Fundamentals of Material Science

Content

Materials are like people – the imperfections make them interesting!

1. Classification and Relevance

- **Classes of Materials**
- **Interdisciplinary Connections to Other Science Branches**

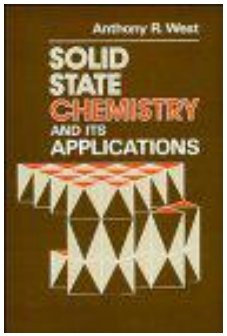
2. Structure of Solid State Materials

- **Principle Concepts and Classifications**
- **Types of Bonding and Influences upon Structure**
- **Ideal Crystals**
- **Real Crystals**
- **Phases and Phase Transitions**
- **Phase Diagrams**

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

Literature

Solid State Chemistry



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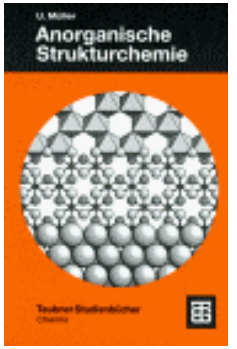
Structural Chemistry



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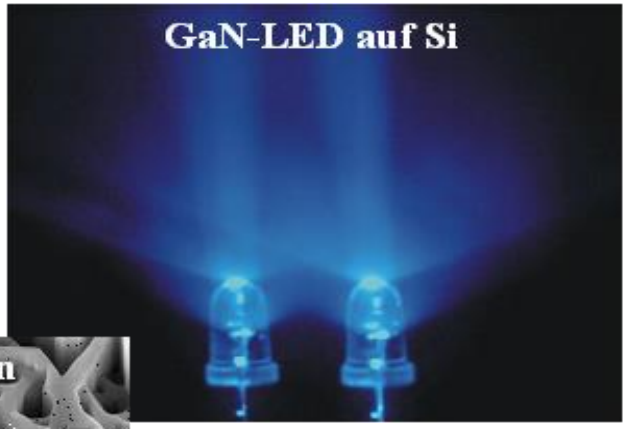
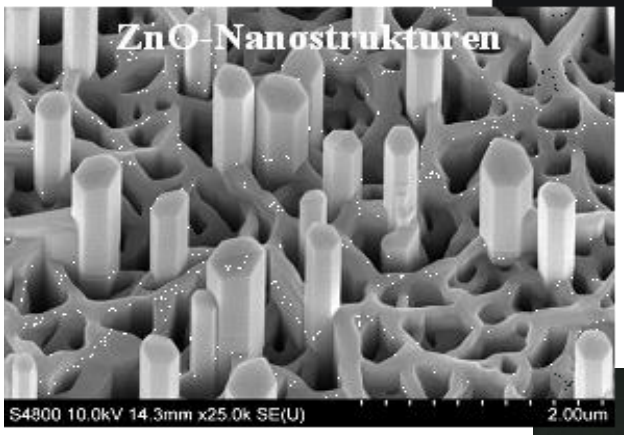
1. Classification and Relevance

Examples for Research on New Materials

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



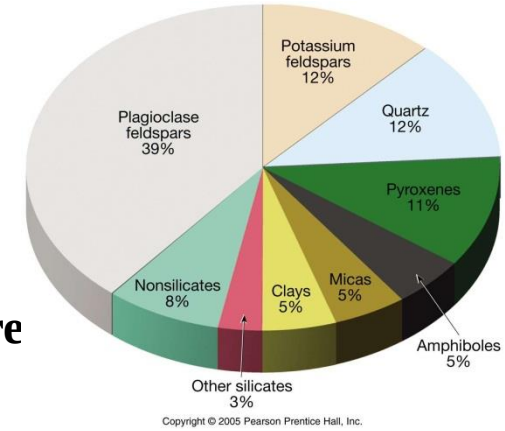
(Zn,Cd,Mg)O
- **UV/blue emitting light sources**
- **Spintronic**
- **Polariton laser**
- **Nanoparticle as emulsion additive**



Nitrides and oxynitrides, e.g.
TaO_xN_y and $(Ba,Sr,Ca)_2Si_5N_8$:Eu
- **Yellow and red pigments**
- **Phosphors for blue LEDs**
- **Hard ceramics: α-SiAlON and ß-SiAlON**

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. TiO_2 (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”

Material class (property)	Compound	(Field of) Application
Metallic conductors	Cu, Ag, Au	Electronics
Low-dimensional metallic conductors	$K_2[Pt(CN)_4]$, $(SN)_x$	
	Hexagonal C_x (graphite)	Electrodes
Semi-conductors	Si, Ge, GaAs	Diodes, transistors, ICs
	Si, $CuInSe_2$	Solar panels (photovoltaic)
	GaAs, AlInGaP, AlInGaN, ZnTe	LEDs, laser diodes, photo diodes
	$Li_{0.05}Ni_{0..95}O$	Thermistors
	Se	Photo conductors
	SnO_2:In	Transparent electrodes
Thermo-electric materials	Bi_2Te_3, PbTe	Thermo-electric cooler
Superconductors	Nb_3Sn	High-power magnets
	$YBaCu_3O_7$	Electric transport without resistance
Ion conductors	$NaAl_{11}O_{17}$ (ß-alumina), Li_3N	Long-life batteries, accumulator
	ZrO_2:Y, ZrO_2:Ca	O_2-sensors (Lambda-probe)

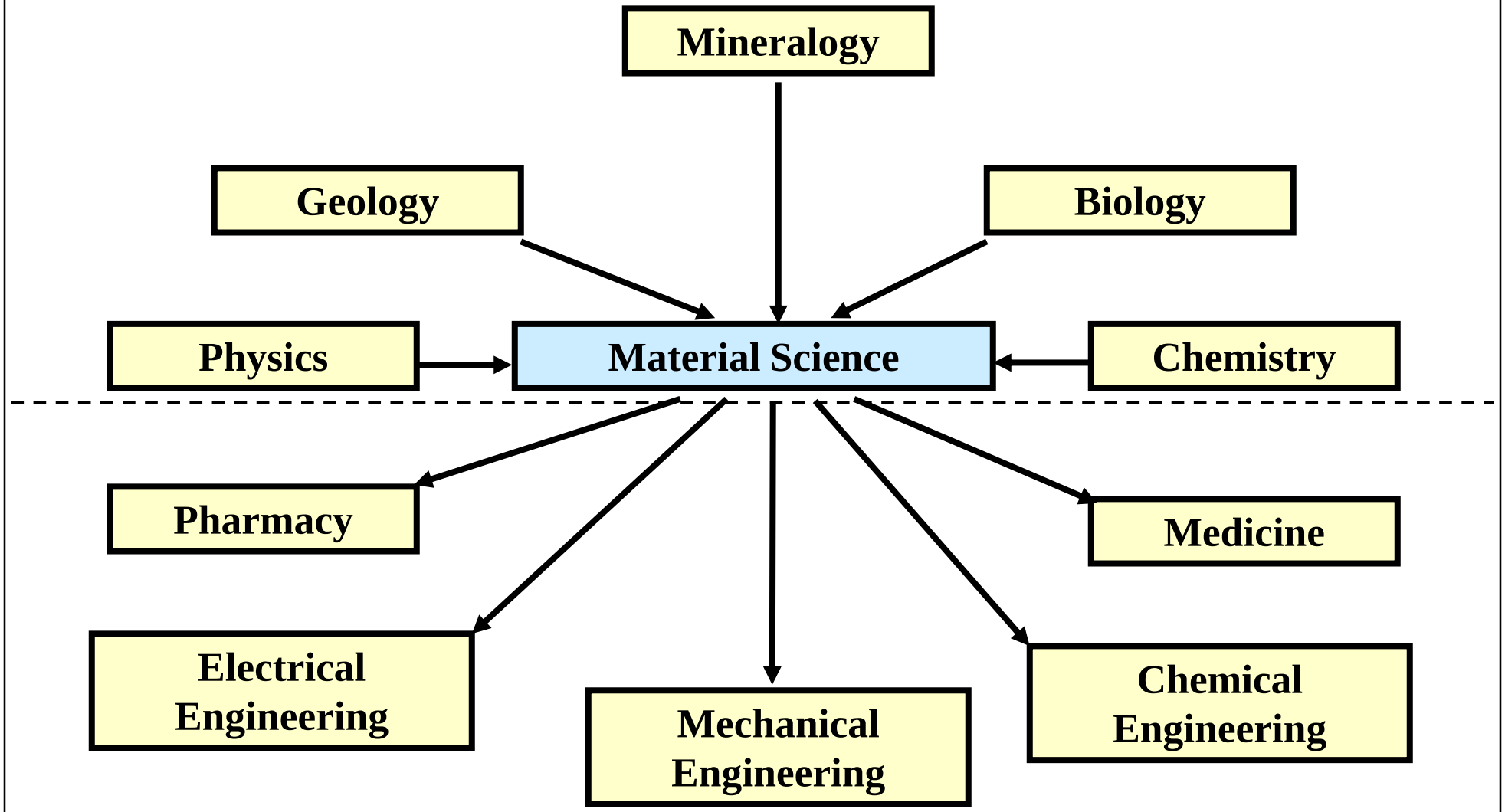
1. Classification and Relevance

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

Material class (property)	Compound	(Field of) Application
Piezo electrics	$Pb(Ti_{1-x}Zr_x)O_3$ (PZT)	Electro acoustic: microphones, speaker
Pyro electrics	ZnO	IR-detectors
Ferro electrics	$BaTiO_3$, $PbTiO_3$, SiO_2	Compensators, sensors
Ferro and Ferri magnets	$Nd_2Fe_{14}B$, $BaFe_{12}O_{19}$, $SmCo_5$	Permanent magnets
	Fe, γ-Fe_2O_3, CrO_2	Audio- and video tapes
	MFe_2O_4 (Ferrite), $ZnFe_2O_4$	Engines, transformers
	$Y_3Fe_5O_{12}$ (YIG)	Information storage
	$FeBO_3$	Magneto optics: modulation of light
Coloured pigments	$CoAl_2O_4$, CdS, Fe_2O_3, TiO_2	Colour filter, dispersion paint
Photoluminescence pigments – UV	$BaMgAl_{10}O_{17}$:Eu, Y_2O_3:Eu	Phosphorescence lamps
– blue	$Y_3Al_5O_{12}$:Ce, $Sr_2Si_5N_8$:Eu	White pcLEDs
Cathodoluminescence pigments	ZnS:Ag, ZnS:Cu, Y_2O_2S:Eu	Cathode ray tube
X-ray luminescence pigments (Scintillators)	$Bi_4Ge_3O_{12}$, Lu_2SiO_5:Ce, Gd2SiO5:Ce, Gd_2O_2S:Pr,Ce,F	Positron emission tomography
Stimulated light emission	Al_2O_3:Cr, Al_2O_3:Ti, $Y_3Al_5O_{12}$:Nd, $Lu_3Al_5O_{12}$:Nd, $LiYF_4$:Pr, YVO_4:Nd	Laser

1. Classification and Relevance

Interconnections to Other Sciences and Engineering

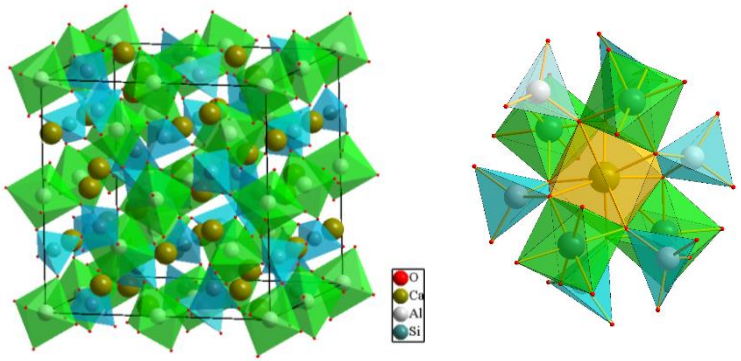


1. Classification and Relevance

Minerals as the basis for material sciences

- **Up to date: ~ 5500 Minerals known from the Earth crust (→ Mineral catalogues)**

- **„Mineral-Inspired Approach“: Search for novel material on the basis of the knowledge of minerals**

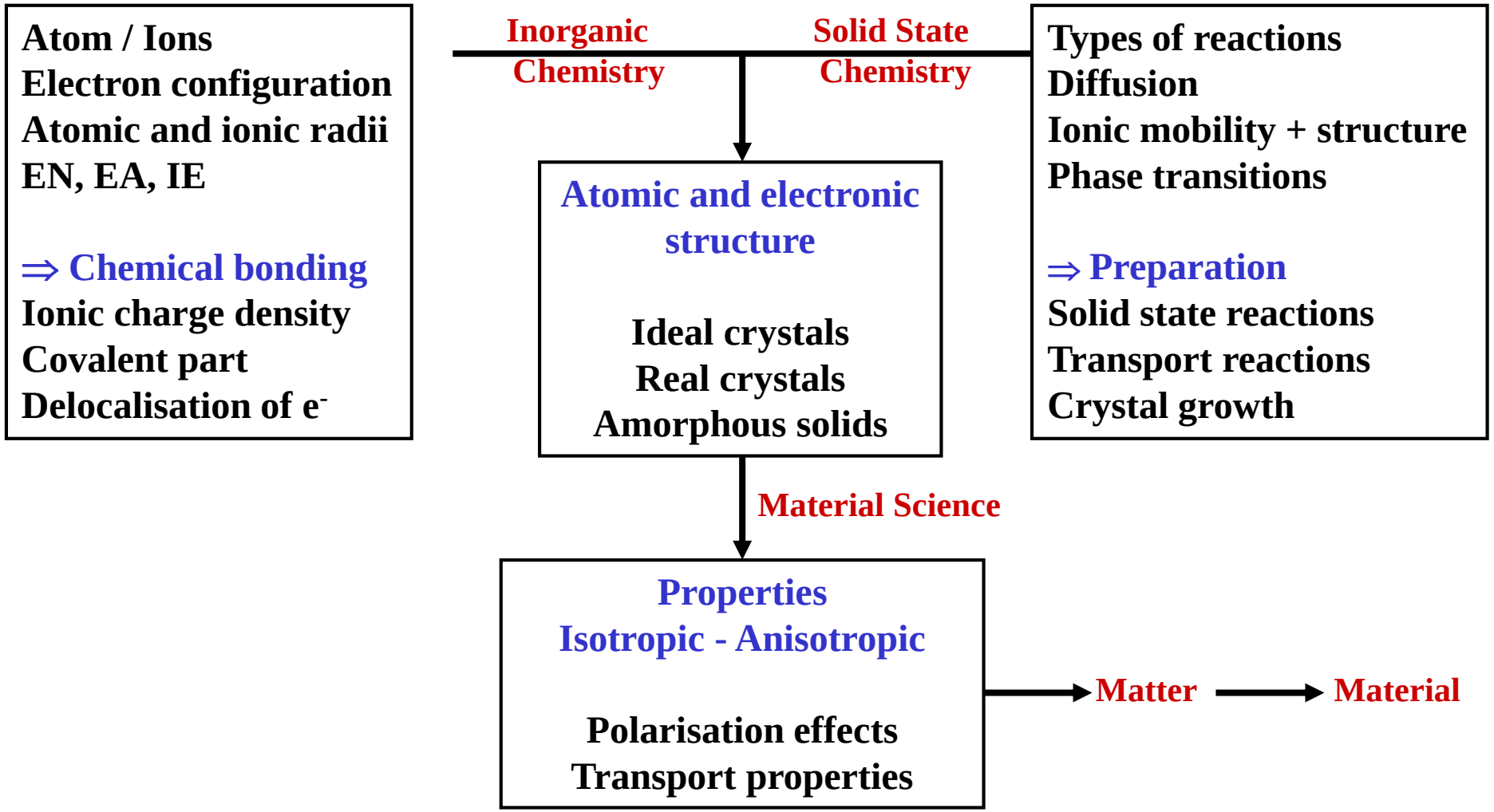


Example: Native Garnets

- **Pyrope** $Mg_3Al_2Si_3O_{12}$
- **Grossular** $Ca_3Al_2Si_3O_{12} \rightarrow Y_3Al_5O_{12}$, $Gd_3Al_5O_{12}$, $Lu_3Al_5O_{12}$, $Y_3Fe_5O_{12}$
- **Uvarovite** $Ca_3Cr_2Si_3O_{12}$
- **Andradite** $Ca_3Fe_2Si_3O_{12}$
- **Spessartine** $Mn_3Al_2Si_3O_{12}$
- **Almandine** $Fe_3Al_2Si_3O_{12}$

1. Classification and Relevance

Linkage to Chemistry



1. Classification and Relevance

Comparison and Differences between Molecular and Solid State Compounds

	Molecular Compounds	Solid State Compounds
Stoichiometry	Daltonides: defined composition	Berthollides: non-stoichiometric, since defects, formation of solid solutions, e.g. alloys, are common
Bonding	Only covalent: directed, short range, localised electrons MO-description, structure prediction	Covalent, ionic, metallic: undirected, long range, band structure, complex structure prediction
Isomerism	Only topological	Polymorphism, phase transitions
Syntheses	Endothermic chemistry: selective con- and destruction, kinetically controlled	Exothermic chemistry: diffusion, thermodynamically controlled
Purification	Volatility facilitates separation	Insoluble, no evaporation without decomposition
Characterisation	IR, MS, NMR	SEM, PSD, TEM, XRD, XRF
Properties	(No) cooperative interactions Structure-effect-correlations → Biochemistry, medicine	Cooperative interactions Structure-properties-correlations → Material science

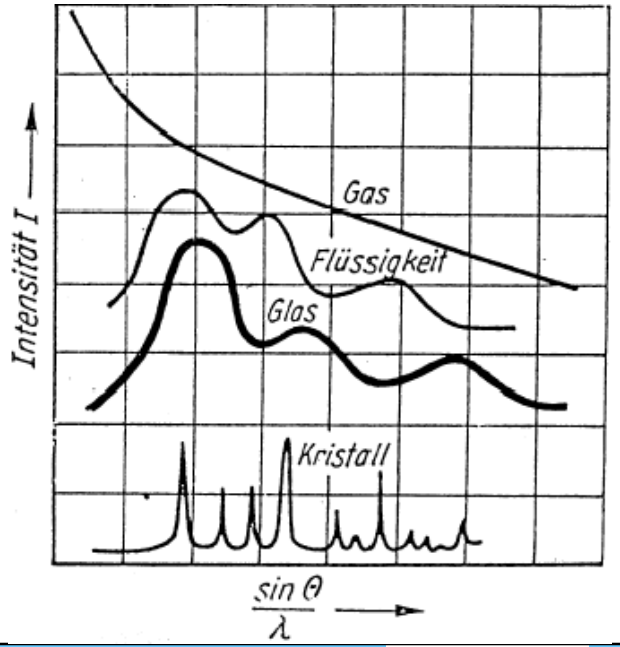
2. Structure of Solid State Materials

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

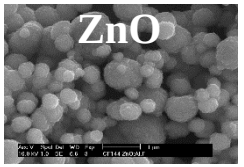
Exp.: Glasses - inorganic (quartz glass, borosilicate glass)
- organic (perspex PMMA, polycarbonate PC)

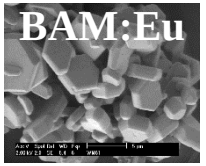
2. Structure of Solid State Materials

Proper Degree

0,1 nm | 1 nm | 10 nm | 100 nm | 1 µm | 10 µm | 100 µm | 1 mm | 10 mm | 100 mm

atoms | cluster | nanocrystals | micro crystals | single crystals





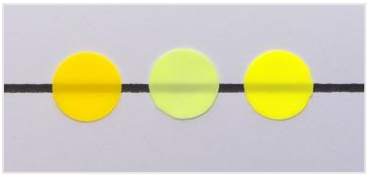
amorphous matter

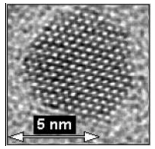
e.g. glasses

nanoceramics

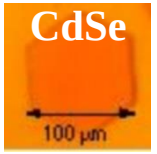
ceramics (opaque)

ceramics (translucent)





supercrystals



ceramics (transparent)

SiO_4^{4-}, PO_4^{3-}-

BO_3^{3-} glasses

windows, filters, lenses

prisms, mirrors

$CdSe$, $CsPbBr_3$

marker, µ-LED displays

$(Y_{1-x}Lu_x)_3Al_5O_{12}$:Ce

LED, laser diodes, FL, CT, PET

$Lu_3Al_5O_{12}:SE^{3+}$

SE = Ce - Yb

solid state laser

high energy physics

2. Structure of Solid State Materials

Classification – Crystal Lattice

Binary 1 type of cations

Ternary 2 types of cations

Quaternary 3 types of cations

No solid solutions!

	Halides	Oxides	Nitrides	Sulphides
Binary	MX MX_2 MX_3 MX_4	M_2O MO M_2O_3 MO_2 M_2O_5 MO_3 M_2O_7 MO_4	M_3N M_3N_2 MN M_3N_4	M_2S MS M_2S_3 MS_2 M_2S_5
Ternary	$M^1M^2X_3$ $M^1M^2X_4$ $M^1M^2X_5$ $M^1M^2X_6$	$M^1{}_2M^2O_2$ $M^1M^2O_3$ $M^1M^2{}_2O_4$ $M^1M^2{}_4O_7$	$M^1M^2N_2$ $M^1M^2{}_2N_5$ $M^{12}M^2{}_5N_8$ $M^1{}_3M^2{}_6N_{11}$	$M^1{}_2M^2S_2$ $M^1M^2S_3$ $M^1M^2{}_2S_4$ $M^1{}_2M^2{}_4S_6$
Quaternary	$M_1M_2M_3X_6$	$M^1M^2{}_2M^3{}_3O_6$ $M^1M^2M^3{}_5O_{10}$ $M^1M^2M^3{}_{10}O_{17}$ $M^1M^2M^3{}_{11}O_{19}$	$M^1M^2M^3N_3$ $M^1M^2M^3{}_4N_7$ $M^1{}_3M^2M^3{}_6N_{11}$ $M^1{}_5M^2{}_5M^3{}_{11}N_{23}$	$M^1{}_2M^2M^3S_4$ $M^1M^2{}_3M^3{}_2S_5$

2. Structure of Solid State Materials

Classification – Survey of the Different Types of Compounds

Group	Type of compound	Examples
A	Elements	A1: Cu-Typ c.c.p., A2: W-type b.c.c., A3: Mg-ype h.c.p., A4: diamond-type
B	AB	B1: NaCl, B2: CsCl, B12: BN
C	AB_2	C4: TiO_2, C6: CdI_2
D	A_mB_n	D1: NH_3
E	More than 2 types of atoms without connecting building units	PbFCl
F	Building units consisting of 2 or 3 atoms	F1: KCN
G	Building units consisting of 4 atoms	G1: $MgCO_3$
H	Building units consisting of 5 atoms	H2: $BaSO_4$
L	Alloys	CuAu
M	Mixed crystals	$(Y,Eu)_2O_3$
O	Organic compounds	O1: CH_4
S	Silicates	Mg_2SiO_4

2. Structure of Solid State Materials

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, Ti_2H, Fe_2N

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.: $La_{1-x}Ce_xPO_4$, $Ca_{1-x}Sr_xS$, $K_{1-x}Rb_x$, $Mo_{1-x}W_x$

Formation of complete solid solutions only, if

1. **Both elements/compounds crystallise in the same type of lattice (isotypic)**
   → Vegard's rule: $a_{AB} = a_A(1-x_B) + a_Bx_B$ 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**

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 extend

Mg_2SiO_4	Forsterite	$Mg_{2-x}Zn_xSiO_4$	$x < 0.4$
Zn_2SiO_4	Willemite	$Zn_{2-x}Mg_xSiO_4$	$x < 0.4$

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

  $Ca^{II}_3Al_2Si^{IV}_3O_{12} \rightarrow (Ca^{II}_{1-a}Y^{III}_a)_3Al_2(Si^{IV}_{1-a}Al^{III}_a)_3O_{12} \rightarrow Y^{III}_3Al_2Al^{III}_3O_{12}$
- Compounds forming complete solid solutions are difficult to gain in their pure borderline stoichiometry

  $\Rightarrow$ compounds of lanthanides, such as $LnPO_4$ (monazite, xenotim) or Ln_2O_3 (bixbyite)

Notation	Chemistry	Material sci.	Laser physics
• $Zn_{2-x}Mn_xSiO_4$	$(Zn,Mn)_2SiO_4$	Zn_2SiO_4:Mn	Mn:Zn_2SiO_4
• $La_{1-x-y}Ce_xTb_yPO_4$	$(La,Ce,Tb)PO_4$	$LaPO_4$:Ce,Tb	Ce,Tb:$LaPO_4$
• $Y_{3-x}Nd_xAl_5O_{12}$	$(Y,Nd)_3Al_5O_{12}$	$Y_3Al_5O_{12}$:Nd	Nd:$Y_3Al_5O_{12}$

2. Structure of Solid State Materials

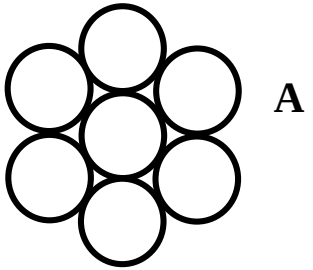
Types of Bonding and Structure Defining Parameters

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

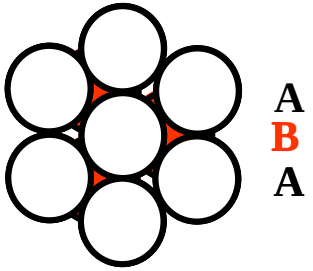
2. Structure of Solid State Materials

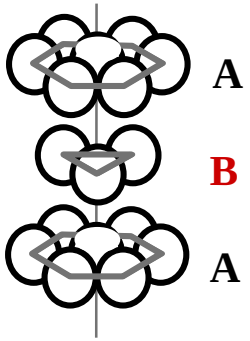
Ideal Crystals – Metallic Structures

Closely packed layer

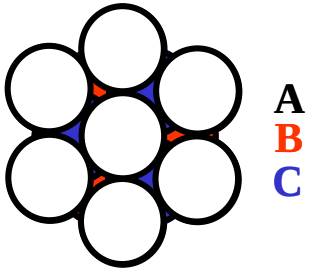


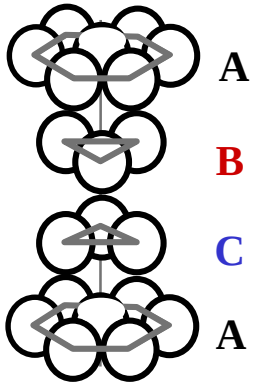
Hexagonal close packing
(h.c.p.)





