
- **Thermal extension coefficient** \( \alpha = 6.5 \times 10^{-6} \text{ K}^{-1} \)
- **Melting point** \( T_m = 1970 \text{ °C} \)
- **Refractive index at 589.3 nm** \( n = 1.830 \)
- **Refractive index at 1.0 µm** \( n = 1.816 \)
- **Hardness acc. to Mohs** 8.5
- **Thermal conductivity** 14 W/mK at 20 °C
- **Optical band gap** \( E_G = 7.0 \text{ eV} \)
- **Body colour** white (colourless)
- **Exciton luminescence** \(~ 300 \text{ nm}\) (Electron-hole pair recombination)

Typical impurities (dopants)

- **Y-site** (dodecahedral) \( \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ce}^{3+} - \text{Lu}^{3+} \)
- **Al-site** (octahedral) \( \text{Sc}^{3+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Fe}^{3+} \)
- **Al-site** (tetrahedral) \( \text{Fe}^{3+}, \text{Si}^{4+}, \text{Ge}^{4} \)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Physical properties of $Y_3Al_5O_{12}$

![Diagram showing the electronic transitions in $Y_3Al_5O_{12}$ and the absorption spectrum after calcination in air for several days.](attachment:image.png)

- **Conduction band**
- **Valence band**

- $E_g \approx 7.0 \text{ eV}$

**Absorption spectrum of YAG after calcination in air for several days**

- Absorption peaks at:
  - $860 \text{ nm}$
  - $650 \text{ nm}$
  - $460 \text{ nm}$

**Energy levels**:

- $V_{o}^{+}$, $V_{o}^{2+}$, $V_{o}^{0}$
- $V_{Y}^{'''}$, $V_{Al}^{''''}$

**Electronic configurations**:

- $2p^2$
- $2s^2$
- $2p^2$

- $E_g \approx 7.0 \text{ eV}$
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Optical properties of $Y_3Al_5O_{12}$
High optical band gap
High refractive index ($n_D = 1.82$)
Low maximal phonon frequency

$Y_3Al_5O_{12}:Ce^{3+}$ (0.5 – 3.0%)
Extremely high crystal field splitting for the excited state $\sim 28000 \text{ cm}^{-1}$ (3.5 eV)
→ dodecahedral coordination of $Ce^{3+}$
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

β-Alumina-structures – MAl$_{11}$O$_{17}$ = M$_2$O·nAl$_2$O$_3$

Layer structures
A Spinel units “Al$_{11}$O$_{16}$”
B Intermediate layers “M-O”
  with M = Na, K, Rb, Cu, Ag, In, Tl

Hexagonal close packing of anions
in spinel units
High ionic mobility of the cations M$^+$ within
the intermediate layers → ionic conductor (cations)

β-Alumina-variations
NaAl$_{11}$O$_{17}$ → (Na$_{1-x}$Ba$_x$)Mg$_x$Al$_{11-x}$O$_{17}$ → BaMgAl$_{10}$O$_{17}$

NaAl$_{11}$O$_{17}$ → (Na$_{1-x}$La$_x$)Mg$_x$Al$_{11}$O$_{17+2x}$ → LaMgAl$_{11}$O$_{19}$ (magnetoplumbit structure!)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

β-Alumina–structures – NaAl₁₁O₁₇

Exp.: BaMgAl₁₀O₁₇

Ba²⁺ exhibits nine-fold coordination (triply capped trigonal prism ⇒ D₃h)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

β-Alumina–structures – NaAl$_{11}$O$_{17}$

Stability of β-alumina phase

Only the biggest cations stabilise the β-alumina structure
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Properties of β-alumina-structures

Very high ionic conductivity, high optical band gap, fissility, anisotropic refraction