Cubic close packing
(c.c.p.)



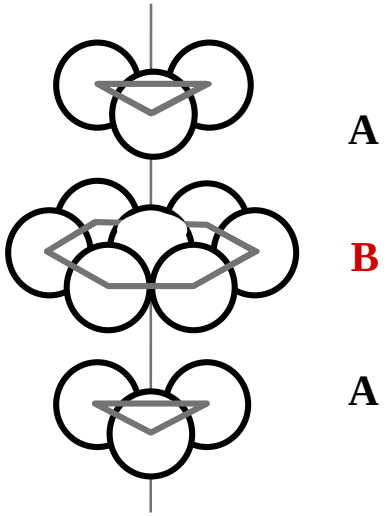


2. Structure of Solid State Materials

Ideal Crystals – Metallic Structures

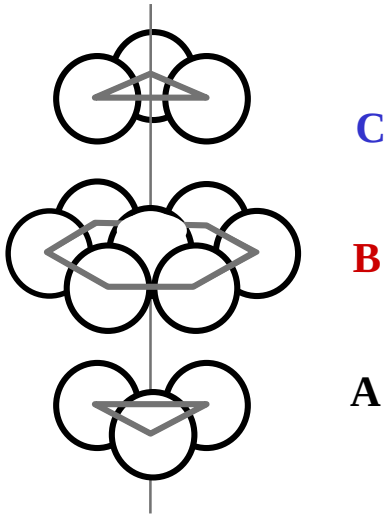
Hexagonal close packing

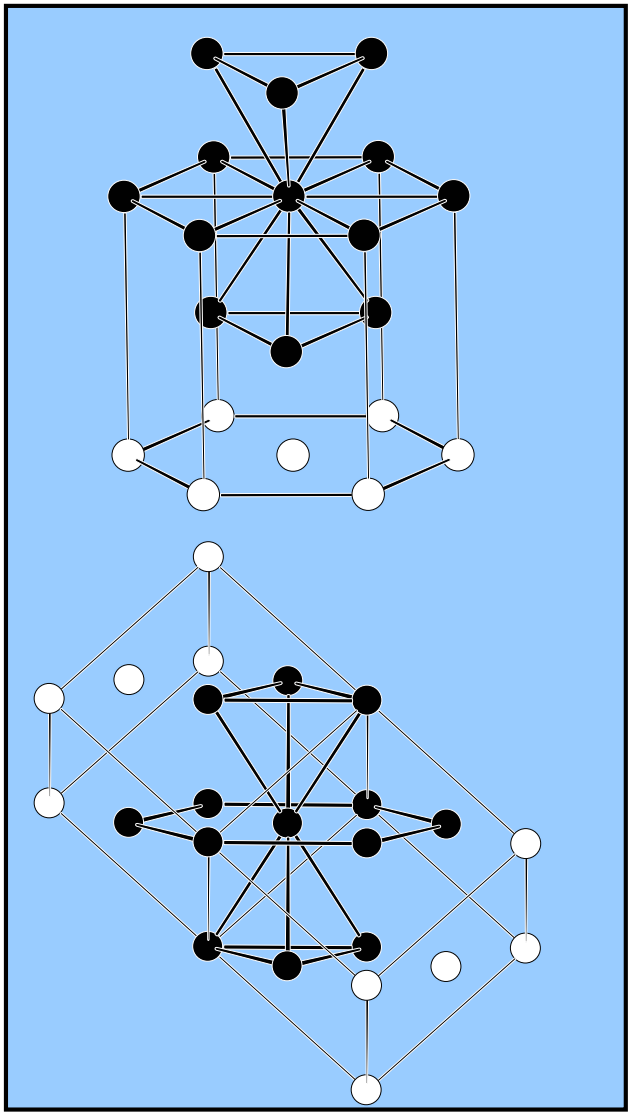
(h.c.p.)



Cubic close packing

(c.c.p.)



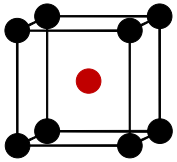


2. Structure of Solid State Materials

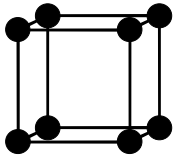
Ideal Crystals – Metallic Structures

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

Cubic body centred



Cubic primitive



Spatial occupation SO

$SO = 4/3 \cdot \pi r^3 \cdot (Z/V)$

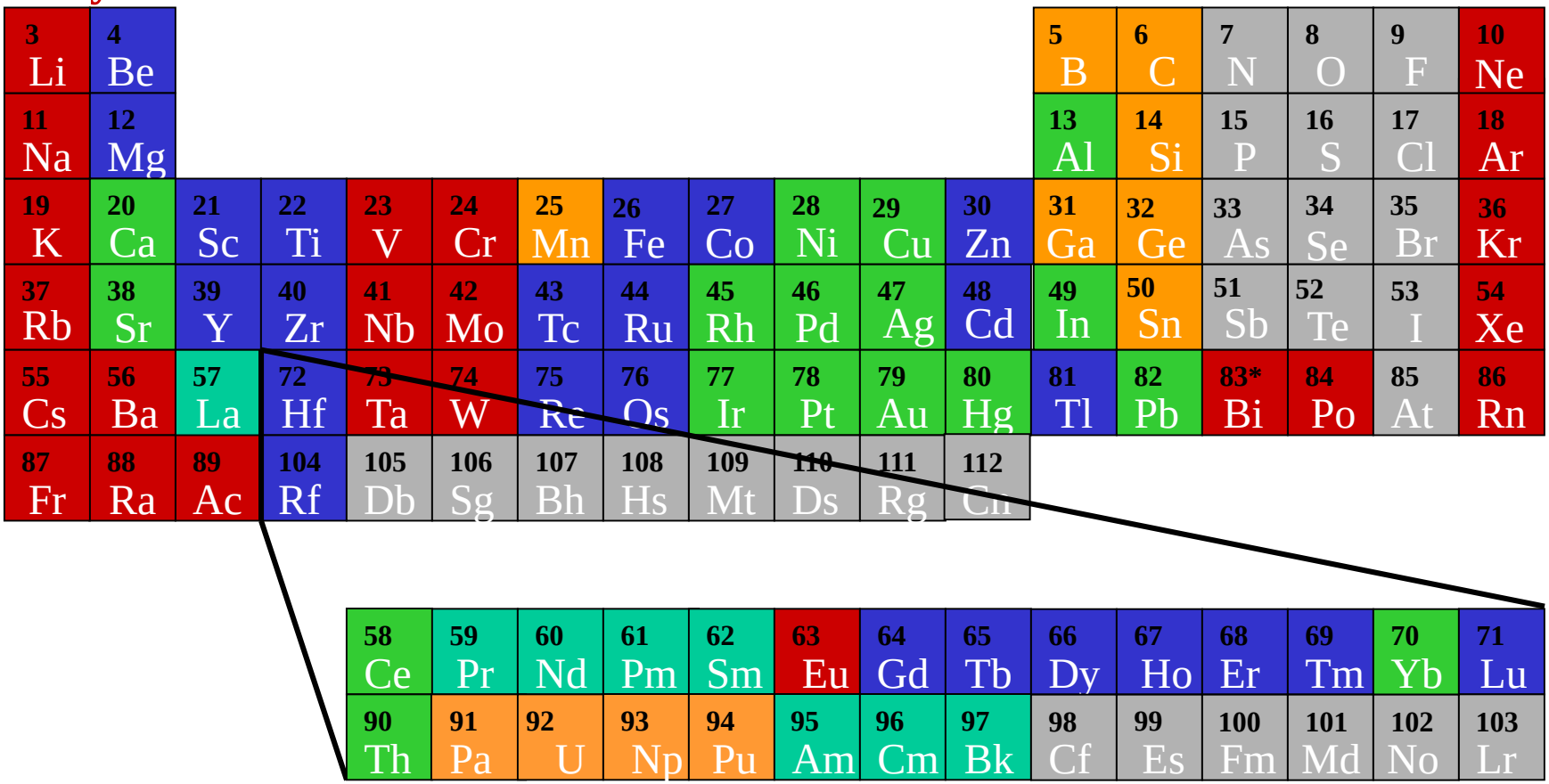
with

r = radius of the spheres

Z = number of spheres per volume

2. Structure of Solid State Materials

Ideal Crystals – Metallic Structures



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

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

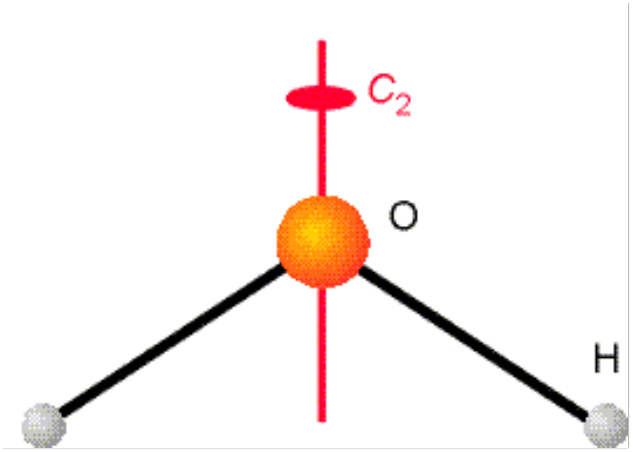
The possible combinations of these symmetry operations results in 32 crystal classes (crystallographic point groups), which can be categorized into 7 crystal systems

2. Structure of Solid State Materials

Ideal Crystals – Symmetry

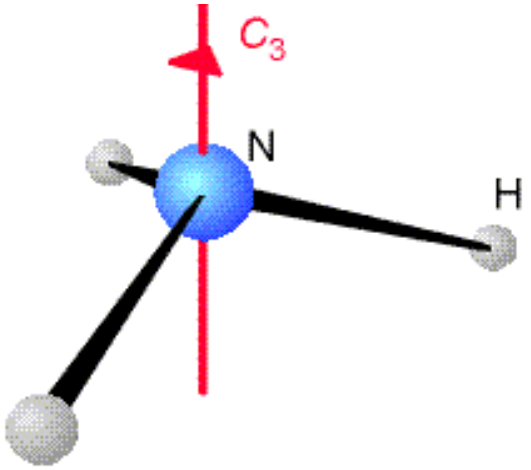
Symmetry element: **Rotation axis**

Symmetry operation: **Rotation**



Examples (molecules)

- **H_2O exhibits a two-fold axis**
  360°/2 = 180°
  After rotation by 180° the atoms appear at the same position as before



- **NH_3 exhibits a three-fold axis**
  360°/3 = 120°
  Atoms appear at their given position after rotation by 120° and 240°

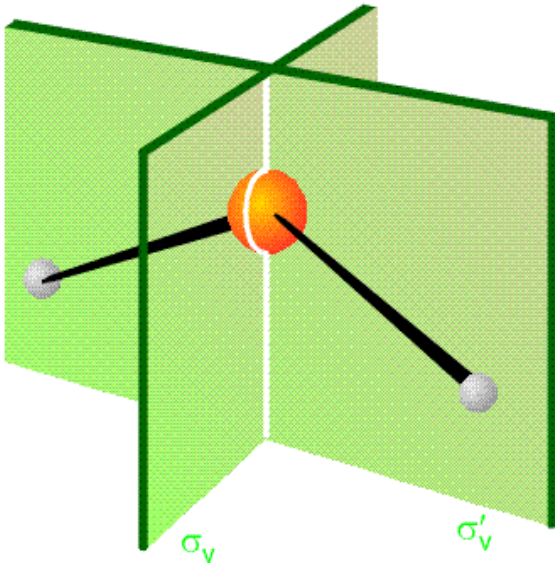
- **XeF_4 exhibits a four-fold axis**
  360°/4 = 90°
  Atoms appear at their given position after rotation by 90°, 180° and 270°

2. Structure of Solid State Materials

Ideal Crystals – Symmetry

Symmetry element: **Mirror plane**

Symmetry operation: **Mirroring**



Examples

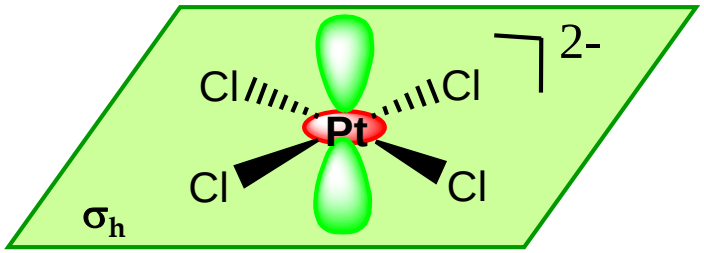
- **H_2O**

  2 mirror planes, perpendicular to one another: σ_v and σ_v'

  including main rotation axis (C_2-axis in this case)

- **Tetrachloro platinum anion $[PtCl_4]^{2-}$**

  1 mirror plane σ_h perpendicular to main rotation axis (C_4-axis in this case)

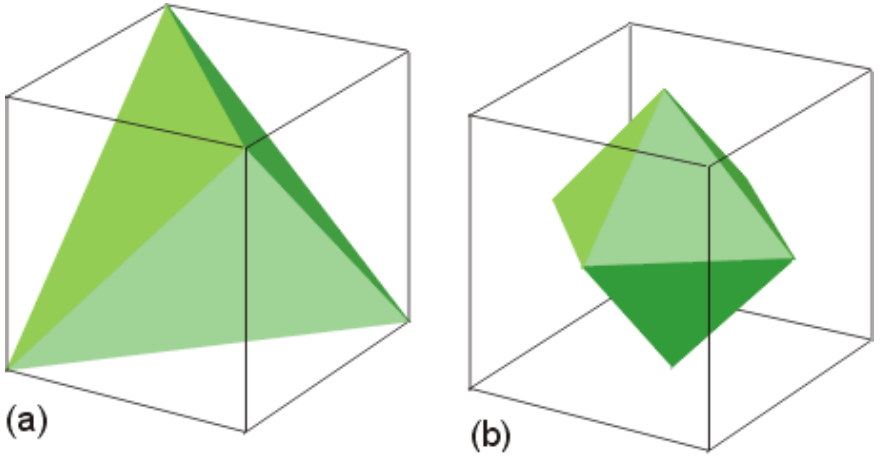


2. Structure of Solid State Materials

Ideal Crystals – Symmetry

Symmetry element: **Point**

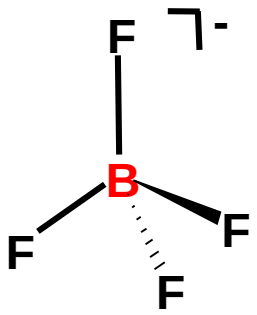
Symmetry operation: **Inversion (mirroring through a point)**

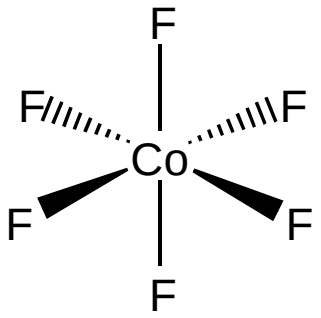


Examples

a) **Octahedra possess a inversion centre**
e.g. $[CoF_6]^{3-}$

b) **Tetrahedra possess no inversion centre**
e.g. $[BF_4]^-$





2. Structure of Solid State Materials

Ideal Crystal – Symmetry (Basic Object with Arbitrary Symmetry)

Crystal system	Crystal classes Hermann-Mauguin	Point groups Schoenflies
Triclinic	1, -1	C_1, C_i
Monoclinic	2, m, 2/m	C_2, C_s, C_{2h}
Orthorhombic	2 2 2, m m 2, m m m	D_2, C_{2v}, D_{2h}
Tetragonal	4, -4, 4/m, 4 2 2	C_4, S_4, C_{4h}, D_4
	4 m m, 4 m, 4/m m m	C_{4v}, D_{2d}, D_{4h}
Trigonal	3, -3, 3 2, 3 m, -3 m	C_3, C_{3i}, D_3, C_{3v}, D_{3d}
Hexagonal	6, -6, 6/m, 6 2 2	C_6, C_{3h}, C_{6h}
	6 m m, -6 m 2, 6/m m m	D_6, C_{6v}, D_{3h}, D_{6h}
Cubic	2 3, m 3, 4 3 2, -4 3 m, m 3 m	T, T_h, O, T_d, O_h

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 (α, β, γ)**

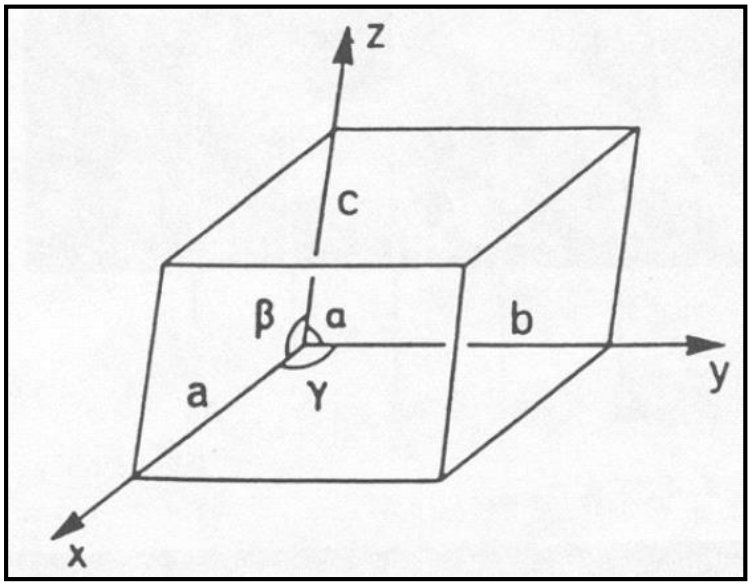
By definition

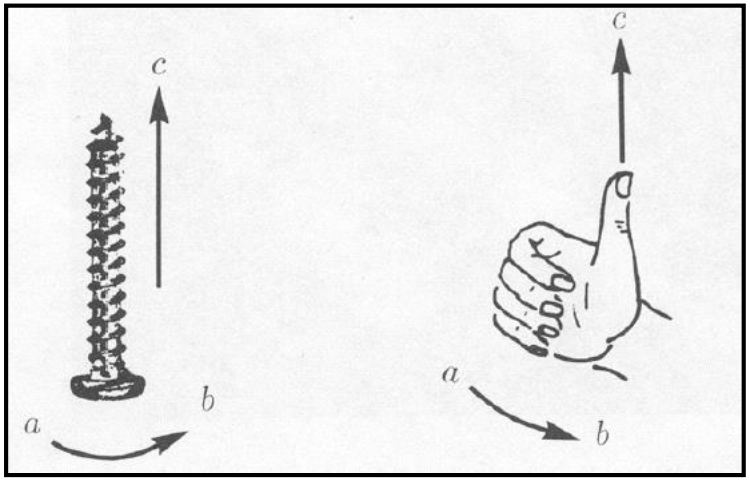
- **α = angle between b and c**
- **β = angle between a and c**
- **γ = angle between a and b**

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**

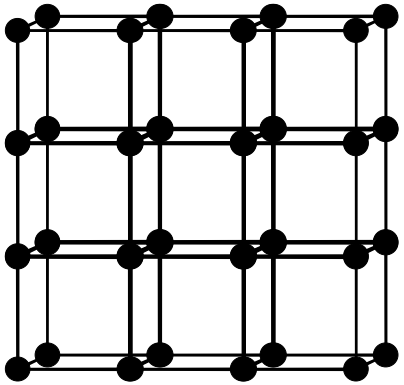




2. Structure of Solid State Materials

Ideal Crystals – Unit Cell

Packing of cubic 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

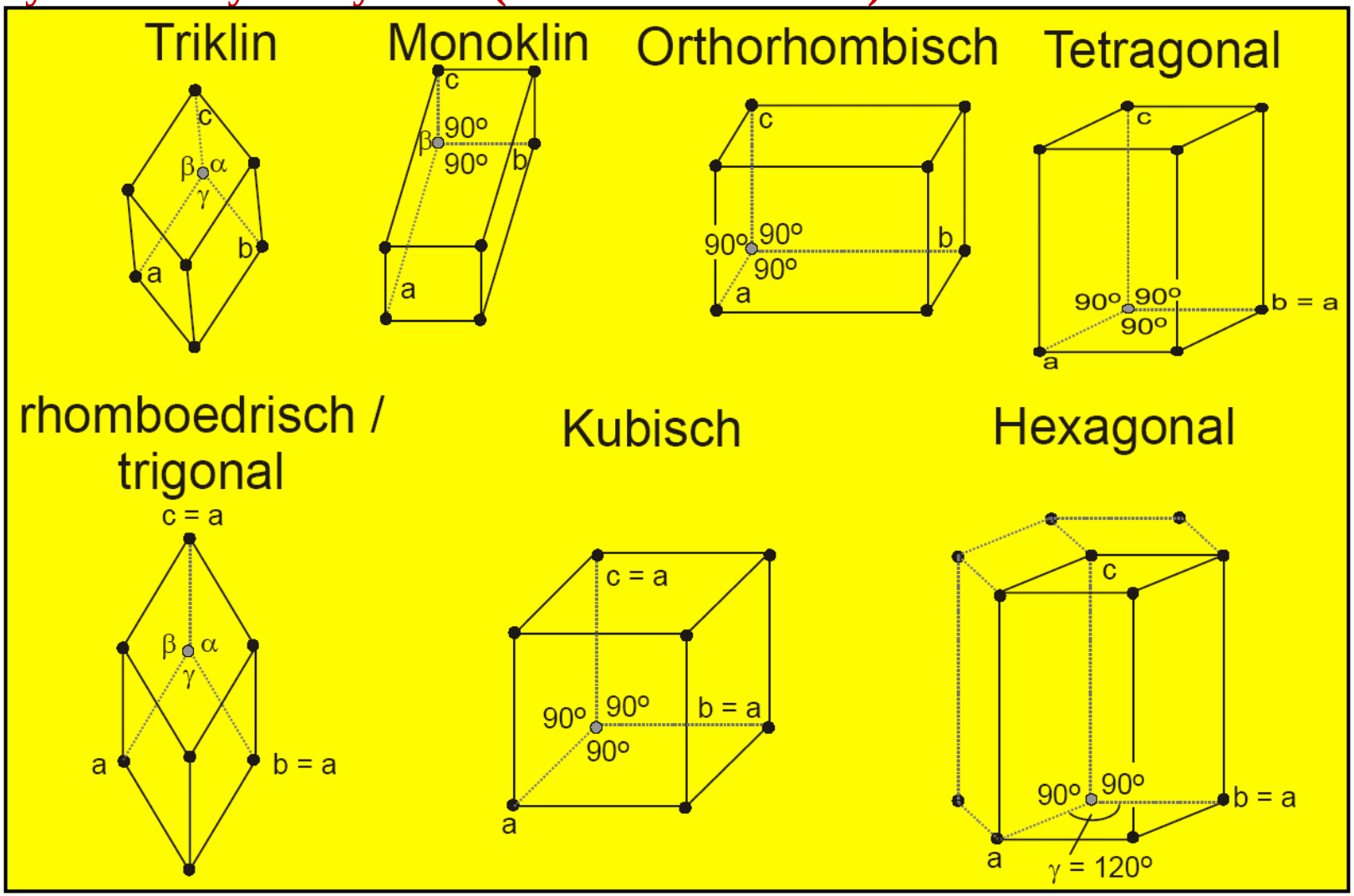
2. Structure of Solid State Materials

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

Cristal system	Unit cell	Minimal symmetry requirements
Triclinic	$\alpha \neq \beta \neq \gamma$ $a \neq b \neq c$	None
Monoclinic	$\alpha = \gamma = 90°, \beta \neq 90°$ $a \neq b \neq c$	Two-fold axis or a symmetry plane
Orthorhombic	$\alpha = \beta = \gamma = 90°$ $a \neq b \neq c$	Combination of three perpendicular two-fold axes or symmetry planes
Tetragonal	$\alpha = \beta = \gamma = 90°$ $a = b \neq c$	Four-fold rotation axis or a four-fold inversion axis
Trigonal	$\alpha = \beta = \gamma \neq 90°$ $a = b = c$	One three-fold axis
Hexagonal	$\alpha = \beta = 90°$ $\gamma = 120°$ $a = b \neq c$	Six-fold rotation axis or a six-fold inversion axis
Cubic	$\alpha = \beta = \gamma = 90°$ $a = b = c$	Four three-fold axes, intersecting under 109.5°

2. Structure of Solid State Materials

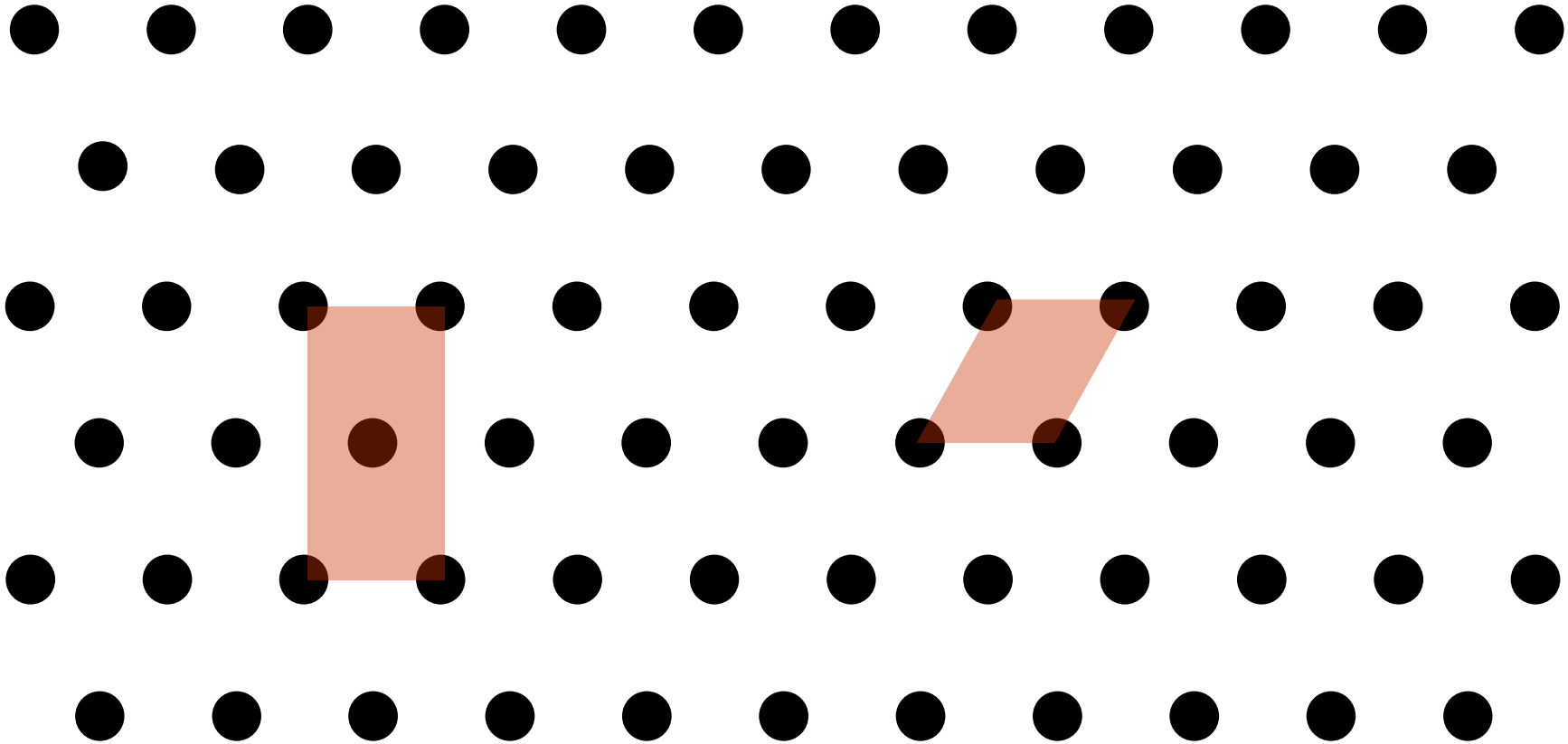
Ideal Crystals – Crystal Systems (Primitive Unit Cell)



2. Structure of Solid State Materials

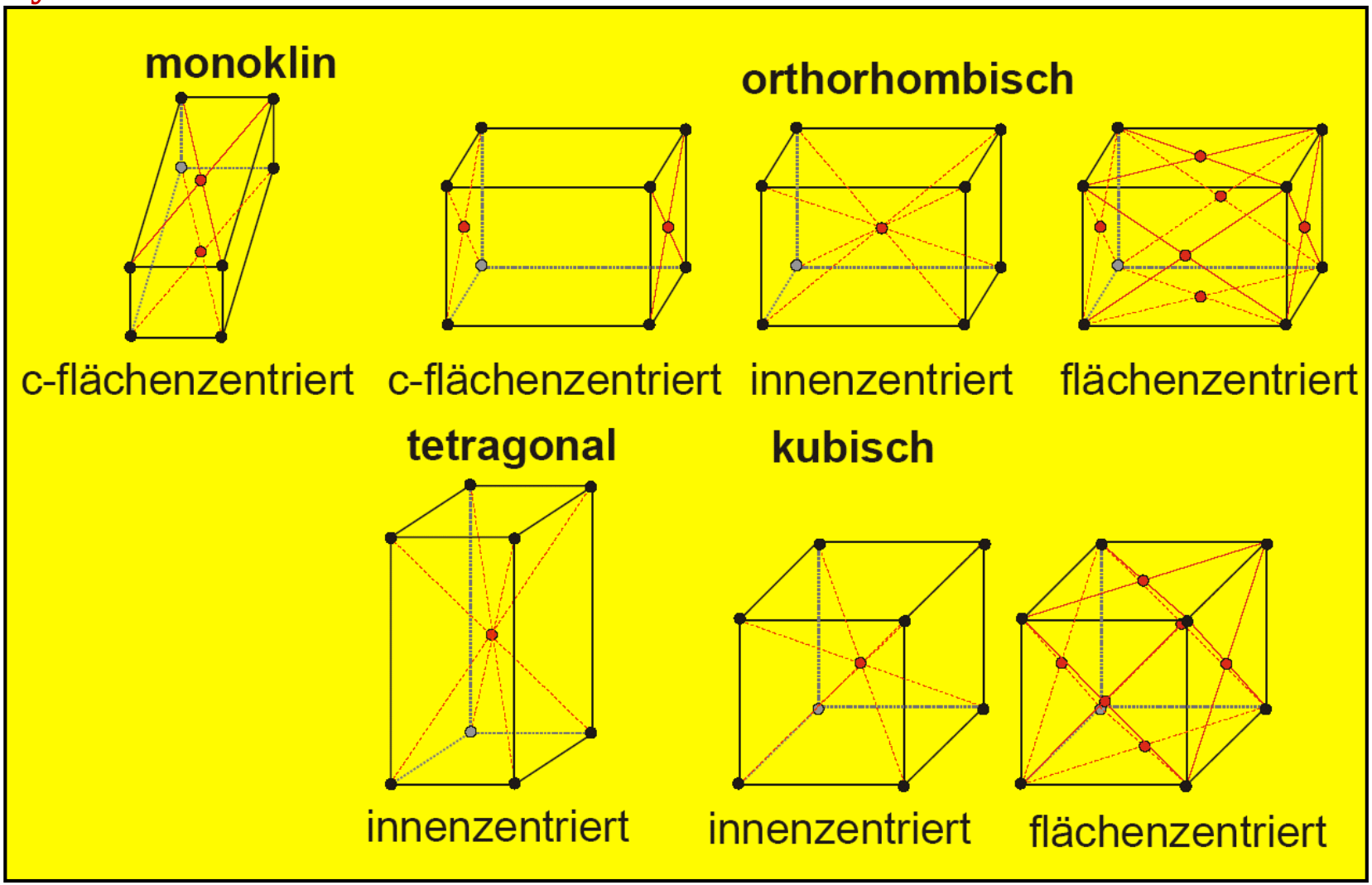
Ideal Crystals – Primitive and Centred Unit (2D: Elementary Knots)

⇒ Complete Occupation of the Space (2D: Area) without Overlapping



2. Structure of Solid State Materials

Ideal Crystals – Primitive and Centred Unit Cell

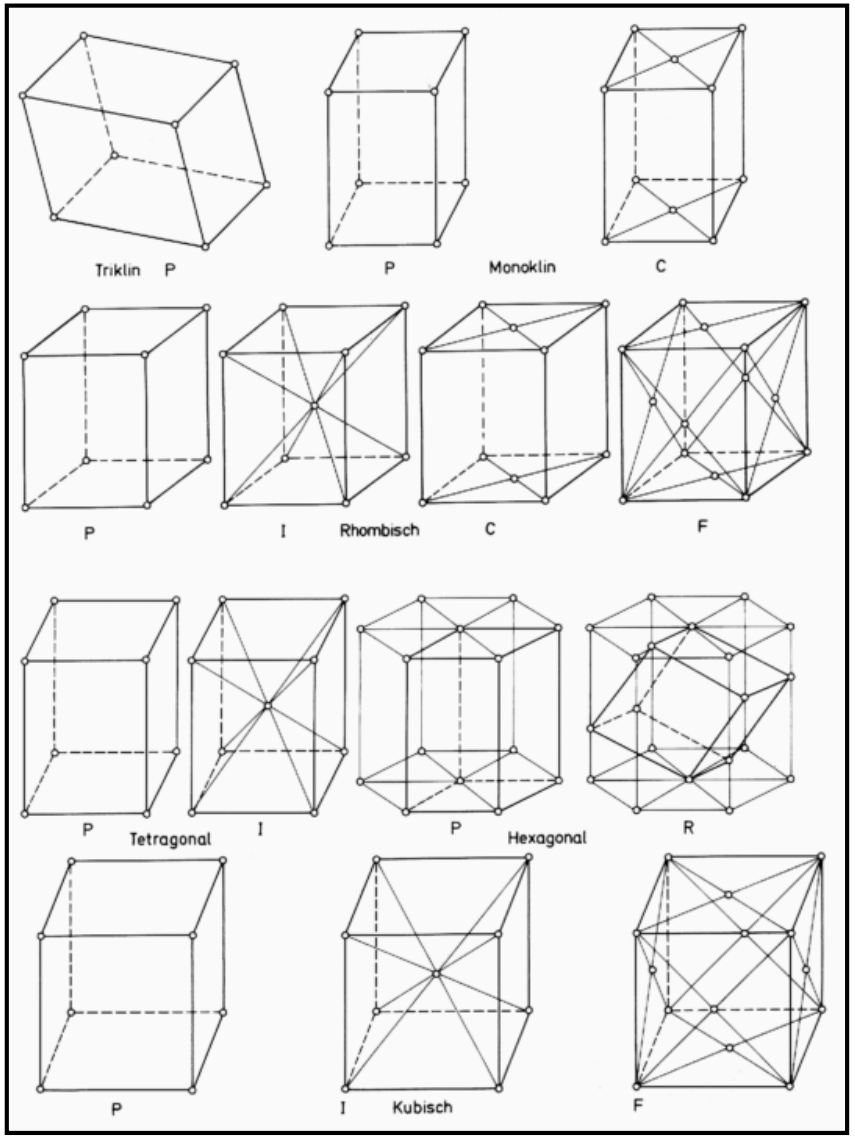


2. Structure of Solid State Materials

Ideal Crystals – Translational Lattices

Crystal system	Allowed lattices
Triclinic	P
Monoclinic	P, C
Orthorhombic	P, F, I, A or B or C
Tetragonal	P, I
Trigonal (Rhombohedral)	P or R
Hexagonal	P
Cubic	P, I, F

⇒ 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

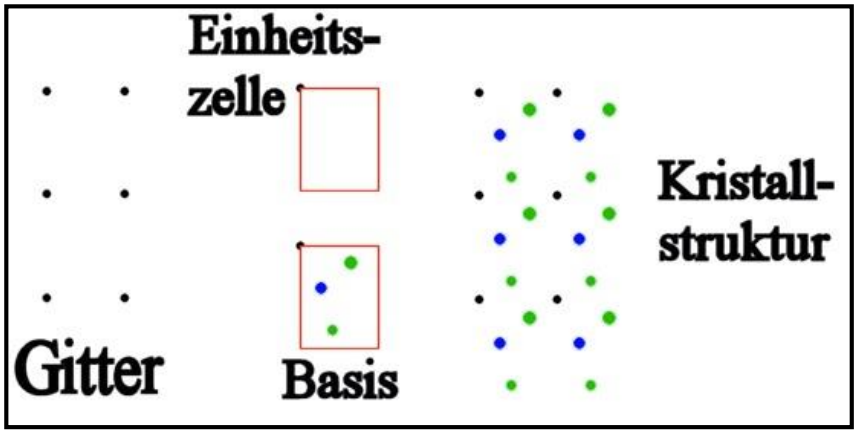
Lattice type	Symbol	Lattice points per unit cell
Primitive	P	1
Body-centred	I	2
Basis face-centred	A, B, C	2
Face-centred	F	4

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)

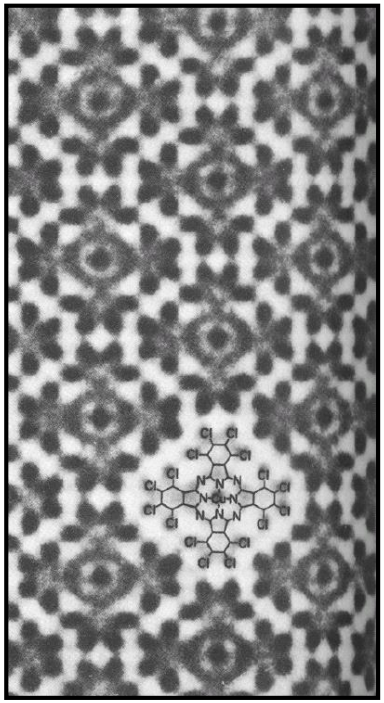
Introduction of a basis (more complex as simpel balls or points)
⇒ Further symmetry elements (8): 1 glide plane, 7 screw axes

2. Structure of Solid State Materials

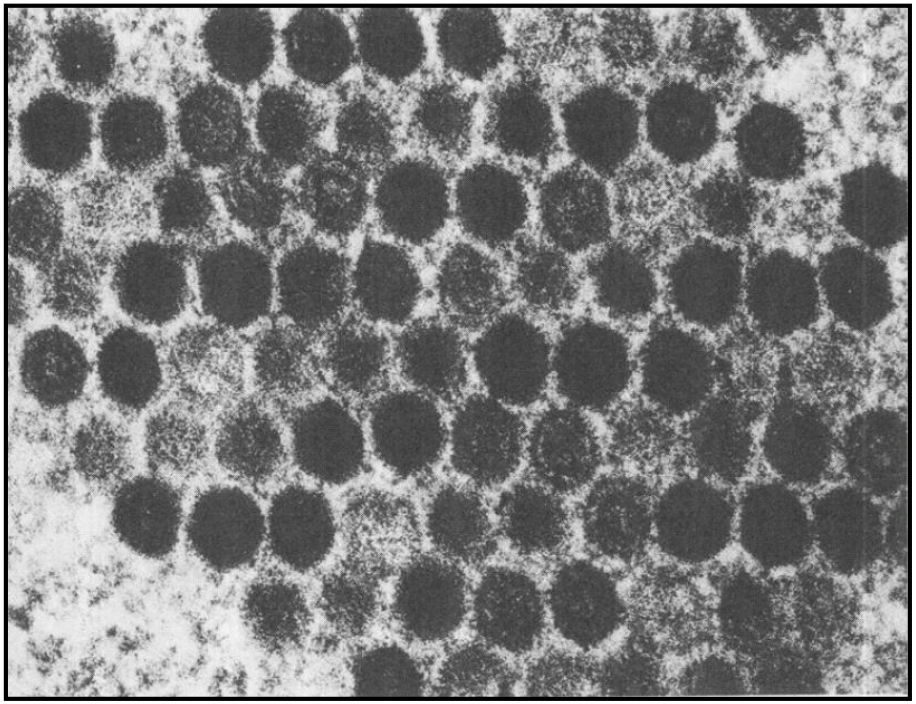
Ideal Crystal - 3-Dimensional Translational Arrangement of Building Blocks

Can be visualized by transmission electron microscopy

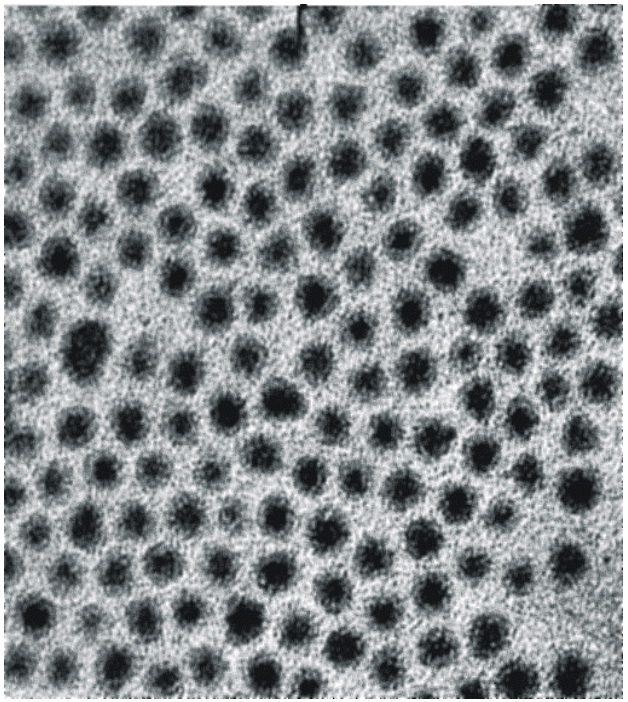
Cu-phthalocyanine



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

Space group	Symmetry Elements
Centrosymmetric	Translation, screw-axes, mirror planes, inversion centres
Non-centrosymmetric	Translation, screw-axes, mirror planes
Chiral	Translation, screw-axes (→ chiral molecules)

General notation

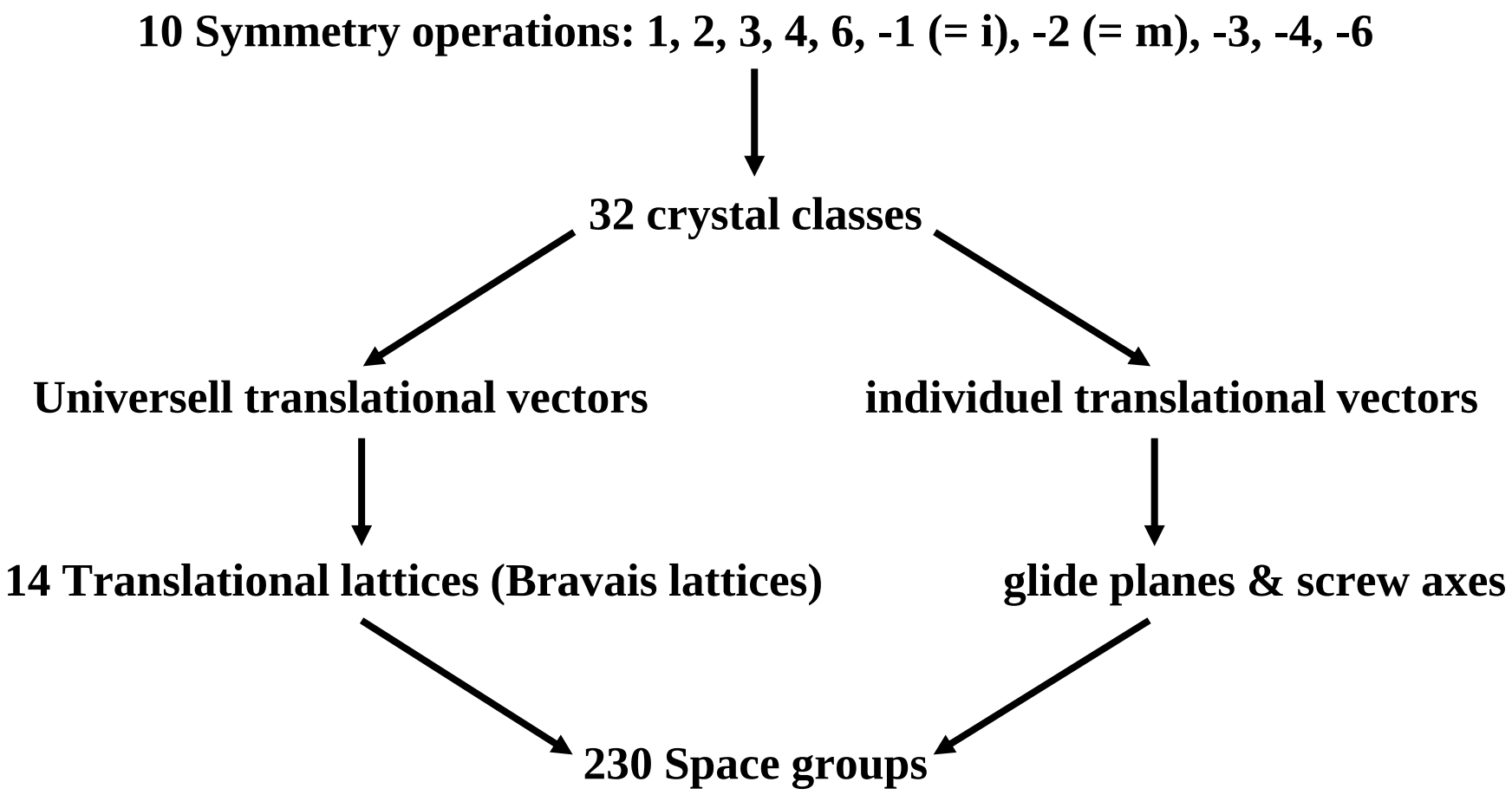
1234 (usually)

Example

Fmmm lattice type F-centred mirror plane perpendicular to a, b and c axis (La_2NiO_4)

2. Structure of Solid State Materials

Ideal Crystal – Space Groups



2. Structure of Solid State Materials

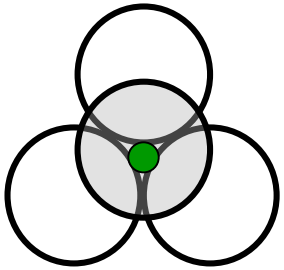
Ideal Crystals – Ionic Structures

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

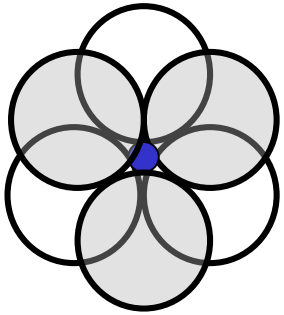
Voids: Tetrahedral or octahedral voids
usually of the cations

	For N packed particles
c.c.p.:	**(N) Octahedral sites**
	(2N) Tetrahedral sites
h.c.p.:	**(N) Octahedral sites**
	(2N) Tetrahedral sites

Tetrahedral void T_+, T_-

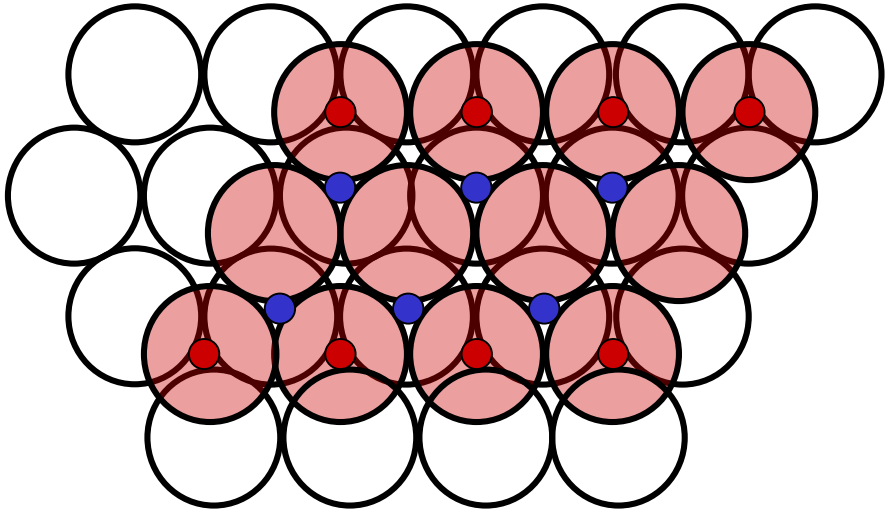


Octahedral void O



2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures



T_+

T_-

T_+

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

Anions - Arrangement	T_+	T_-	O	Structure type
c.c.p. (ABCABC...)	-	-	1	NaCl (common salt)
	1	-	-	ZnS (zinc blende)
	1/8	1/8	1/2	$MgAl_2O_4$ (spinel)
	-	-	1/2	$CdCl_2$
	1	-	-	$CuFeS_2$ (chalcopyrite)
	-	-	1/3	$CrCl_3$
	1	1	-	K_2O (antifluorite)
h.c.p. (ABAB...)	-	-	1	NiAs
	1	-	-	ZnS (wurtzite)
	-	-	1/2	CdI_2
	-	-	1/2	TiO_2 (rutile)
	-	-	1/3	Al_2O_3 (corundum)
	1/8	1/8	1/2	Mg_2SiO_4 (olivin)
	1	-	-	ß-Li_3PO_4
	1/2	1/2	-	γ-Li_3PO_4