Application as
• Solid electrolyte in batteries
• Phosphor in gas discharge lamps (fluorescence lamps and PDP’s)

\[
\begin{align*}
\text{BaMgAl}_{10}\text{O}_{17} & \rightarrow (\text{Ba}_{1-x}\text{Eu}_x)\text{MgAl}_{10}\text{O}_{17} \quad \rightarrow \text{blue} \\
\text{BaMgAl}_{10}\text{O}_{17} & \rightarrow \text{Ba(Mg}_{1-y}\text{Mn}_y)\text{Al}_{10}\text{O}_{17} \quad \rightarrow \text{green} \\
\text{BaMgAl}_{10}\text{O}_{17} & \rightarrow \text{BaMg(Al}_{10-z}\text{Cr}_z)\text{O}_{17} \quad \rightarrow \text{deep red} \\
\text{BaMgAl}_{10}\text{O}_{17} & \rightarrow (\text{Ba}_{1-x}\text{Eu}_x)(\text{Mg}_{1-y}\text{Mn}_y)\text{Al}_{10}\text{O}_{17} \rightarrow \text{cyan}
\end{align*}
\]
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Phosphors with β-alumina structure

BaMgAl$_{10}$O$_{17}$:Cr$^{3+}$

BaMgAl$_{10}$O$_{17}$:Mn$^{2+}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Excitation at</th>
<th>$\lambda_{\text{max}}$ at</th>
<th>$x$</th>
<th>$y$</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{3+}$</td>
<td>190 nm</td>
<td>694 nm</td>
<td>0.596</td>
<td>0.257</td>
<td>3d$^3$-3d$^3$</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>180 nm</td>
<td>515 nm</td>
<td>0.146</td>
<td>0.722</td>
<td>3d$^5$-3d$^5$</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Phosphors with β-alumina structure: Emission spectra of BaMgAl_{10}O_{17}:Eu^{2+},Mn^{2+}

- **Eu^{2+}** is incorporated on Ba^{2+}-sites and there absorbs the incoming UV-radiation → allowed [Xe]4f^{7} – [Xe]4f^{6}5d^{1}-interconfigurational transition
- **Energy transfer from Eu^{2+} to Mn^{2+},** whereby the efficiency of the energy transfer depends on the Mn^{2+}-concentration and thus the average distance between Eu^{2+} - Mn^{2+} → Mn^{2+} emission [Ar]3d^{5} – [Ar]3d^{5}-intraconfigurational transition
Ideal Crystal - Ionic Structures

Phosphors with β-alumina-structure: energy migration after excitation with UV-radiation

Host structure → ET → Eu$^{2+}$([Xe]4f$^6$5d$^1$) → ET → Mn$^{2+}$([Ar]3d$^5$*)

Sensitizer for Mn$^{2+}$ luminescence

CB

$E_g = 7.0 \text{ eV}$

(≤ 180 nm)

VB

170 nm
4f$^6$5d$^1$
250 nm
310 nm
4f$^7$(8S$^{7/2}$)

ET

450 nm

3d$^5$*

515 nm

515 nm

3d$^5$
2. Structure of Solid State Materials

**Ideal Crystal - Ionic Structures**

ABX$_3$–structures – CaCO$_3$ (calcite)

Trigonal crystal system

\[ Z = 6 \]

\[ \rho = 2.71 \text{ g/cm}^3 \]

Thermodynamically most stable form of calcium carbonate

**Examples**

CaCO$_3$, CoCO$_3$

ScBO$_3$, FeBO$_3$, InBO$_3$

LuBO$_3$, YBO$_3$ (high temperature modification)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

ABX₃-structures – CaCO₃

Polymorphism

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>ρ [g/cm³]</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>6</td>
<td>2.71</td>
<td>trigonal</td>
</tr>
<tr>
<td>Vaterite</td>
<td>2</td>
<td>2.65</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Aragonite</td>
<td>4</td>
<td>2.93</td>
<td>orthorhombic</td>
</tr>
</tbody>
</table>

Biomineralisation of CaCO₃

- Amorphous: CaCO₃-storage in organisms
- Calcite: otholiths
- Aragonite: coccoliths (calcareous shells) in foraminiferes
- Calcite/aragonite/chitin/protein as composite:
  - nacre (seashell, pearl)
- Mn²⁺ luminescence: calcite 610 nm, aragonite 560 nm (stronger crystal field)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