2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB-Structures – NaCl (kitchen salt)

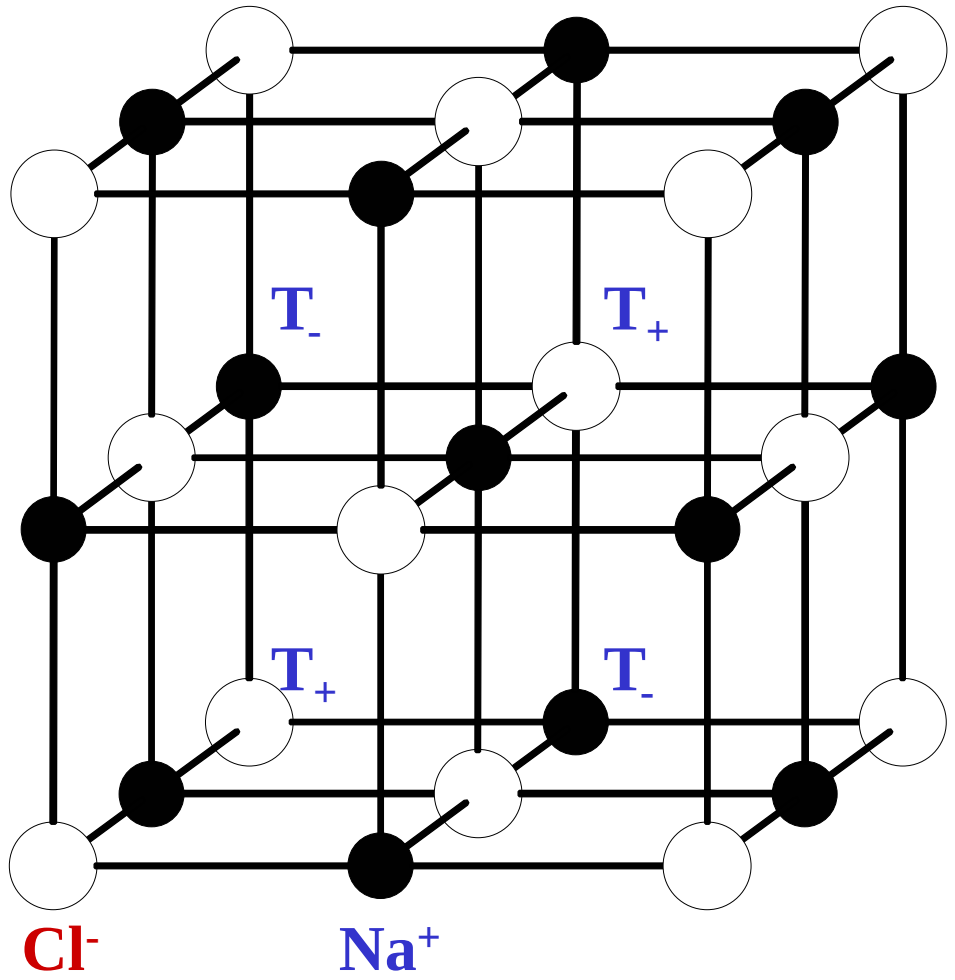
Cubic close packing of anions

Coordination 6 : 6
N = 4

Site	Occupation
O	Na^+
T_+	empty
T_-	empty

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



2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

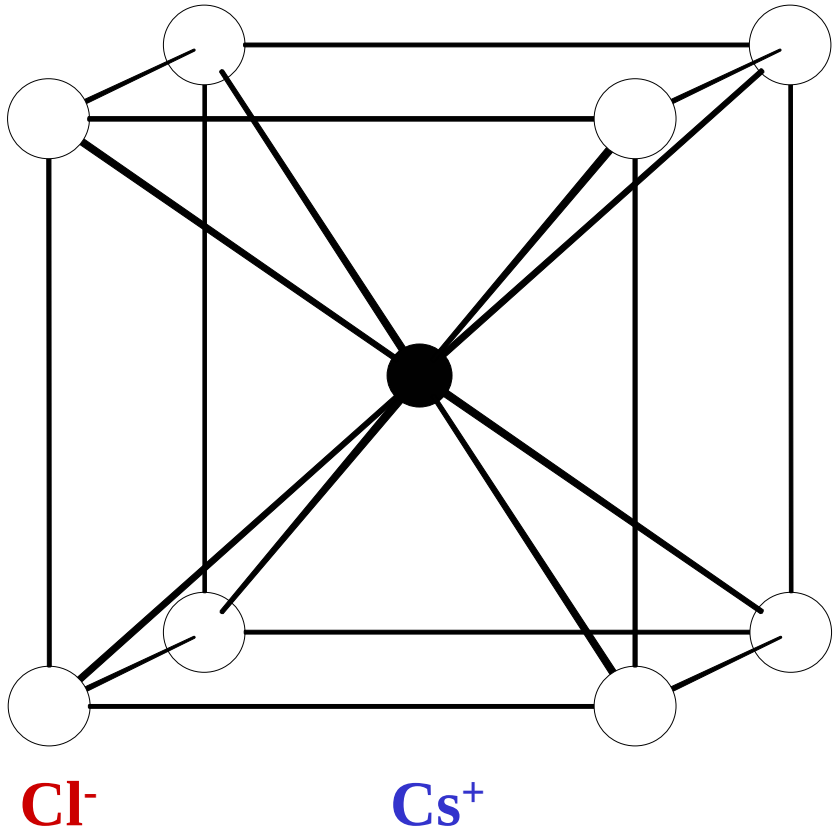
AB-Structures – CsCl (caesium chloride)

Cubic primitive packing of anions

Coordination 8 : 8
N = 1

Examples

- **CsCl, CsBr, CsI, CsCN**
- **TlCl, TlBr, TlI**
- **NH_4Cl, NH_4Br**



2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB-Structures – ZnS (zinc blende or sphalerite)

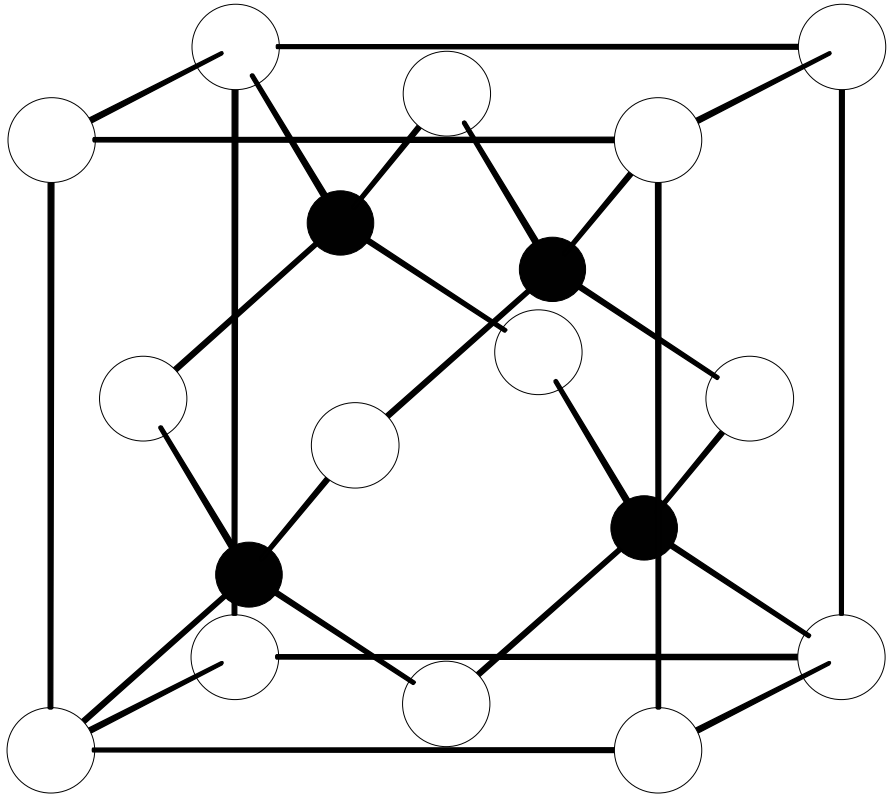
Cubic close packing of anions

Coordination 4 : 4
N = 4

Site	Occupation
O	empty
T_+	Zn^{2+}
T_-	leer

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)

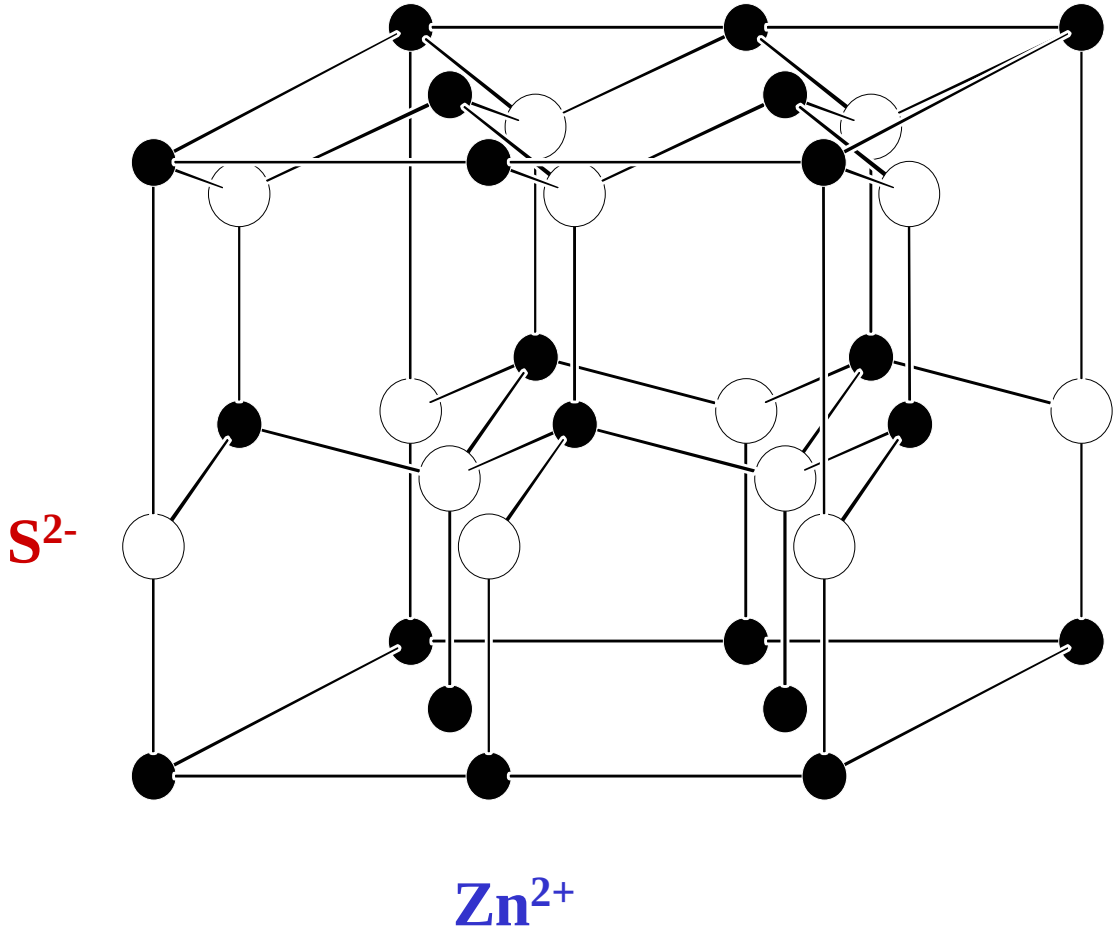
Hexagonal close packing of anions

Coordination 4 : 4
N = 4

Site	Occupation
O	empty
T_+	Zn^{2+}
T_-	empty

Examples

- ZnO, ZnS, ZnSe, ZnTe
- BeO, SiC
- CdS, CdSe
- MnS
- AlN, GaN, InN



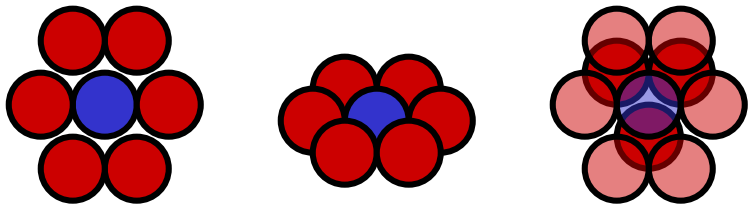
2. Structure of Solid State Materials

Ideal Crystals – Influence of the Ionic Radii

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

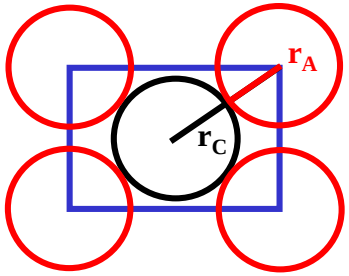
Ratio	CN	Geometry
1	12	Cubeoctahedron
0.732 - 0.999	8	Cube
0.414 - 0.732	6	Octahedron
0.225 - 0.414	4	Tetrahedron

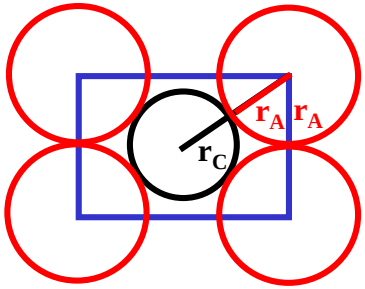
r_{Cation}/r_{Anion} = 1 is found in many metallic crystals and in some ionic crystals with extremely large cations, i.e. Cs^+

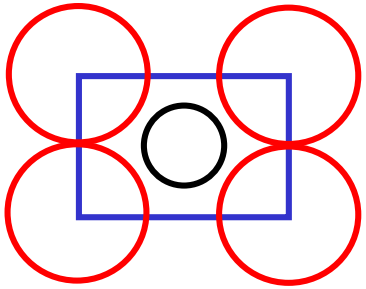


2. Structure of Solid State Materials

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

$(r_C + r_A)/r_A = \sqrt{3}/1$

$r_C/r_A = \sqrt{3}/1 - 1 = 0.732$

Anions can not get closer to the cation

$r_C/r_A < 0.732$

Example	r_C/r_A
CsCl	0.94
CsBr	0.87
TlCl	0.83
CsI	0.79

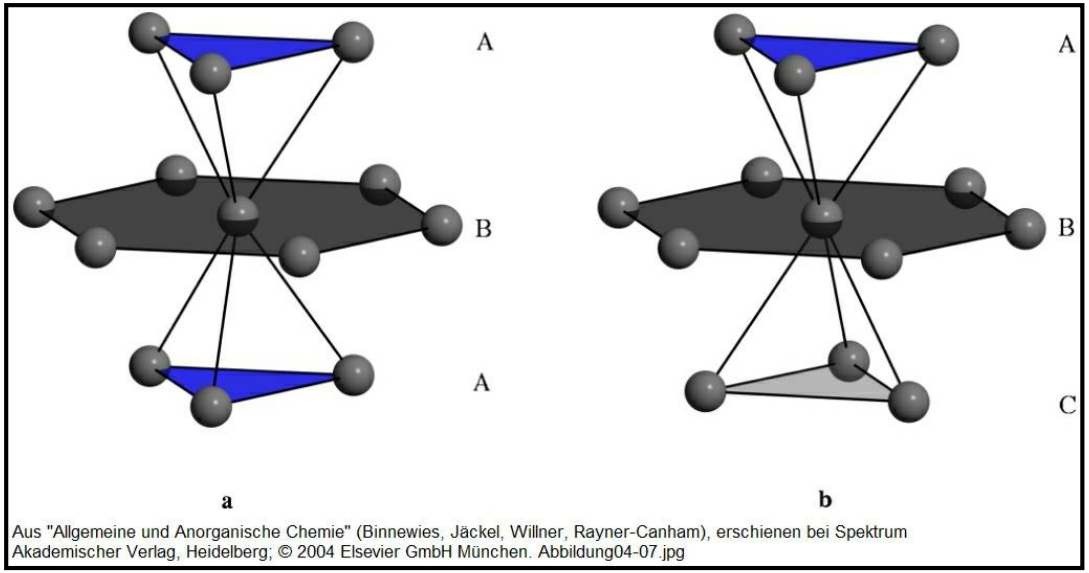
2. Structure of Solid State Materials

Ideal Crystals – For $0.414 < r_C/r_A < 0.732$ Cations Are Coordinated Octahedrally

The structure type depends on the packing of the anions

Anion packing	hexagonal close	cubic close
Layer sequence	ABABAB	ABCABCABC
Structure type	NiAs-type	NaCl-type

Example	r_C/r_A
KBr	0.71
KI	0.64
NaCl	0.56
NaBr	0.52
NaI	0.47



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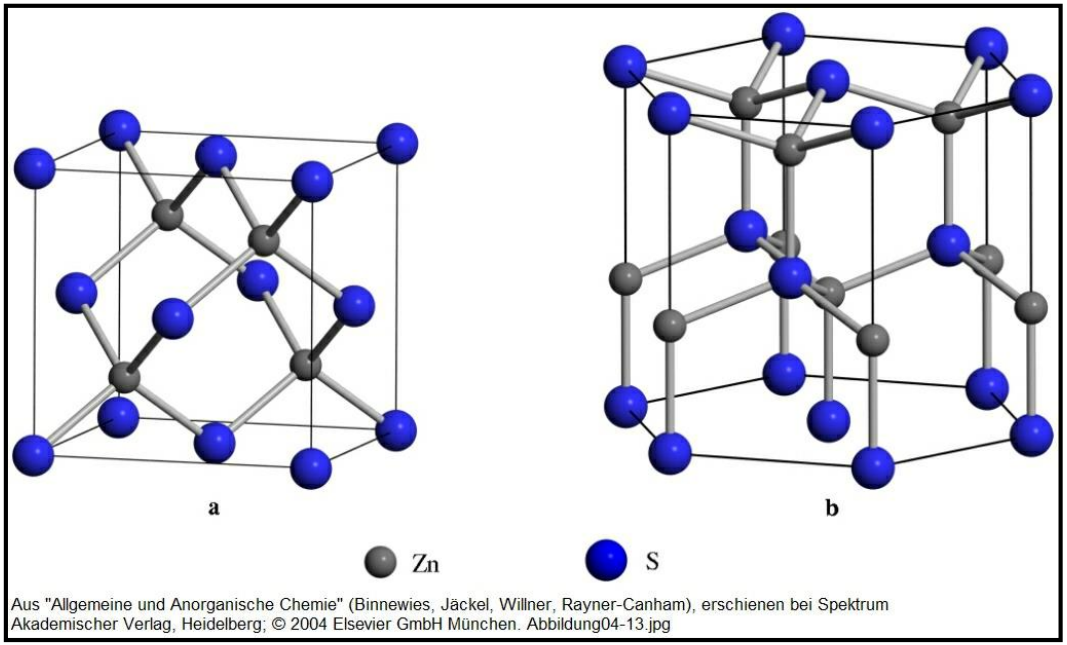
2. Structure of Solid State Materials

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

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

Anion packing	**cubic close**	**hexagonal close**
Layer sequence	**ABCABCABC**	**ABABAB**
Structure type	**Zinc blende-type**	**Wurtzite-type**

Example	r_C/r_A
BeO	0.25
BeS	0.19



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2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

AB_2-Structures – CaF_2 (Flussspat or fluorite)

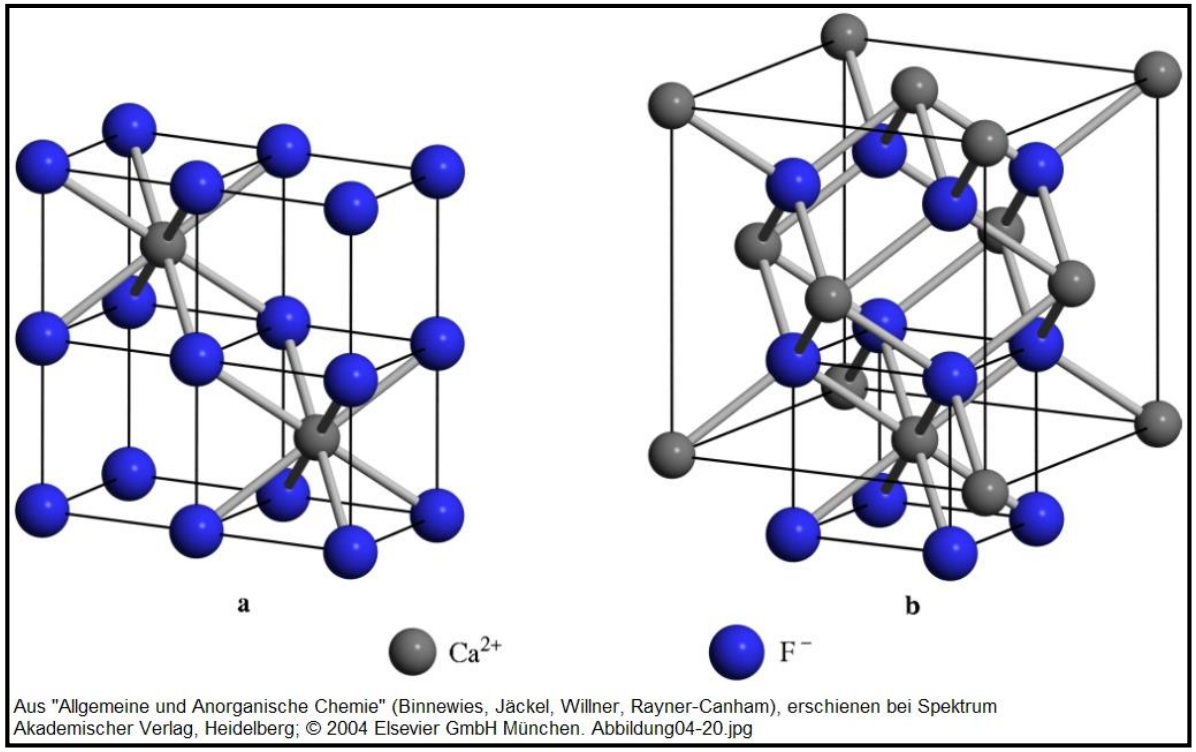
Cubic close packing of cations

Coordination 8 : 4
N = 4

Site	Occupancy
O	empty
T_+	F^-
T_-	F^-

Example

- **CaF_2, SrF_2, BaF_2**
- **$CrCl_2$, $BaCl_2$, $SrBr_2$**
- **Li_2O, Li_2S, Li_2Se, Li_2Te**



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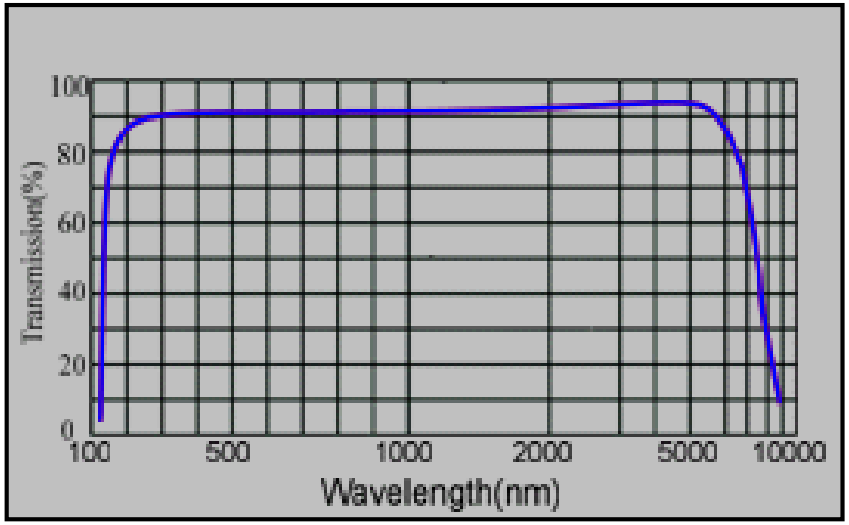
2. Structure of Solid State Materials

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)**



no UV **under UV**

2. Structure of Solid State Materials

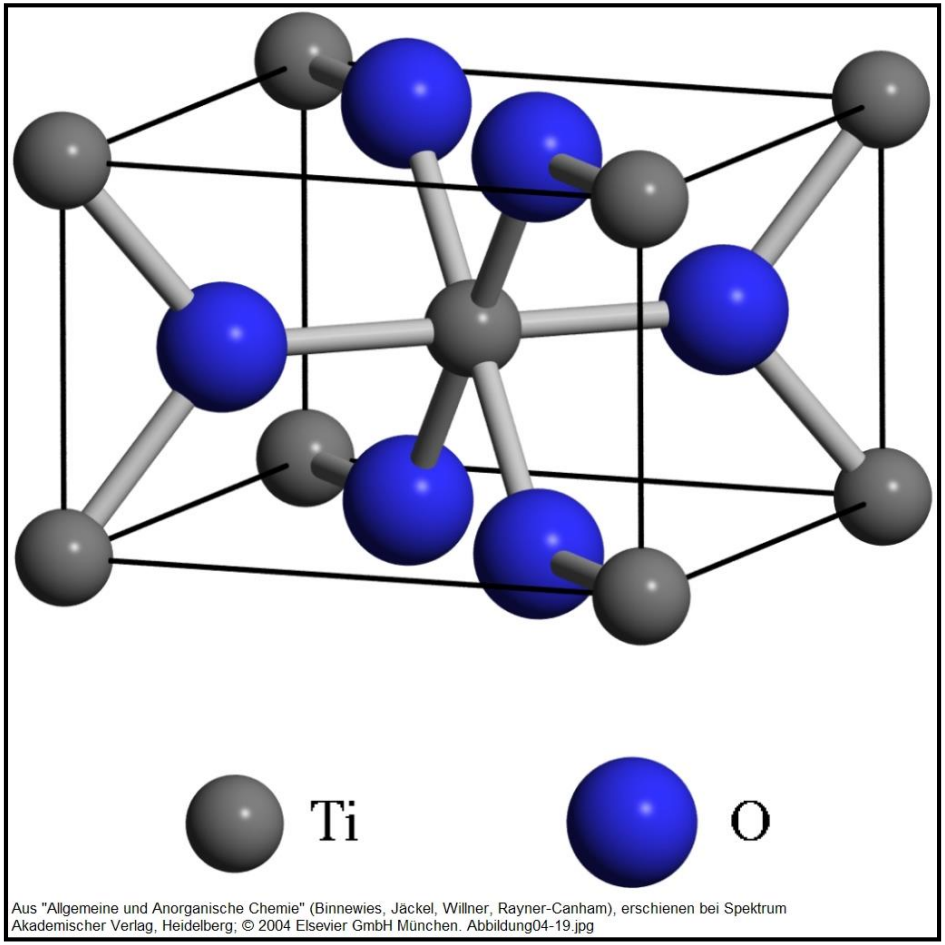
Ideal Crystals – Ionic Structures

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



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Examples

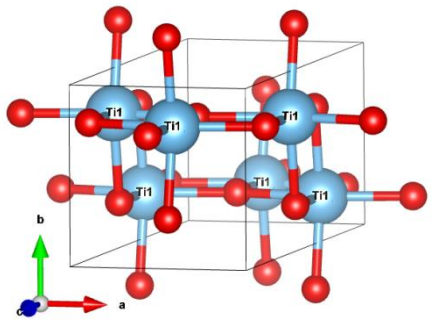
- **GeO_2, SnO_2, PbO_2**
- **MgF_2, MnF_2, FeF_2, CoF_2, NiF_2, ZnF_2, PdF_2**
- **TiO_2, CrO_2, ß-MnO_2, NbO_2, TaO_2, MoO_2, WO_2**

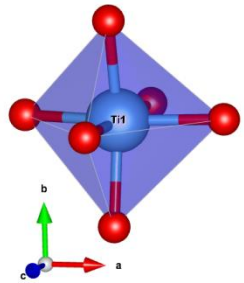
2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

Polymorphism of TiO_2 (anatase and brookite are metastable)

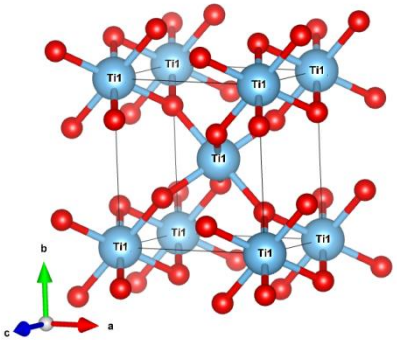
Anatase (tetragonal)

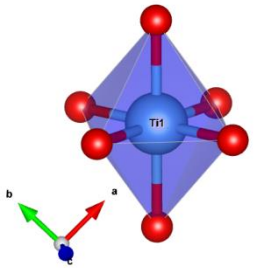




4 mutual edges

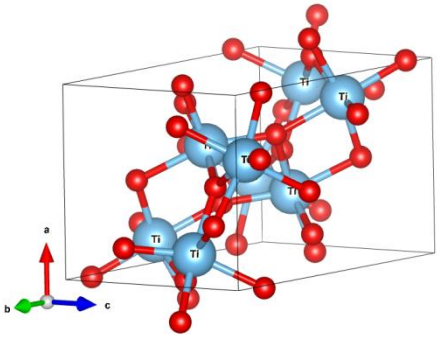
Rutile (tetragonal)

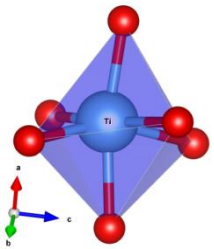




2 mutual edges

Brookite (orthorhombic)





3 mutual edges

2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

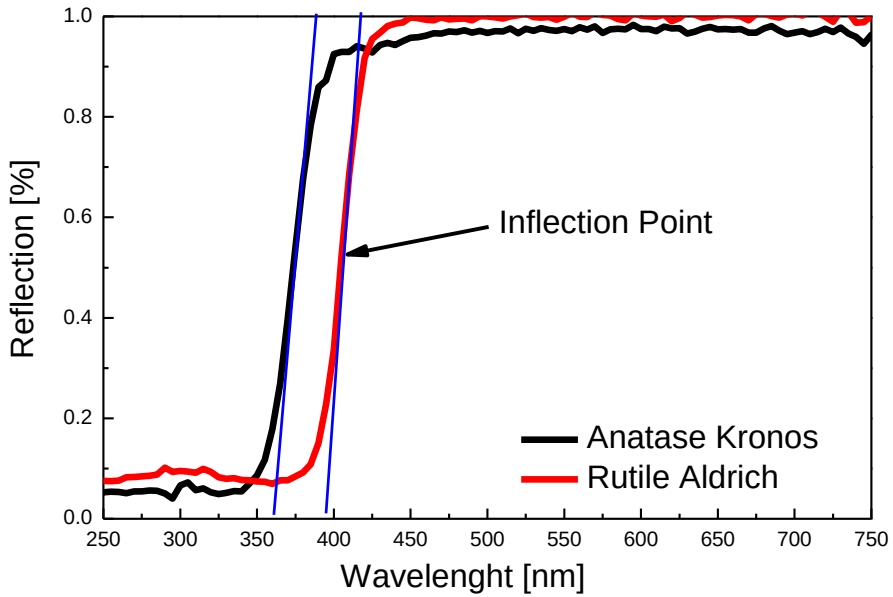
Properties of TiO_2 (rutile and anatase)

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**



2. Structure of Solid State Materials

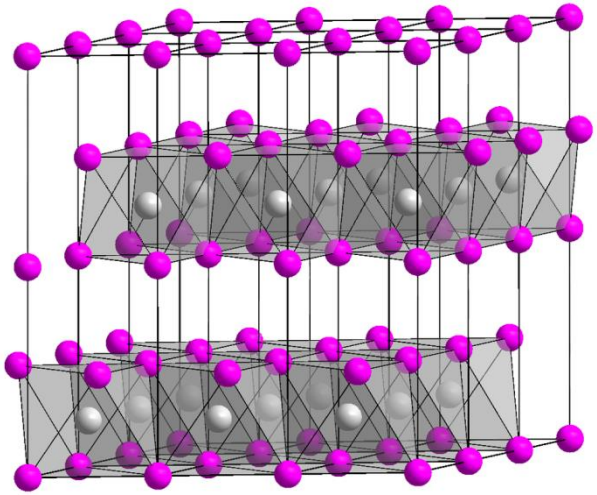
Ideal Crystals – Ionic Structures

AB_2-Structures – CdI_2 (cadmium iodide)

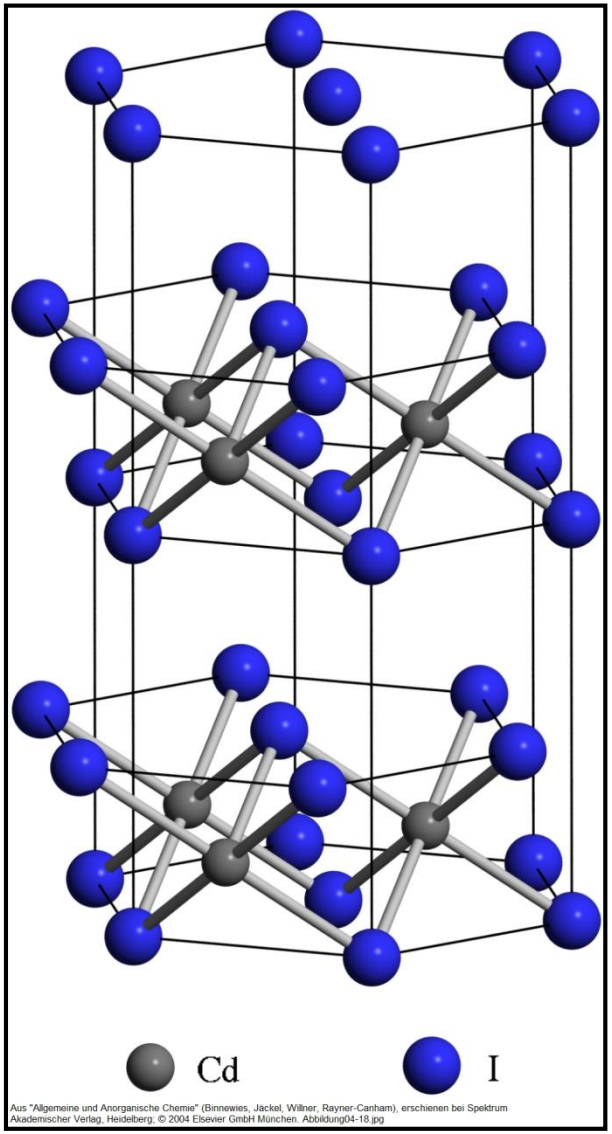
Hexagonal close packing of anions, layer structure

Coordination 6 : 3
N = 3

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



Source: Orci – own work with diamond 3



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Examples

- **CdI_2, MgI_2, CaI_2, TiI_2, VI_2, MnI_2, FeI_2, ZnI_2**
- **$TiBr_2$, VBr_2, $MnBr_2$, $FeBr_2$, $CoBr_2$**
- **$Mg(OH)_2$, $Ca(OH)_2$, $Fe(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$**

2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

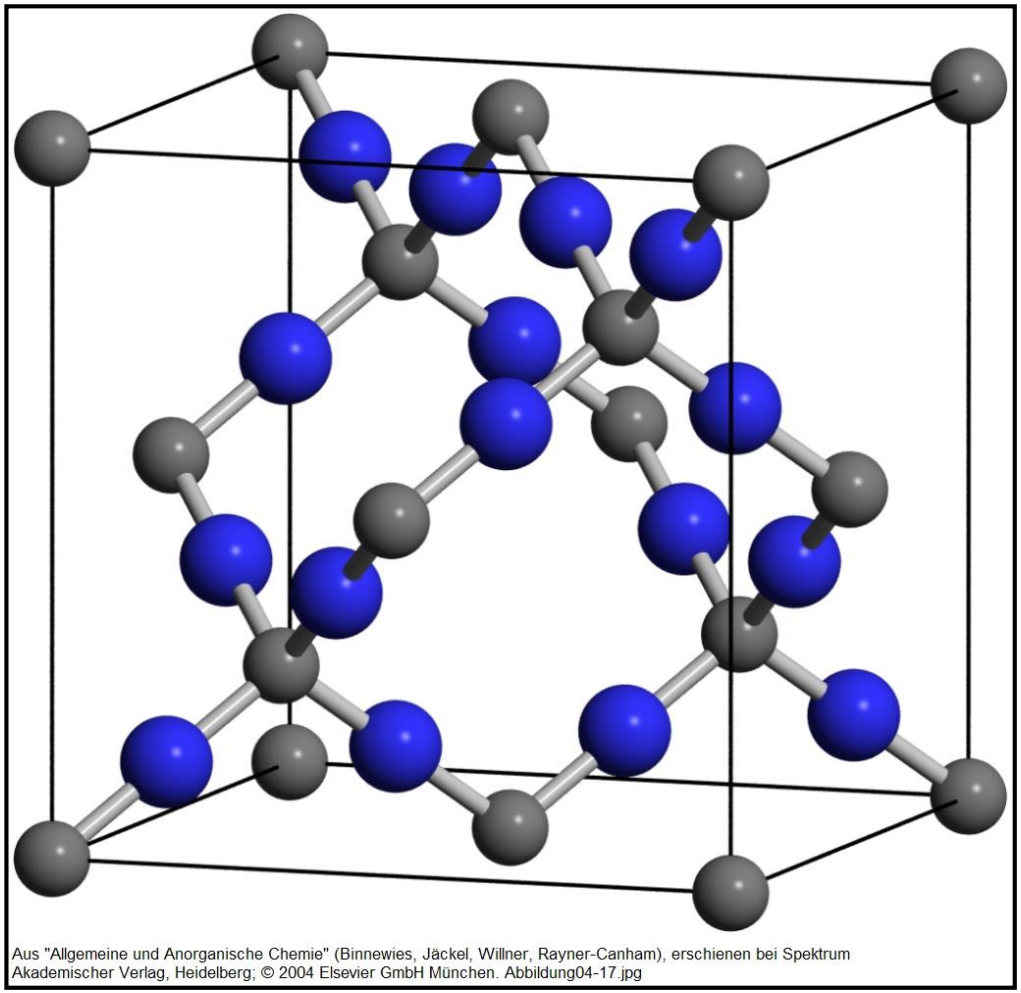
AB_2-Structures – SiO_2 (ß-cristobalite)

Can be derived formally from cubic close packing (Si occupies Zn^{2+} and S^{2-} positions of zinc blende structure)

Coordination 4 : 2
N = 8

<u>Examples</u>

- **BeF_2**
- **SiO_2**



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ß-cristobalite is a modification of SiO_2 as α-quartz, ß-quartz and ß-tridymite

2. Structure of Solid State Materials

Ideal Crystals – Ionic Structures

A_2B_3-Structures – α-Al_2O_3 (corundum)

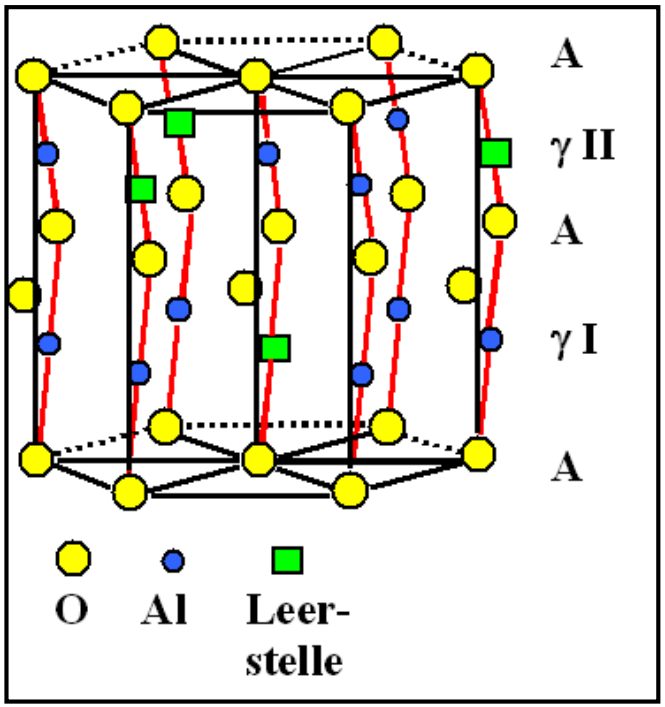
Distorted hexagonal close packing of anions

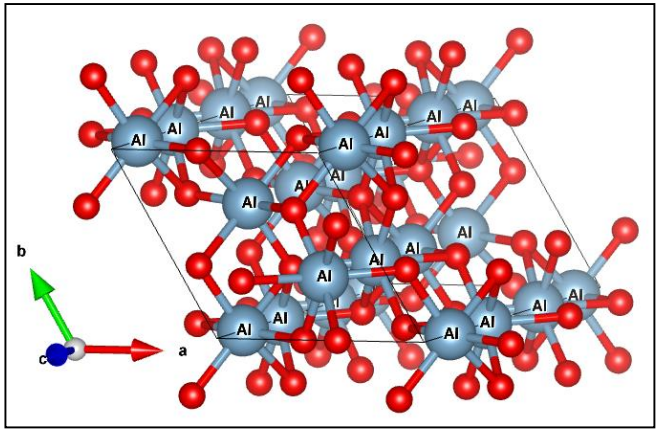
Coordination 6 : 4
N = 4
Al^{3+} is distorted octahedrally coordinate!

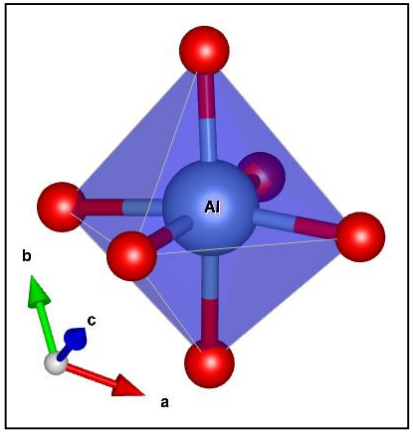
Site	Occupancy
O	2/3 Al^{3+}
T_+	empty
T_-	empty

Examples

- **α-Al_2O_3, α-Ga_2O_3**
- **Ti_2O_3, V_2O_3, Cr_2O_3, α-Fe_2O_3**
- **Rh_2O_3**





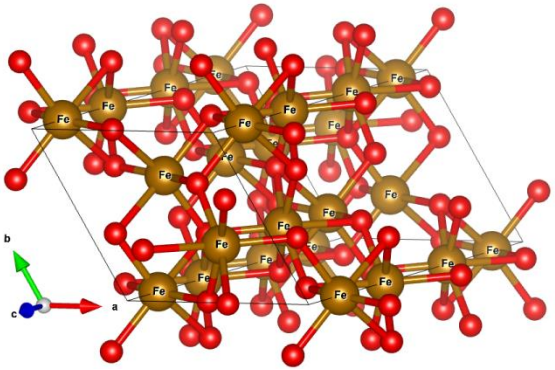


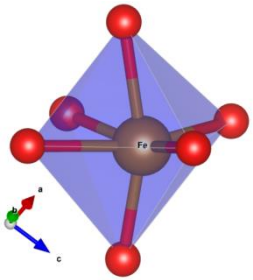
2. Structure of Solid State Materials

Ideal Crystals - Ionic Structures

A_2B_3-Structures – polymorphism of Fe_2O_3

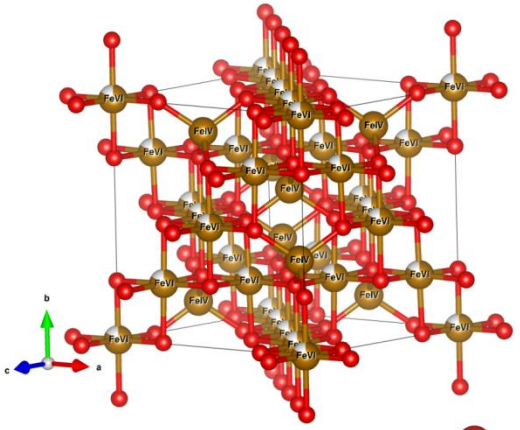
α-Fe_2O_3 (trigonal, corundum)

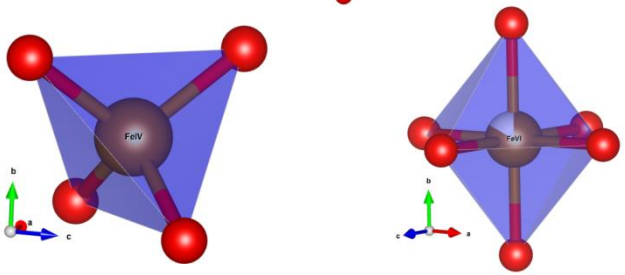




Antiferromagnetic (not magnetic)
E_g = 2.2 eV (red crystals)

γ -Fe_2O_3 (cubic, metastable)





Ferromagnetic (strongly magnetic)
E_g = 2.0 eV (black crystals)

2. Structure of Solid State Materials

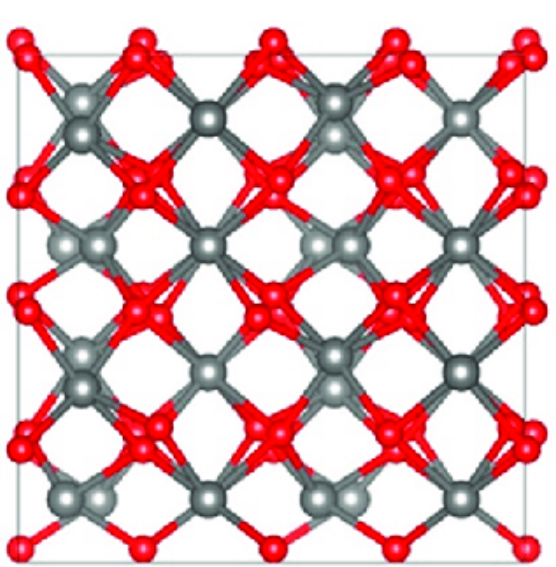
Ideal Crystals - Ionic Structures

A_2B_3 Structures – α-Mn_2O_3 (cubic, Bixbyite)

Distorted cubic-dense anion packaging

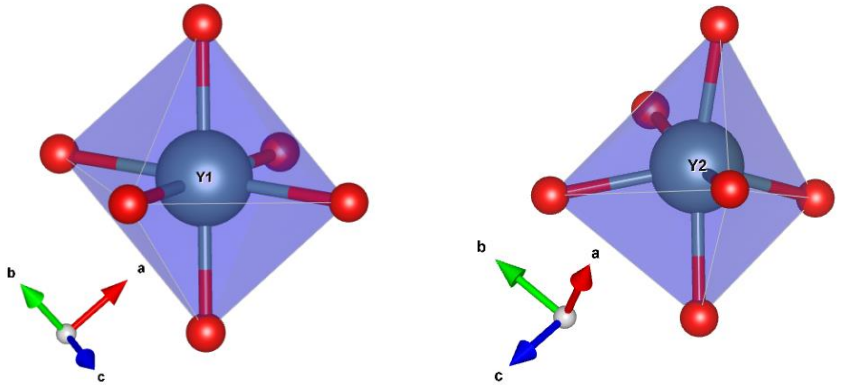
Coordination 6 : 4
Z = 16 (80 Atoms perunit cell)
Two Mn^{3+} sites with octahedral coordination:

a) S_6-Lage (8) with inversion symmetry
b) C_2-Lage (24) without inversion symmetry



Examples

- **V_2O_3**
- **In_2O_3, Tl_2O_3**
- **Sc_2O_3, Y_2O_3, Ln_2O_3 (Ln = Gd - Lu)**



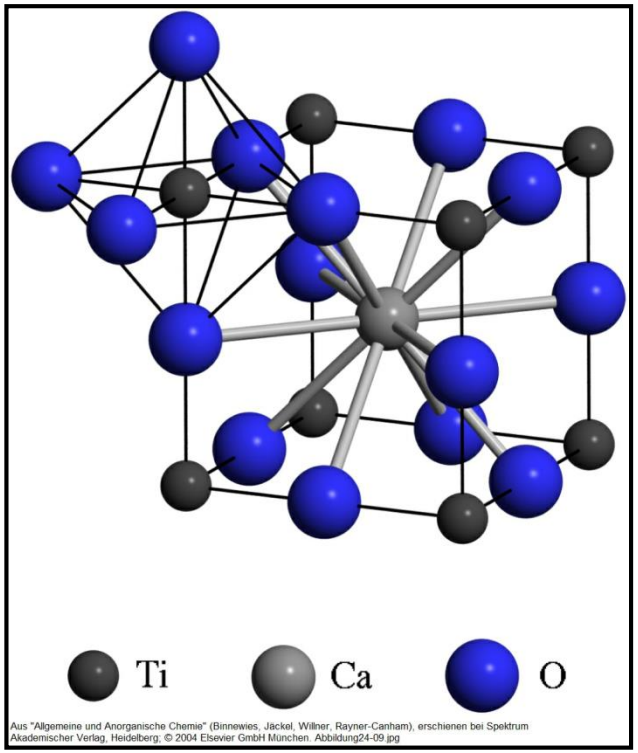
2. Structure of Solid State Materials

Ideal Crystals - Ionic Structures

ABX_3–Structures – $CaTiO_3$ (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 TiO_6-octahedra, where Me^{2+} is twelve-fold coordinate