ABX₃–structures – YBO₃

Polymorphism

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>ρ [g/cm³]</th>
<th>Crystal system</th>
<th>Anion</th>
<th>CN (Y³⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite (ht-type) 6</td>
<td>6.86</td>
<td>trigonal</td>
<td>[BO₃]³⁻ units</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>“YBO₃” (lt-type) 2</td>
<td>7.40</td>
<td>hexagonal</td>
<td>[B₃O₉]⁹⁻ rings</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

Δᵗᴴ° = 12.1 kJ/mol

Eₘ = 1386 kJ/mol  lt → ht transition

Eₘ = 568 kJ/mol  ht → lt transition

2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

ABX₃-structures – YBO₃

Calcite-type ([BO₃]³⁻ units) “YBO₃”- or lt-type ([B₃O₉]⁹⁻ rings)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

ABX₃-structures – YBO₃

Eu³⁺ activated phosphors, e.g. LnBO₃:Eu (Ln = Y, In, Gd, Lu)

- The emission spectrum is dominated by a intraconfigurational transition: \([\text{Xe}]4f^6(5D_0) \rightarrow [\text{Xe}]4f^6(7F_J)\)
  \[\Rightarrow\] several narrow lines between 585 and 710 nm (orange - red)

- Rel. intensity of emission lines = \(f(\text{symmetry, covalence})\)
  Inversion symmetry \(5D_0 \rightarrow 7F_1\) strongest
  No inversion symmetry \(5D_0 \rightarrow 7F_2\) strongest

  Strong ionic character \(5D_0 \rightarrow 7F_4\) weak
  (borates, phosphates)

  Strong covalent character \(5D_0 \rightarrow 7F_4\) strong
  (aluminates, vanadates, sulphides)
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

**ABX$_3$-structures – YBO$_3$**

**Calcite- or ht-type**
Y$^{3+}$ on octahedral sites

**“YBO$_3$“- or lt-type**
Y$^{3+}$ on dodecahedral sites, where Y1 is not distorted and Y2 is

---

**LuBO$_3$ : Eu (Calcite)**

- Emission spectrum
- Excitation spectrum

---

**LuBO$_3$ : Eu (YBO$_3$ -Type)**

- Emission spectrum
- Excitation spectrum
Real Crystals - Definition

Real crystal = ideal crystal (mathematical ideal, incl. vibrations + elastic deformations) + defects (violation of symmetry)

Defects = intrinsic defects and extrinsic defects (dopants)

- 0-dimensional defects (point defects)
  Violation of symmetry on atomic scale

- 1-dimensional defects (line defects)
  Violation of symmetry along a line

- 2-dimensional defects (area defects)
  Symmetry violation for every point lying upon an area

- 3-dimensional defects (spatial defects)
  Any point in a given volume exhibits different symmetry
2. Structure of Solid State Materials

Real Crystals - 0-dim. Defects (Point Defects)

Intrinsic defects (construction errors)

- Vacancy ("V")
- Self-interstitial ("i")

In ionic crystals, intrinsic defects lead to relative charges, that must be compensated

a) By a electron ⇒ colour centre
   Exp.: SiO₂
b) By 2ⁿᵈ defect with opposite charge
   ⇒ Schottky-defect
   Exp.: BeO, MgO, MX
c) By a ion with matching charge on a interstitial
   ⇒ Frenkel-defect
   Exp.: AgCl, AgBr, CaF₂
2. Structure of Solid State Materials

Real Crystals - 0-dim. Defects (Point Defects)

Extrinsic defects (dopants)
- Substitutional impurity atom
  → only if charge and size match
- Interstitial impurity atom
  often in cases of small cations

Physical effects of atomic vacancies (point defects)
- Colour
- Luminescence
- Magnetism
- Electrical conductivity
- Diffusion processes through a swap of positions
  are important for solid state chemistry and solid electrolytes
2. Structure of Solid State Materials

Real Crystals - 0-dim. Defects (Point Defects)

Diffusion processes through positional exchange using the example of silver chloride

Formation of Frenkel-defects

\[
\text{AgCl} \rightarrow \text{Ag}_{1-x}V_{\text{Ag}}\text{Ag}_x\text{Cl} \quad (\text{defect equation})
\]

→ Cation migration via interstitials \(i\)