Coordination 12 : 6 : 2
N = 1



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Example

- **$CaTiO_3$, $SrTiO_3$, $BaTiO_3$, $PbTiO_3$**
- **KIO_3**
- **$LaVO_3$, $LaCrO_3$, $LaFeO_3$, $LaCoO_3$**

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 $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ show the highest permittivity values (ε_r up to 7000), for comparison: H_2O $\varepsilon_r = 78$**

Applications in

⇒ **Capacitors**

⇒ **Membranes (Speakers)**

⇒ **Sensors (microphones)**

⇒ **Micro nozzles (inkjet printer)**

2. Structure of Solid State Materials

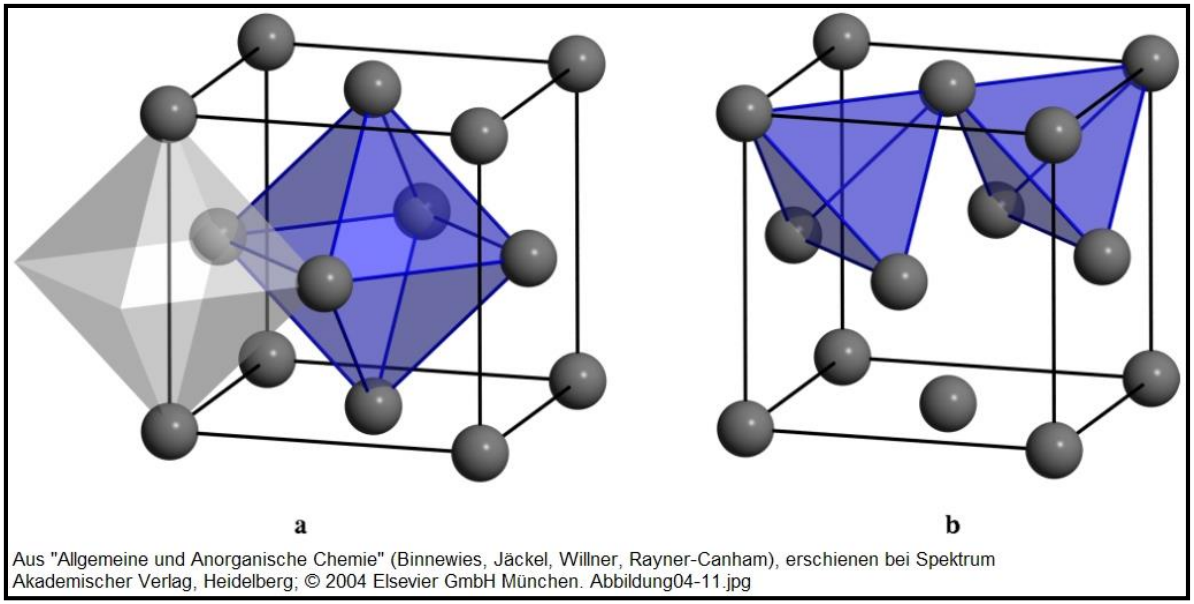
Ideal Crystal - Ionic Structures

AB_2X_4–Structures – $MgAl_2O_4$ (spinel)

Cubic close packing of anions

Coordination 4 : 6 : 4
N = 8

Site	Occupancy
O	1/2
T_+	1/8
T_-	1/8



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Examples

$MgAl_2O_4$, $MnAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$
$CuCr_2S_4$, $CuCr_2Se_4$, $CuCr_2Te_4$
$MgIn_2O_4$, $MgIn_2S_4$

2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

AB_2X_4–Structures – $MgAl_2O_4$ (spinel)

Ordinary spinels	Inverse spinels	Mixtures
$[A]^{tet}[B]_2^{oct}O_4$	$[B]^{tet}[A,B]^{oct}O_4$	$[B_xA_{1-x}]^{tet}[A_xB_{1-x}]^{oct}O_4$
$\gamma = 0.0$	$\gamma = 1.0$	$\gamma = x$ with $0.0 < x < 1.0$
Examples:		
$MgAl_2O_4$	$MgFe_2O_4$	$MnFe_2O_4$
$CoAl_2O_4$	$FeFe_2O_4$ (= Fe_3O_4)	$NiAl_2O_4$
$FeAl_2O_4$	$CoFe_2O_4$	
$CoCo_2O_4$ (= Co_3O_4)	$NiFe_2O_4$	
$MnMn_2O_4$ (= Mn_3O_4)	$CuFe_2O_4$	

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

- Ionic radius
- Coulomb energy
- Covalent character
- Crystal field stabilisation energy

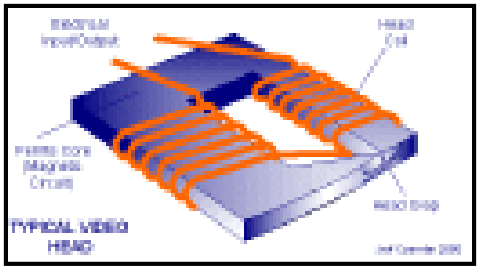
2. Structure of Solid State Materials

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: Fe_3O_4 **magnetite**
Ferroelectrics: $M^{2+}Fe_2O_4$ **ferrite**



<u>Prerequisites for good ferroelectrics</u>

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

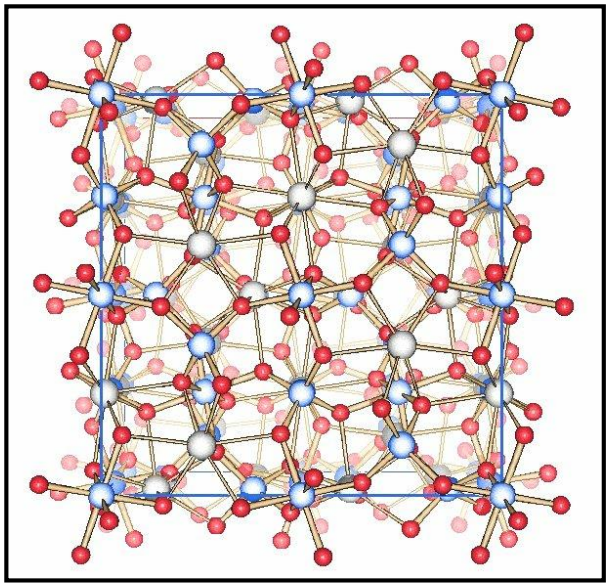
Ideal Crystal - Ionic Structures

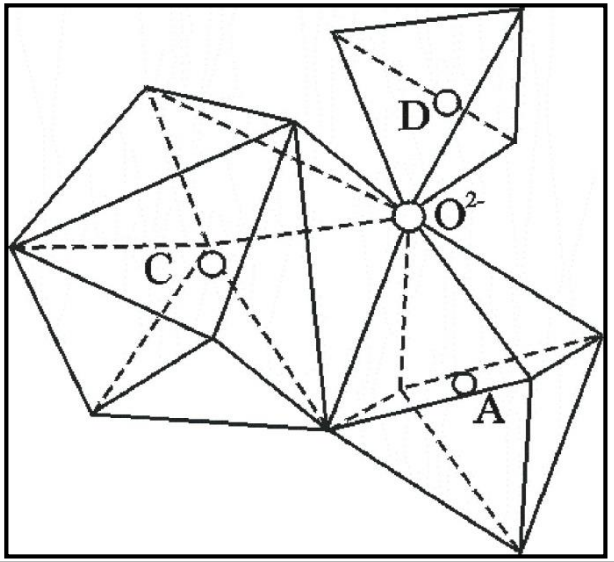
Garnet $C^{II}_3A^{III}_2(Si^{IV}O_4)_3$

Isle silicates (neso silicates) with
$[SiO_4]^{4-}$ or $[TO_4]^{4-}$-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!

Mineral	Composition
Pyrop	$Mg_3Al_2Si_3O_{12}$
Grossular	$Ca_3Al_2Si_3O_{12}$
Almandine	$Fe_3Al_2Si_3O_{12}$
Spessartin	$Mn_3Al_2Si_3O_{12}$





2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Garnet variations $C^{II}_3A^{III}_2(Si^{IV}O_4)_3$

$Ca_3Al_2Si_3O_{12}$ (Grossular) → $(Ca_{1-a}Y_a)_3Al_2(Si_{1-a}Al_a)_3O_{12}$ → $Y_3Al_2Al_3O_{12}$ (YAG)

$Ca_3Fe_2Si_3O_{12}$ (Andradite) → $(Ca_{1-a}Y_a)_3Fe_2(Si_{1-a}Fe_a)_3O_{12}$ → $Y_3Fe_2Fe_3O_{12}$ (YIG)

$Ca_3Cr_2Si_3O_{12}$ (Uwarowit)

$Y_3Al_5O_{12}$ (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
	→	$Ca_2LuM^e_2Al_3O_{12}$	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

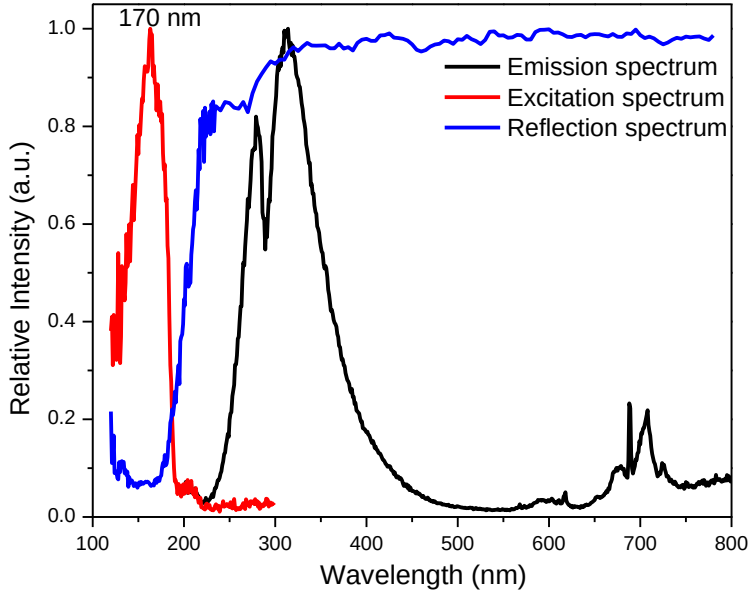
Physical properties of $Y_3Al_5O_{12}$ (YAG: Yttrium Aluminium Garnet)

Density	$\rho = 4.55$ g/cm^3
Thermal extension coefficient	$\alpha = 6.5*10^{-6}$ K^{-1}
Melting point	$T_m = 1970$ °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	$E_G = 7.0$ eV
Body colour	white (colourless)
Exciton luminescence (Electron-hole pair recombination)	~ 300 nm

Typical impurities (dopants)

Y-site	(dodecahedral)	Mg^{2+}, Ca^{2+}, Ce^{3+} - Lu^{3+}
Al-site	(octahedral)	Sc^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}
Al-site	(tetrahedral)	Fe^{3+}, Si^{4+}, Ge^4

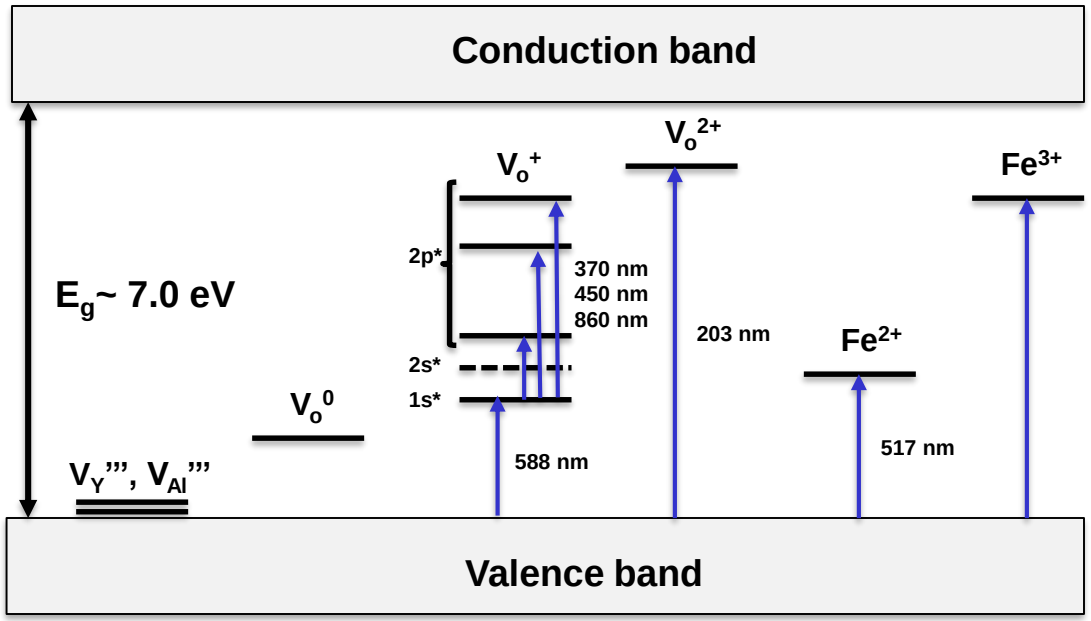
Exciton luminescence of YAG



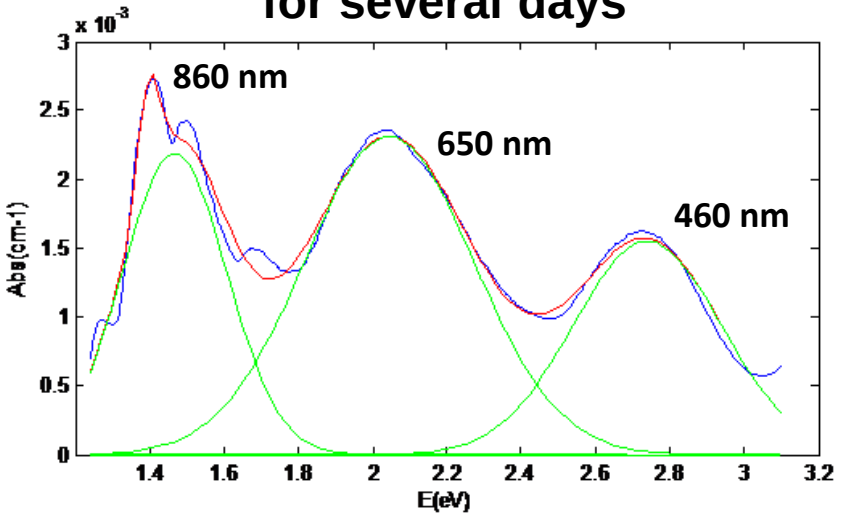
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Physical properties of $Y_3Al_5O_{12}$



Absorption spectrum of YAG after calcination in air for several days

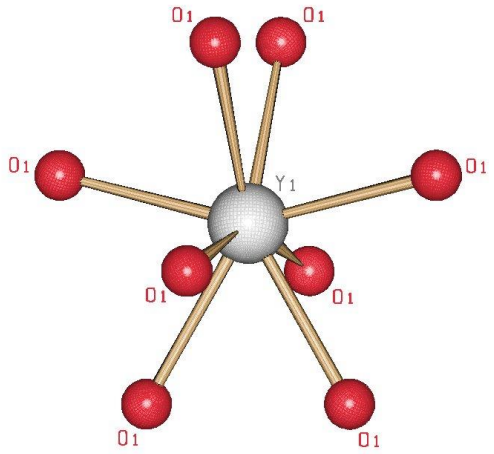


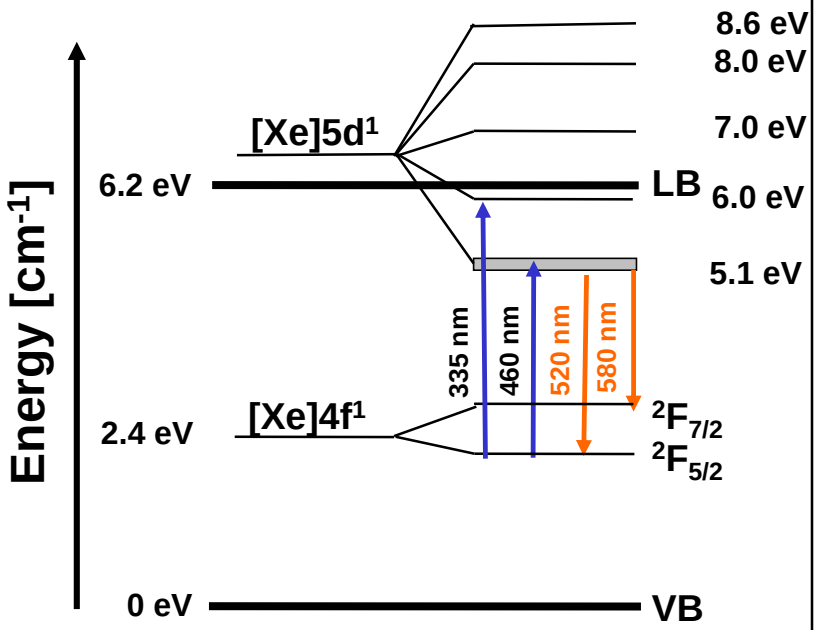
2. Structure of Solid State Materials

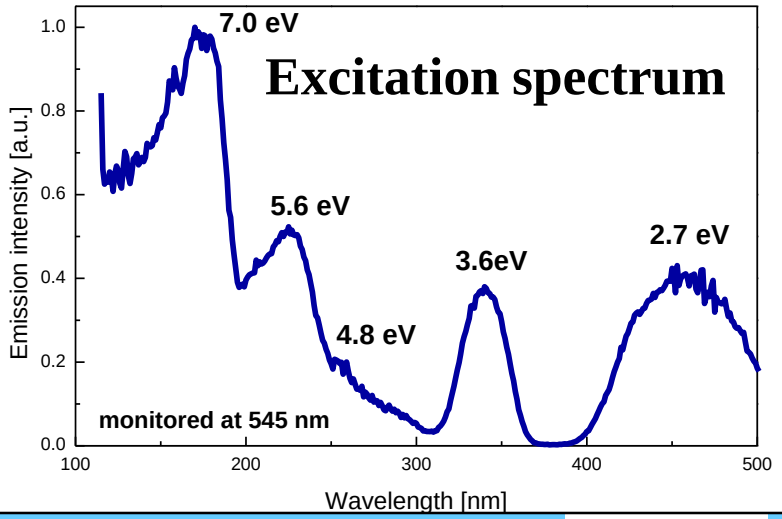
Ideal Crystal - Ionic Structures

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 ~ 28000 cm^{-1} (3.5 eV)
→ dodecahedral coordination of Ce^{3+}

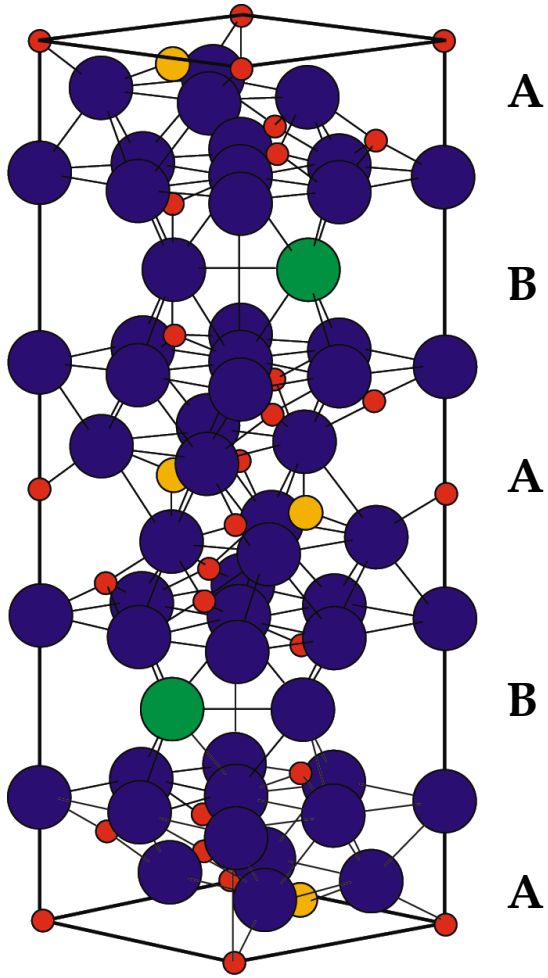






2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures



ß-Alumina–structures – $MAl_{11}O_{17} = M_2O{\cdot}nAl_2O_3$

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)

ß-Alumina-variations

$NaAl_{11}O_{17} \rightarrow (Na_{1-x}Ba_x)Mg_xAl_{11-x}O_{17} \rightarrow BaMgAl_{10}O_{17}$

$NaAl_{11}O_{17} \rightarrow (Na_{1-x}La_x)Mg_xAl_{11}O_{17+2x} \rightarrow LaMgAl_{11}O_{19}$ (magnetoplumbit structure!)

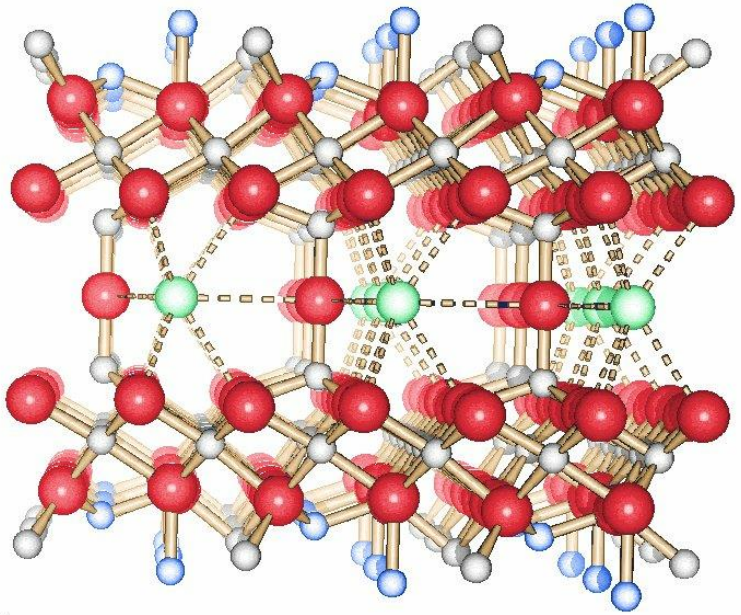
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

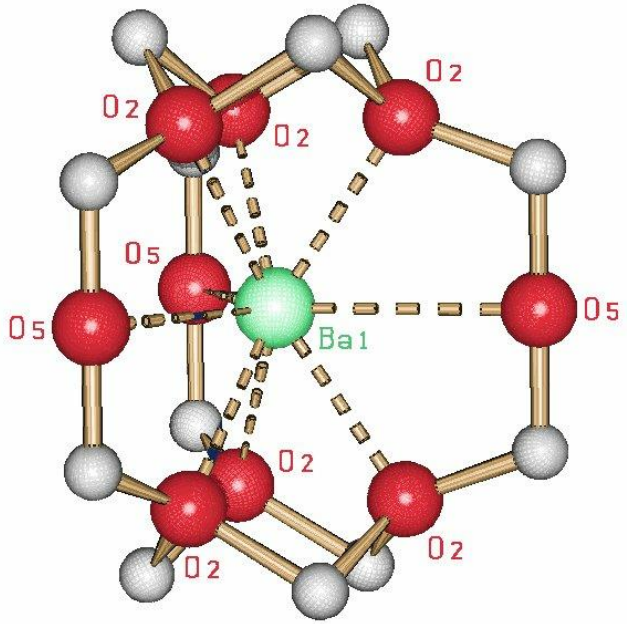
ß-Alumina–structures – $NaAl_{11}O_{17}$

Exp.: $BaMgAl_{10}O_{17}$

Layer structure



Ba^{2+} surrounding



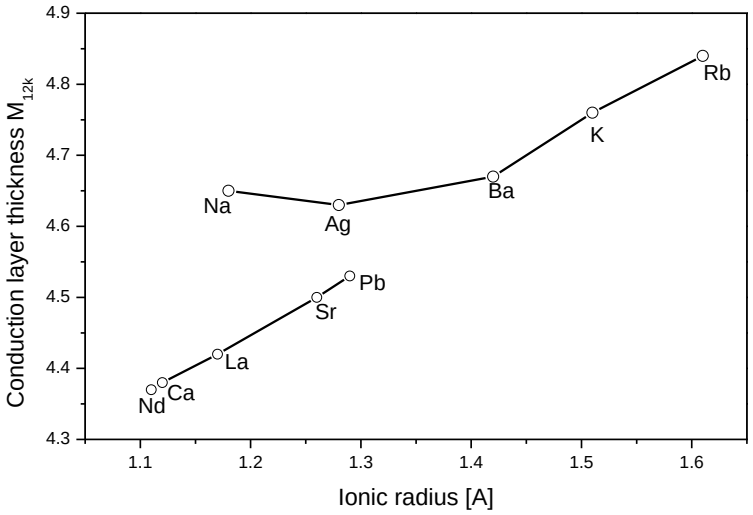
Ba^{2+} exhibits nine-fold coordination (triply capped trigonal prism $\Rightarrow$ D_{3h})

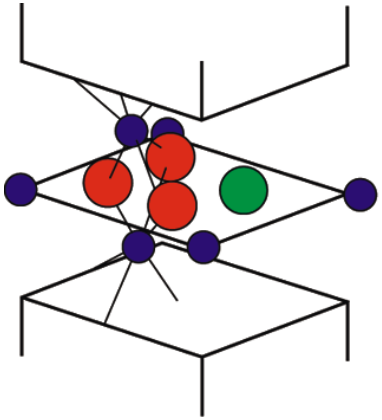
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

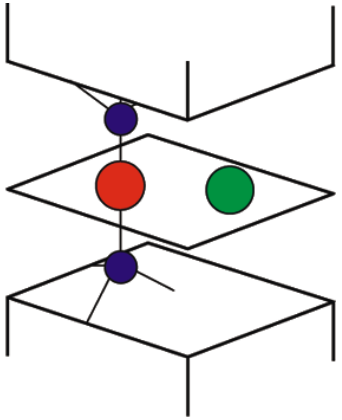
ß-Alumina–structures – $NaAl_{11}O_{17}$

Stability of ß-alumina phase





Magnetoplumbit (mirror symmetry)



β-Alumina (centrosymmetric)

Only the biggest cations stabilise the ß-alumina structure

2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

Properties of ß-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)**

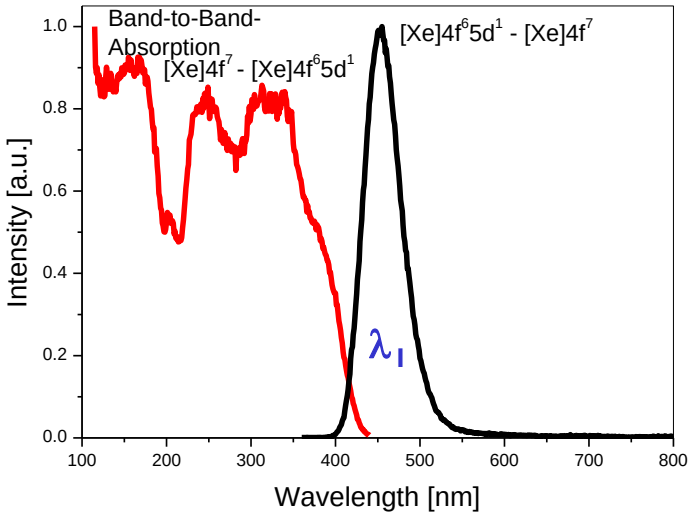
$BaMgAl_{10}O_{17} \rightarrow (Ba_{1-x}Eu_x)MgAl_{10}O_{17}$ → **blue**

$BaMgAl_{10}O_{17} \rightarrow Ba(Mg_{1-y}Mn_y)Al_{10}O_{17}$ → **green**

$BaMgAl_{10}O_{17} \rightarrow BaMg(Al_{10-z}Cr_z)O_{17}$ → **deep red**

$BaMgAl_{10}O_{17} \rightarrow (Ba_{1-x}Eu_x)(Mg_{1-y}Mn_y)Al_{10}O_{17}$ → **cyan**

Luminescence spectra of $BaMgAl_{10}O_{17}$:Eu

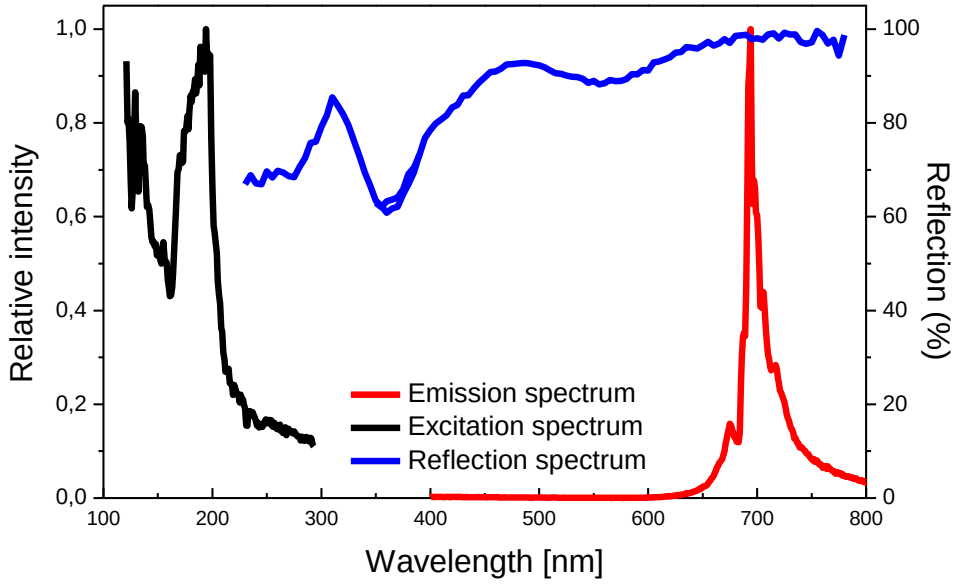


2. Structure of Solid State Materials

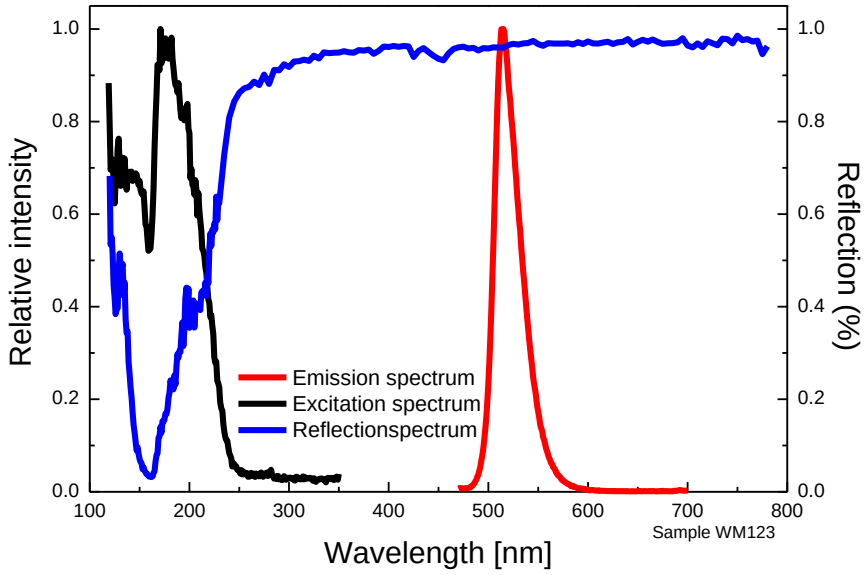
Ideal Crystal - Ionic Structures

Phosphors with ß-alumina structure

$BaMgAl_{10}O_{17}:Cr^{3+}$



$BaMgAl_{10}O_{17}:Mn^{2+}$

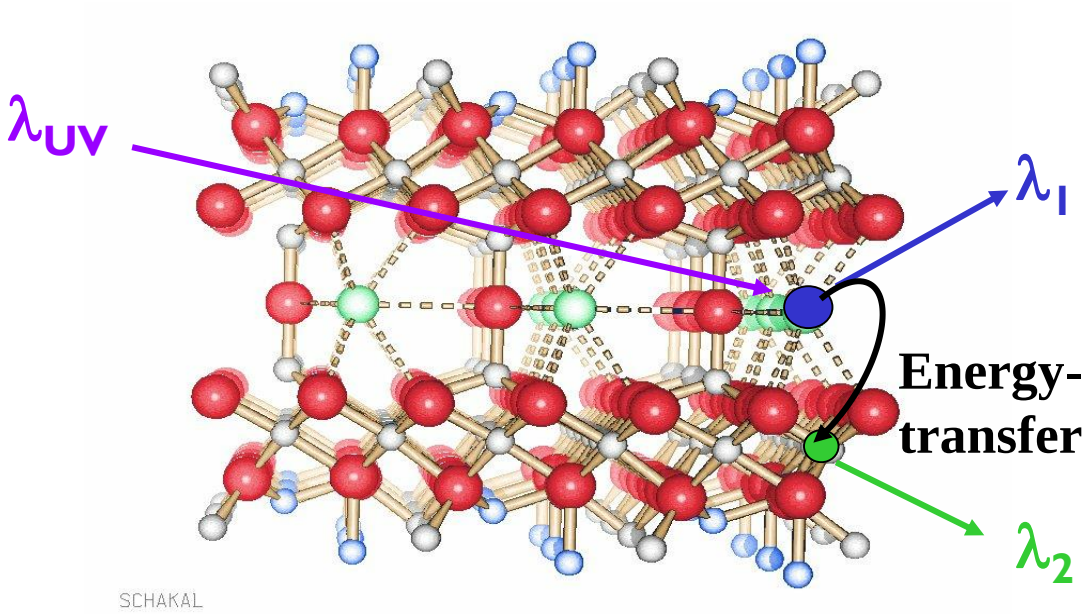


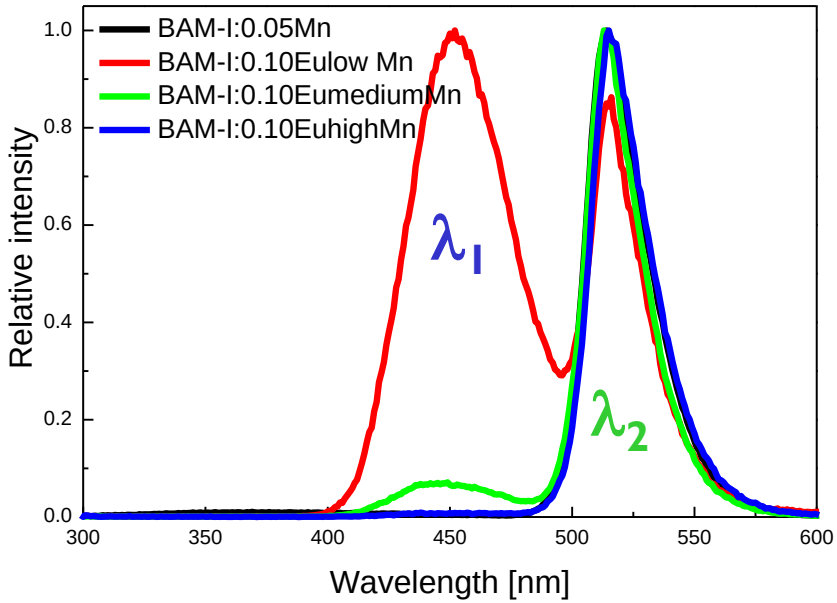
$BaMgAl_{10}O_{17}$:	Excitation at	λ_{max} at	x	y	Transition
Cr^{3+}	190 nm	694 nm	0.596	0.257	$3d^3$-$3d^3$
Mn^{2+}	180 nm	515 nm	0.146	0.722	$3d^5$-$3d^5$

2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

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



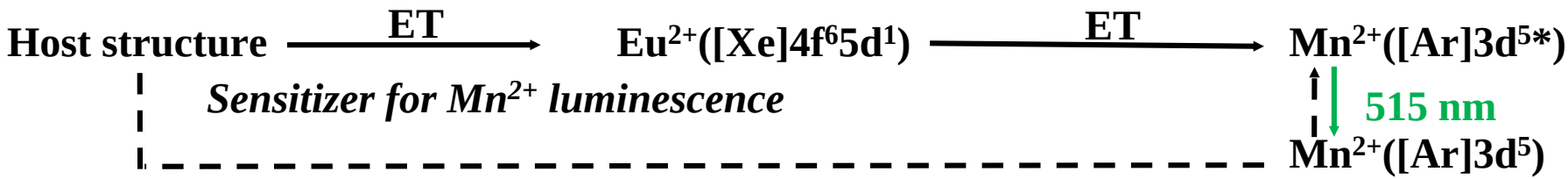


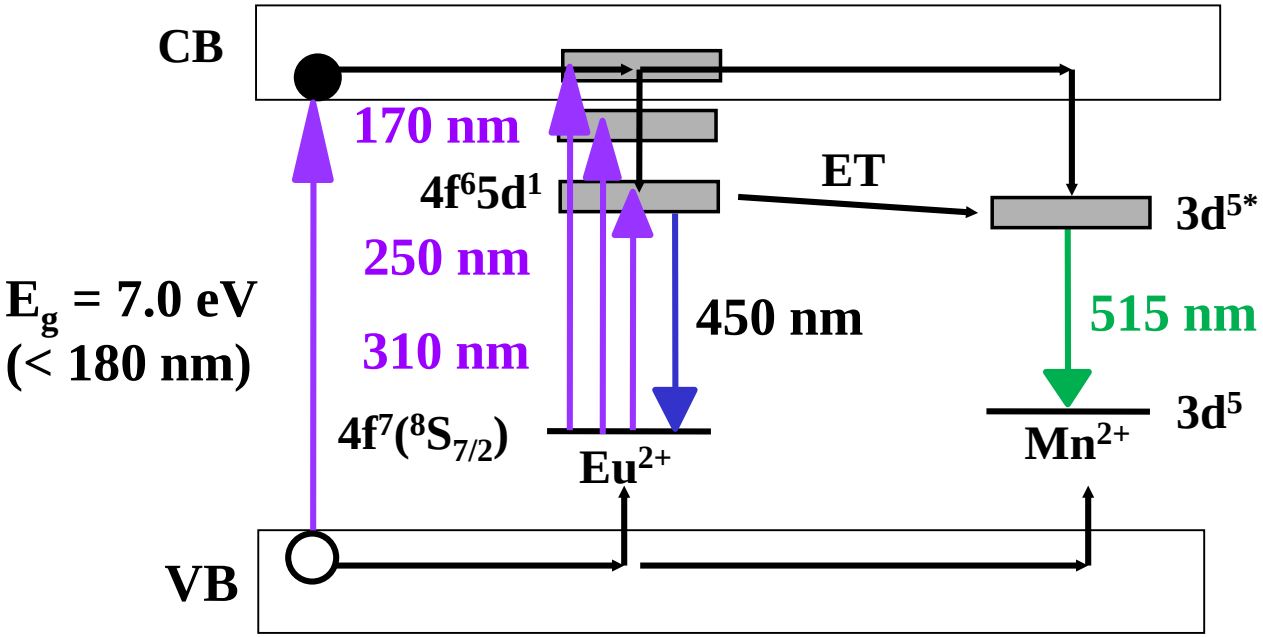
- **Eu^{2+} is incorporated on Ba^{2+}-sites and there absorbs the incoming UV-radiation**
  → allowed $[Xe]4f^7$ – $[Xe]4f^65d^1$-interconfigurational transition
- **Energy transfer from Eu^{2+} to Mn^{2+}, whereby the efficiency of the energy transfer depends on the Mn^{2+}-concentration and thus the average distance between Eu^{2+} - Mn^{2+}**
  → Mn^{2+} emission $[Ar]3d^5$ – $[Ar]3d^5$-intraconfigurational transition

2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

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



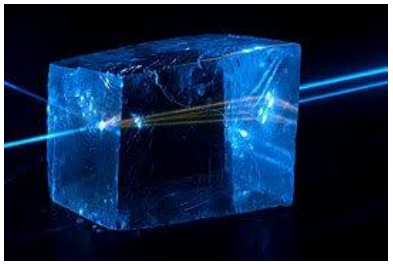


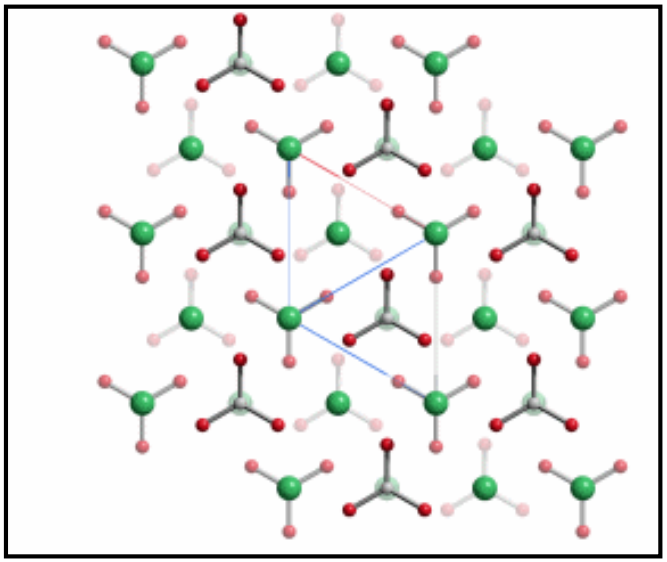
2. Structure of Solid State Materials

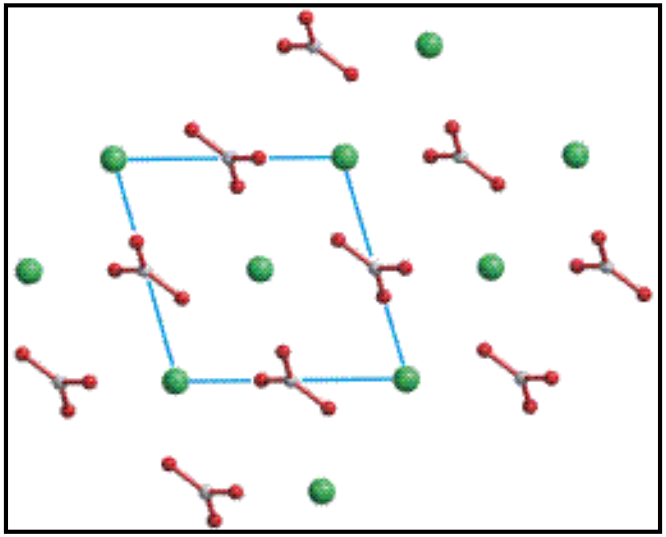
Ideal Crystal - Ionic Structures

ABX_3 Structures – $CaCO_3$ (calcite)

Trigonal crystal system
Z = 6
$\rho = 2.71\ g/cm^3$
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

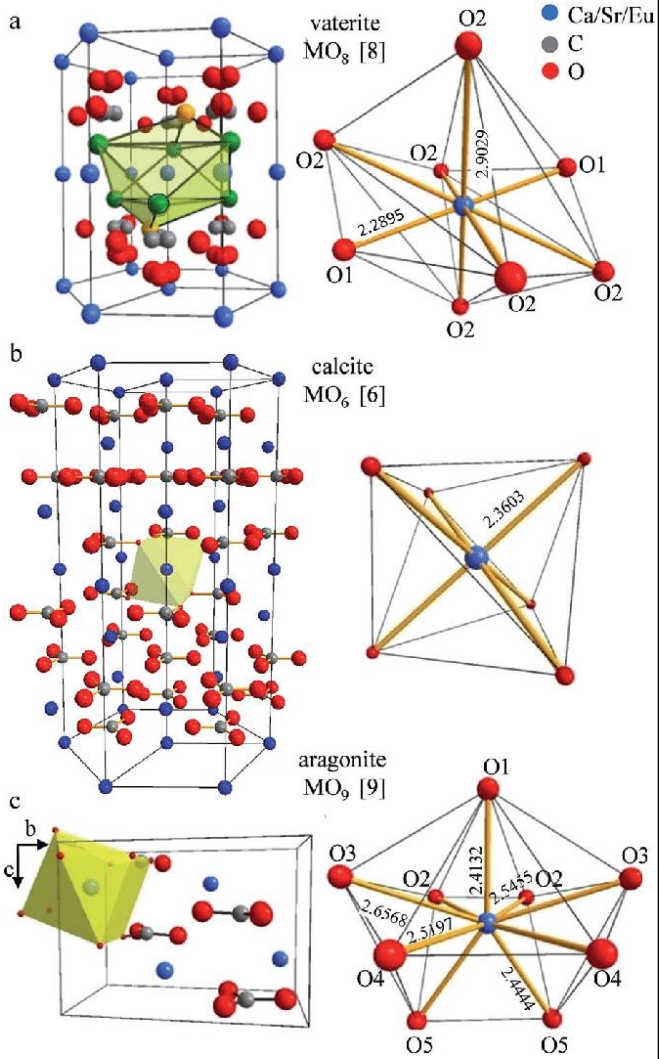
ABX_3 Structures – $CaCO_3$

Polymorphism

	Z	ρ [g/cm³]	Crystal system	CN
Calcite	6	2.71	trigonal	6
Vaterite	2	2.65	hexagonal	8 + 8
Aragonite	4	2.93	orthorhombic	9

Biomineralisation of $CaCO_3$

- Amorphous: $CaCO_3$-storage in organisms
- Calcite: otholiths
- Aragonite: coccoliths (calcareous shells) in foraminiferes
- Calcite/aragonite/chitin/protein as composite: nacre (seashell, pearl)
- Mn^{2+} luminescence: calcite 610 nm
  aragonite 560 nm (stronger crystal field)



Lit.: J. Materials Chemistry C 2 (2014) 46)

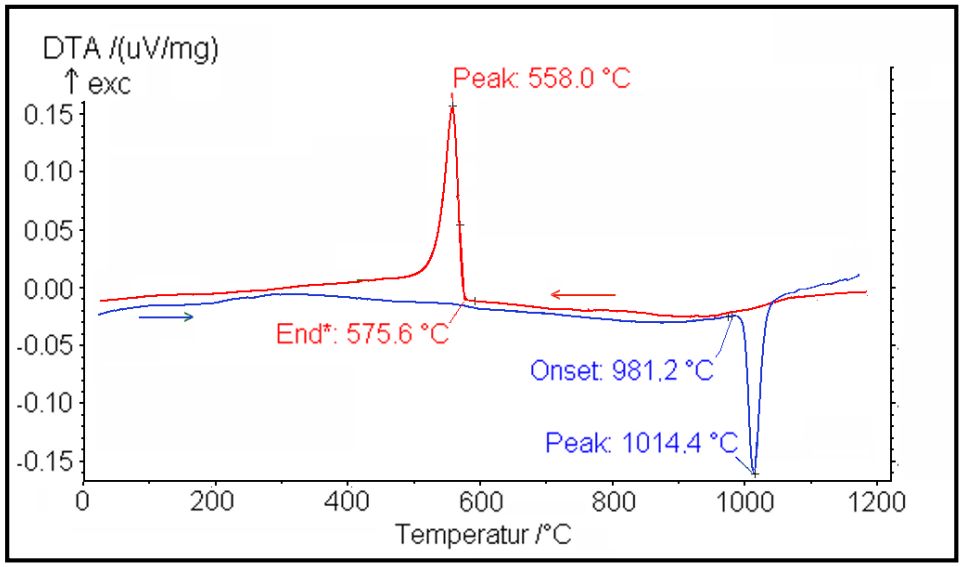
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

ABX_3–structures – YBO_3

Polymorphism

	Z	ρ [g/cm³]	Crystal system	Anion	CN (Y^{3+})
Calcite (ht-type)	6	6.86	trigonal	$[BO_3]^{3-}$ units	6
"YBO_3" (lt-type)	2	7.40	hexagonal	$[B_3O_9]^{9-}$ rings	8



$\Delta_{tr}H° = 12.1$ kJ/mol

$E_a = 1386$ kJ/mol lt → ht transition

$E_a = 568$ kJ/mol ht → lt transition

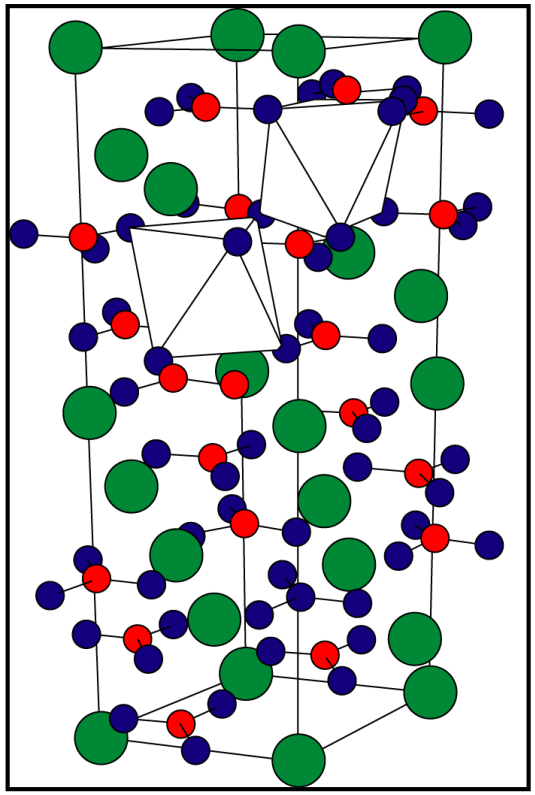
(J. Plewa, T. Jüstel, Phase Transition of YBO_3, J. Therm. Analysis and Calorimetry 88 (2007) 531)