→ Ionic conductivity in crystals
2. Structure of Solid State Materials

Real Crystals - 0-dim. Defects (Point Defects)

Kröger-Vink-notation using the example of a NaCl-crystal

\[ K^x_K \quad A^x_A \quad \text{Cations or anions on correct lattice positions.} \]
\[ \text{Neutral against the ideal lattice (}) \]
\[ Na^x_{Na} \quad Cl^x_{Cl} \]

\[ V_K \quad V^*_A \quad \text{Cation or anion vacancies with a} \]
\[ \text{effective charge of 1- (•) or 1+ (•) } \]
\[ V_{Na} \quad V^*_{Cl} \]
Real Crystals - 0-dim. Defects (Point Defects)

Kröger-Vink-notation using the example of a NaCl-crystal

$K_i^*$ Interstitial cation with a effective charge of 1+ ($\bullet$) $Na_i^*$

$A_i^*$ Interstitial anion with a effective charge of 1- ($\cdot$) $Cl_i^*$

$Ca_{Na}^*$ Substituted Ca-cation (2+) on Na-site with a effective charge of 1+ ($\ast$)

$Br_{Cl}^x$ Substituted Br-anion (2+) on Cl-site with a effective charge of 0 ($\times$)

e$^*$ electron

h$^*$ hole
2. Structure of Solid State Materials

Real Crystals - 0-dim. Defects (Point Defects) in Oxides

Some defect types:

1. Oxygene defects $V_O$: Oxygene deficiency in oxides comprising easily reducible cations $\rightarrow$ MnO$_{2-x}$, CeO$_{2-x}$, PrO$_{2-x}$, TbO$_{2-x}$, PuO$_{2-x}$

2. Metal defects $V_M$: Metal deficiency in oxides in easily oxidisable cations $\rightarrow$ Fe$_{1-y}$O, Mn$_{1-y}$O, Co$_{1-y}$O

3. Oxygene onto interstitials $O_i$: Oxygene excess compounds, easily oxidisable cations $\rightarrow$ UO$_{2+x}$

4. Metals onto interstitials $M_i$: Defect type in metal deficient oxides along with $V_M$ $\rightarrow$ Fe$_{1-y}$O (Koch-Cohen-Cluster)
Real Crystals - 1-dim. Defects (Line Defects)

Dislocations are the only one dimensional defects in crystals

Dislocations are responsible for the plastic ductility (sliding) of crystalline materials, and thus for the mechanical properties of all metals in particular.
2. Structure of Solid State Materials

Real Crystals - 1-dim. Defects (Line Defects)

Dislocations confine the single crystalline areas in polycrystalline ceramics and thus influence the physical properties, such as conductivity and quantum efficiency of phosphors, e.g. $\text{Y}_2\text{O}_3$:Eu (cubic bixbyite structure)

Dislocation density in real crystals

Dislocation-free silicon
for semiconductors $r = 0 \ \text{cm}^{-2}$

"Good" single crystals
for laboratories: $r \sim (10^3 \text{ - } 10^5) \ \text{cm}^{-2}$

Normal crystals including polycrystalline materials: $r \sim (10^5 \text{ - } 10^9) \ \text{cm}^{-2}$

Highly deformed crystals: $r$ up to $10^{12} \ \text{cm}^{-2}$

HR-TEM image of a $\text{Y}_2\text{O}_3$ crystal
2. Structure of Solid State Materials

Real Crystals - 2-dim. Defects (Area Defects)

Area defects are loosely defined as all sorts of interfaces between two bodies (particles, crystallites)
⇒ Phase boundaries: Interface between two different bodies (phases)
⇒ Grain boundaries: Interface between identical but arbitrarily oriented crystals
⇒ Stacking faults: Interface between two identical and specifically oriented crystals
⇒ Surfaces → surface energy $\gamma$ [J/cm$^2$] → f(particle size)

The surface energy is a measure for the reactivity of the surface and is responsible for the different behaviour of nano- and macro-crystals in terms of their thermodynamic properties, i.e. melting point

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma$ [mJ/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>300</td>
</tr>
<tr>
<td>Fe</td>
<td>700</td>
</tr>
<tr>
<td>W</td>
<td>1450</td>
</tr>
</tbody>
</table>
2. Structure of Solid State Materials

Real Crystals - 2-dim. Defects (Area Defects)

Surfaces: The interface is not sharply defined, since the surface can be modified by chemical processes, such as oxidation

Air

<table>
<thead>
<tr>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
</tr>
</tbody>
</table>

Stacking faults
Occur in cubic face-centred structures for example

Normal stacking sequence:
ABCABCABCABC

With stacking fault:
ABCABCACABC

Leads to the formation of grain boundaries

Grain boundaries: Most crystals are polycrystalline and therefore possess a large number of crystalline areas, that are divided by grain boundaries
2. Structure of Solid State Materials

Real Crystals - 3-dim. Defects (Spatial Defects)

- **Voids**
  - Filled by vacuum or gas (gas bubble)
  - Cosmology: Density fluctuations

- **Micro cracks**
  - Are treated as 2-dimensional defects

- **Precipitations**
  - Completely different phase, fully embedded within the matrix of the crystal (filled voids)
  - Examples:
    - SiO$_2$-particles in Si
    - CuAl$_2$ in Al
    - C (graphite) in cast iron

Voids in stainless steel
For comparison $\downarrow \times 10^{28}$
2. Structure of Solid State Materials

Phases and Phase Transitions

Phase: Homogeneous material system in a well defined thermodynamic state

The macroscopically observable phase state, i.e. for a one-component system, the states of aggregation solid (s), liquid (l) and gaseous (g), is a function of independent state variables, namely temperature $T$ and pressure $P$

For a two- or multi-component system, the phase state is additionally dependent on the composition $x$, whereby the solid phase can “freeze out” at a variety of different compositions.

Additionally, a given composition can exist in different crystal structures (polymorphism).

The phase state has a impact on dependent state variables (functions), such as $V$, $U$, $H$, $S$, $F$, $G$, polarisation, magnetisation, electrical resistance, ferroelectricity, etc.
Phases and Phase Transitions

Phase Transitions
Upon a change of one of the independent variables \((p, T, x)\), a non-differentiable point occurs in at least one of the state functions, e.g. \(G(p, T)\)

Phase transitions of the first order show a discontinuity in the first derivation of the state functions

- Melting of Hg\((s)\) at \(-39 \, ^\circ C\)
- Vaporisation of NH\(_3\)(l) at \(-33 \, ^\circ C\)
- Sublimation of CO\(_2\)(s) at -78 \, ^\circ C\)
Phases and Phase Transitions

Phase Transitions

Upon a change of one of the independent variables (p, T, x), a non-differentiable point occurs in at least one of the state functions, e.g. G(p,T)

Phase transitions of the second order show a discontinuity in the second derivation of the state functions

- Glass transition of polystyrene at ca. 100 °C
- Transition to superconducting solid phase of metals (4.15 K for Hg)
2. Structure of Solid State Materials

Phase Diagrams of Aggregate States: pT-Diagrams

Phase diagram of CO$_2$

Phase diagram of H$_2$O

Lit.: Chemie in unserer Zeit 37 (2003) 32
Phase Diagrams – Solid Solutions

Complete miscibility in solid state

Prerequisites
1. The pure materials must crystallise in the same crystal structure (isotypic)
2. The (an-) cations should be of comparable size
3. The individual components of a solid solution should exhibit similar chemical behaviour

Example
System Ag-Au
2. Structure of Solid State Materials

Phase Diagrams – Solid Solutions

Limited miscibility in solid state

Example
System Cu-Ag

Solubility
- 15 atom percent Cu in Ag
- 5 atom percent Ag in Cu
Phase Diagrams – Solid Solutions

No miscibility

Example
System Al$_2$O$_3$-CaO
(important for concrete)

Formation of following compounds

- Al$_2$O$_3$ cubic
- CaAl$_{12}$O$_{19}$ hexagonal
- CaAl$_4$O$_7$ monoclinic
- CaAl$_2$O$_4$ monoclinic
- Ca$_{12}$Al$_{14}$O$_{33}$ cubic
- Ca$_3$Al$_2$O$_6$ cubic
- CaO cubic