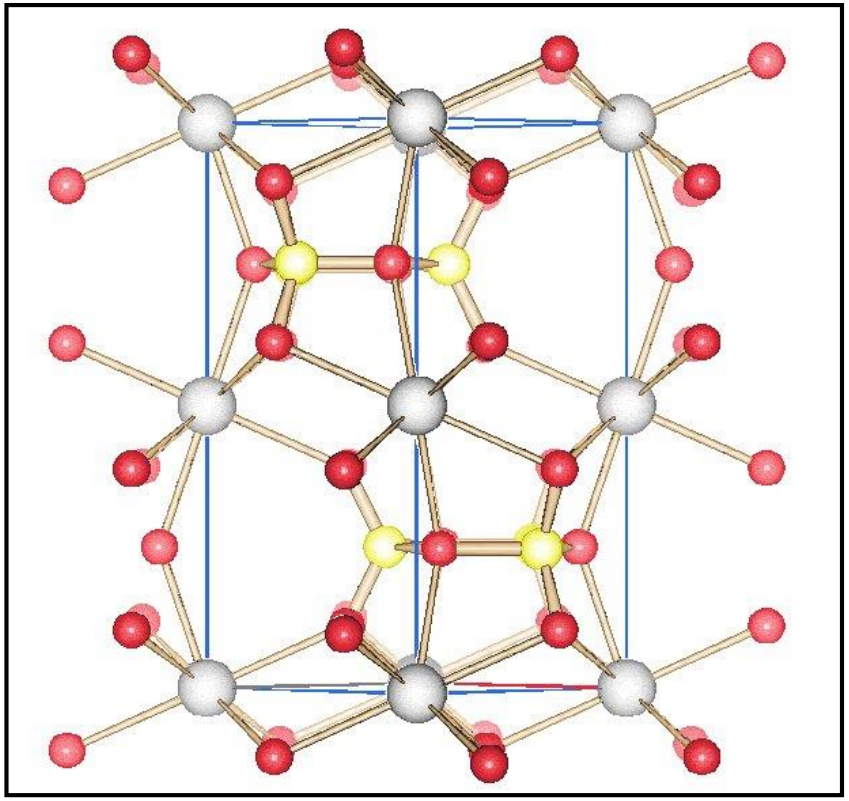
2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

ABX_3–structures – YBO_3

Calcite-type ($[BO_3]^{3-}$ units) "YBO_3"- or lt-type ($[B_3O_9]^{9-}$ rings)





2. Structure of Solid State Materials

Ideal Crystal - Ionic Structures

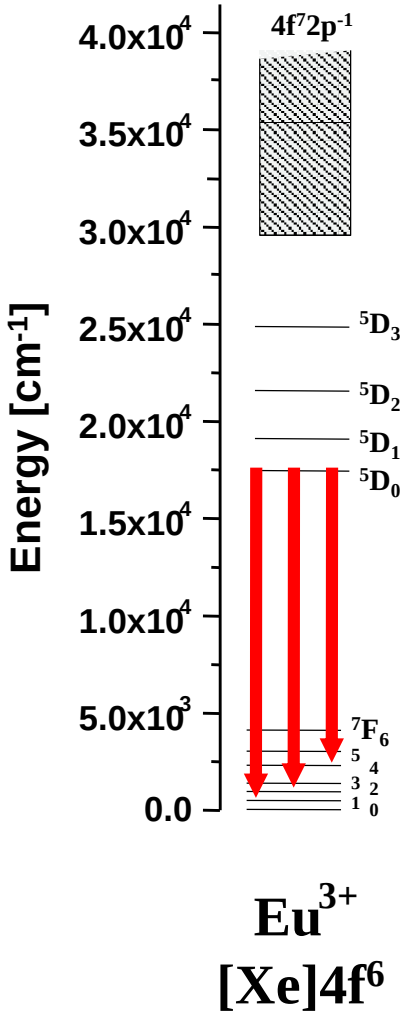
ABX_3–structures – YBO_3

<u>Eu^{3+} activated phosphors, e.g. $LnBO_3$:Eu (Ln = Y, In, Gd, Lu)</u>

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

- **Rel. intensity of emission lines = f(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)



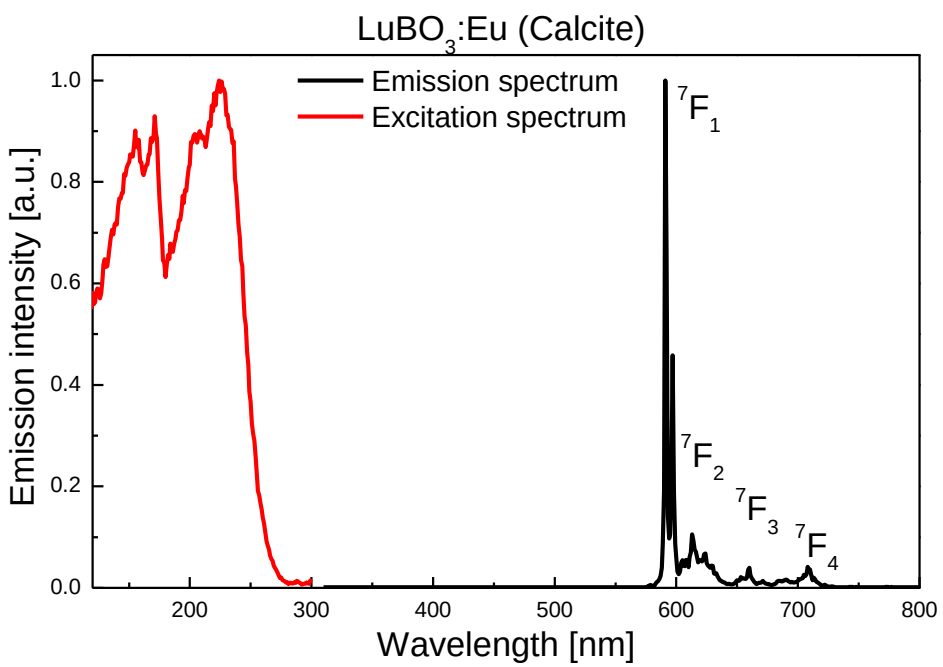
2. Structure of Solid State Materials

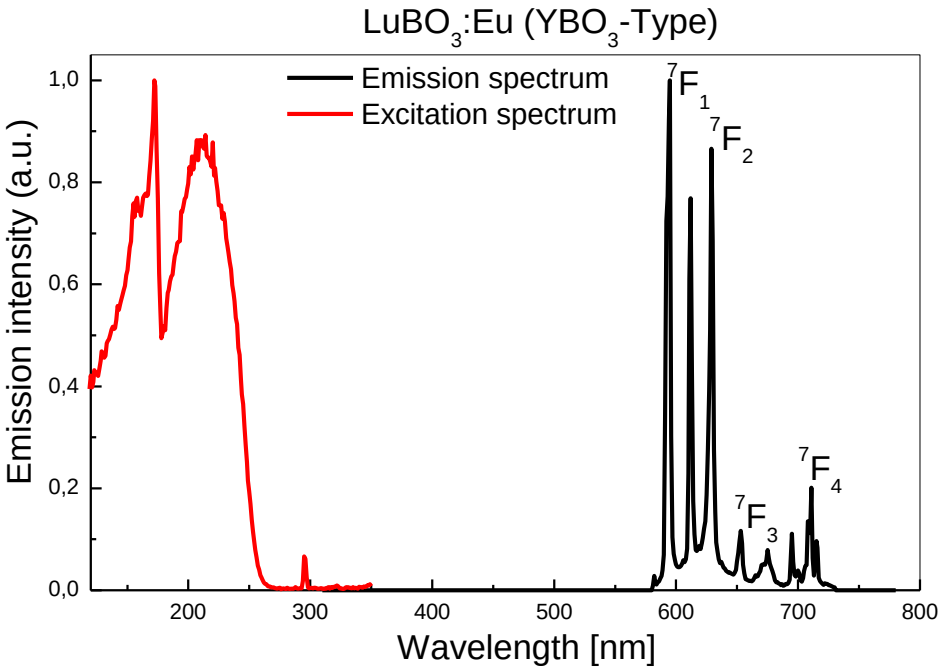
Ideal Crystal - Ionic Structures

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





2. Structure of Solid State Materials

Real Crystals - Definition

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

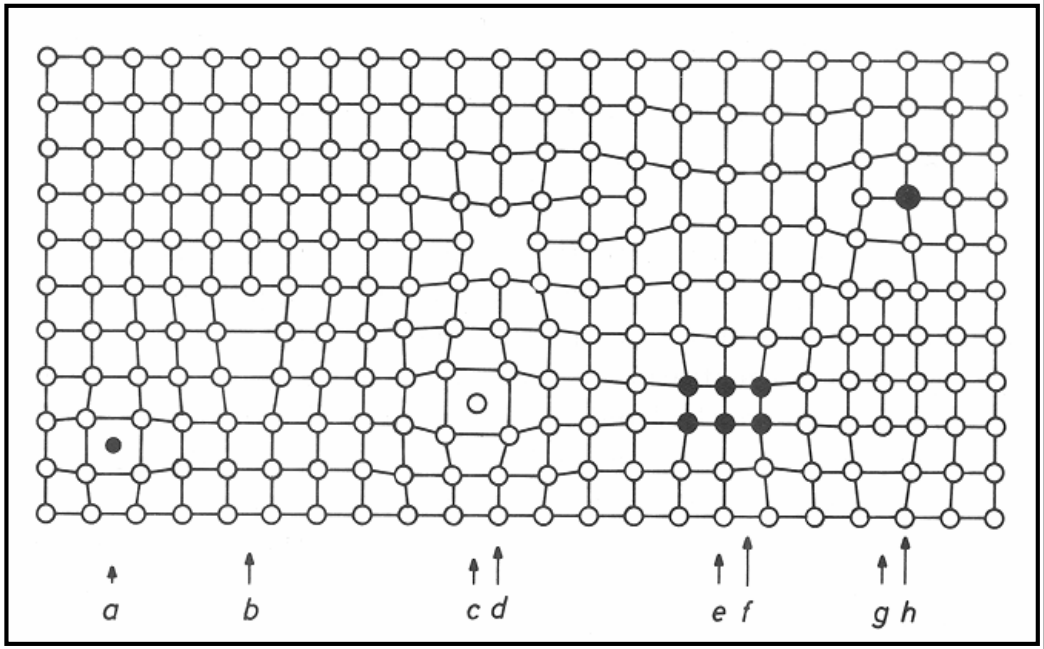
Defects = intrinsic defects and extrinsic defects (dopants)

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

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

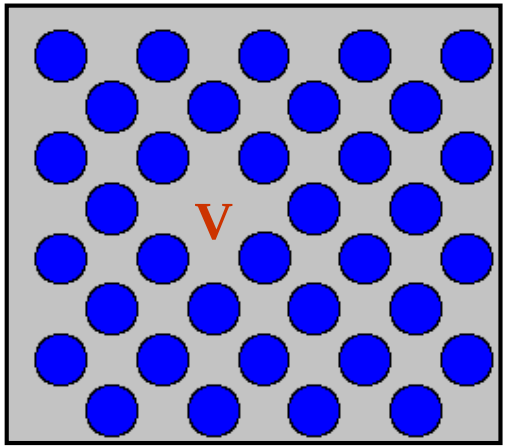
2-dimensional defects (area defects)
Symmetry violation for every point lying upon an area

3-dimensional defects (spatial defects)
Any point in a given volume exhibits different symmetry



2. Structure of Solid State Materials

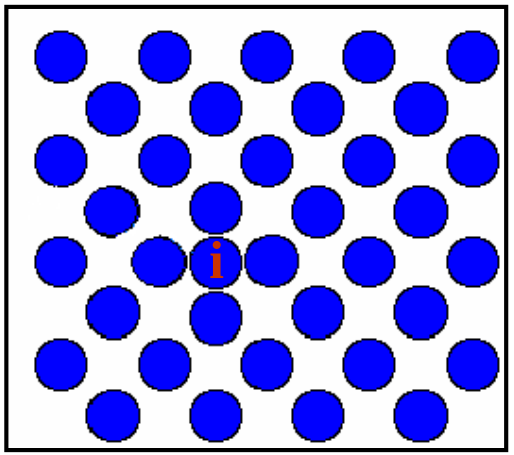
Real Crystals - 0-dim. Defects(Point Defects)



Intrinsic defects (construction errors)

- **Vacancy (“V”)**
- **Self-interstitial (“i”)**

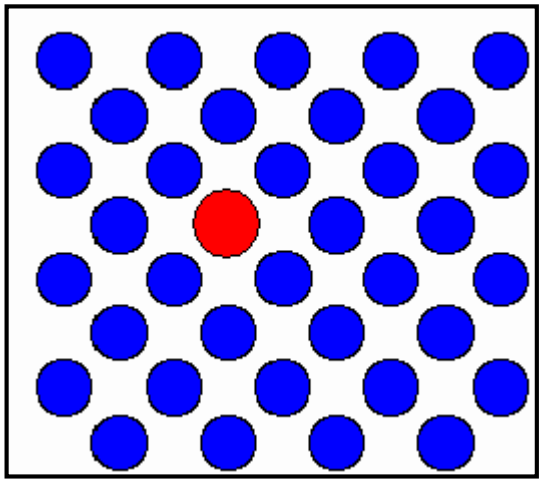
In ionic crystals, intrinsic defects lead to relative charges, that must be compensated

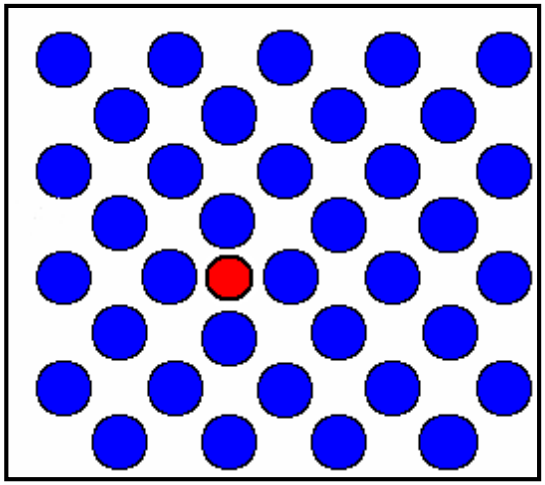


a) By a electron ⇒ colour centre
Exp.: SiO_2
b) By 2nd defect with opposite charge
⇒ Schottky-defect
Exp.: BeO, MgO, MX
c) By a ion with matching charge on a interstitial
⇒ Frenkel-defect
Exp.: AgCl, AgBr, CaF_2

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)

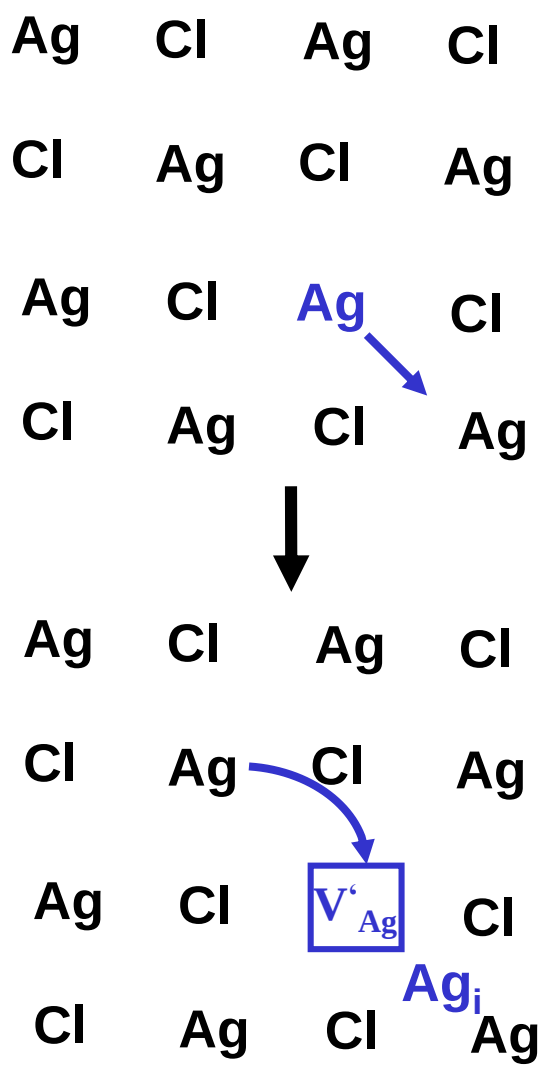
Diffusion processes through positional exchange using the example of silver chloride

Formation of Frenkel-defects

$AgCl \rightarrow Ag_{1-x}V_{Agx}Ag_{ix}Cl$ (defect equation)

→ Cation migration via interstitials i

→ Ionic conductivity in crystals



2. Structure of Solid State Materials

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

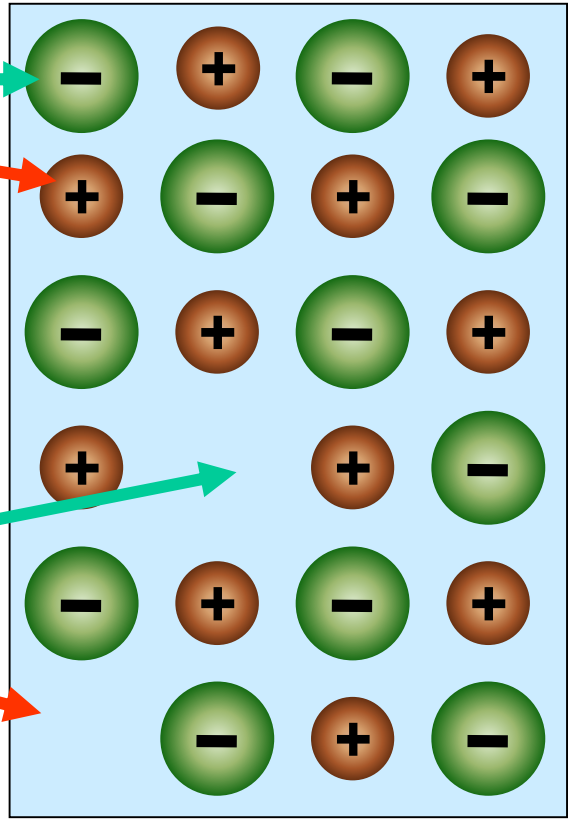
Kröger-Vink-notation using the example of a NaCl-crystal

K^{x}_{K} A^{x}_{A} **Cations or anions on correct lattice positions.**
Neutral against the ideal lattice (^{x})

Na^{x}_{Na} Cl^{x}_{Cl}

V'_{K} $V^{\bullet}_{A}$ **Cation or anion vacancies with a effective charge of 1- ($'$) or 1+ ($^{\bullet}$)**

V'_{Na} $V^{\bullet}_{Cl}$



2. Structure of Solid State Materials

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

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

$K^{\bullet}_{i}$ Interstitial cation with a effective charge of 1+ ($^{\bullet}$) $Na^{\bullet}_{i}$

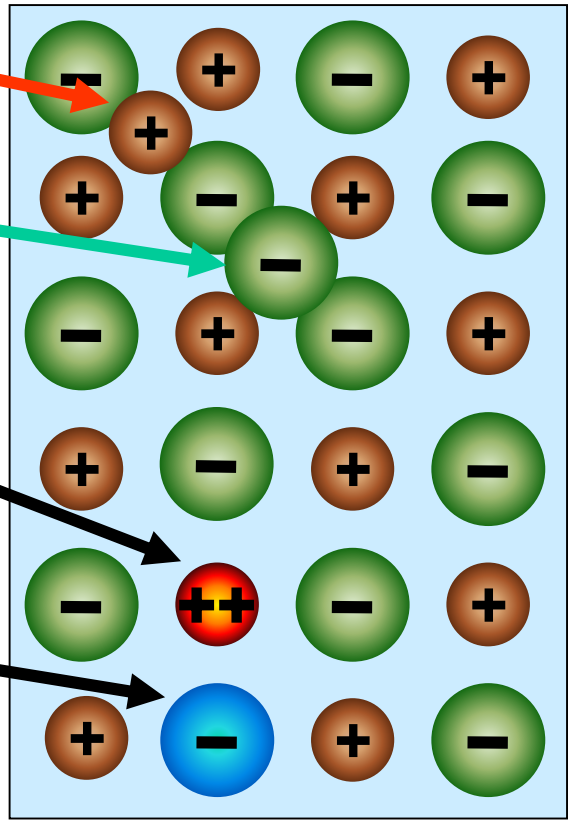
A'_{i} Interstitial anion with a effective charge of 1- ($'$) Cl'_{i}

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

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

e' electron

$h^{\bullet}$ 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 → 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 → $Fe_{1-y}O$, $Mn_{1-y}O$, $Co_{1-y}O$**

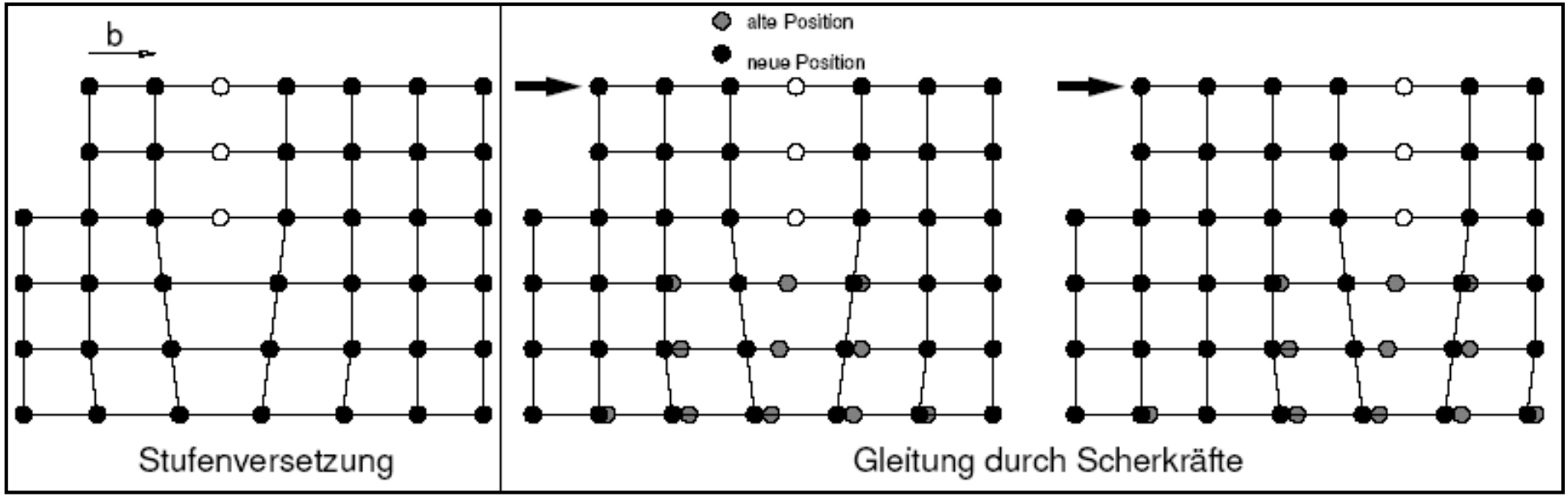
3. **Oxygene onto interstitials O_i: Oxygene excess compounds, easily oxidisable cations → UO_{2+x}**

4. **Metals onto interstitials M_i: Defect type in metal deficient oxides along with V_M → $Fe_{1-y}O$ (Koch-Cohen-Cluster)**

2. Structure of Solid State Materials

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. Y_2O_3:Eu (cubic bixbyite structure)

<u>Dislocation density in real crystals</u>

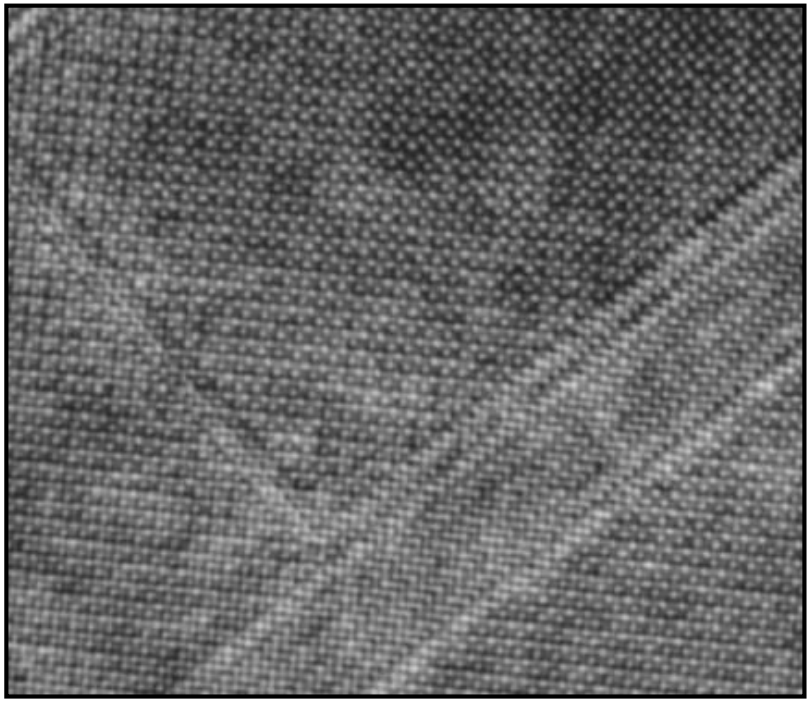
Dislocation-free silicon
for semiconductors r = 0 cm^{-2}

"Good" single crystals
for laboratories: r ~ (10^3 - 10^5) cm^{-2}

Normal crystals including polycrystalline materials: r ~ (10^5 - 10^9) cm^{-2}

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

HR-TEM image of a Y_2O_3 crystal



2. Structure of Solid State Materials

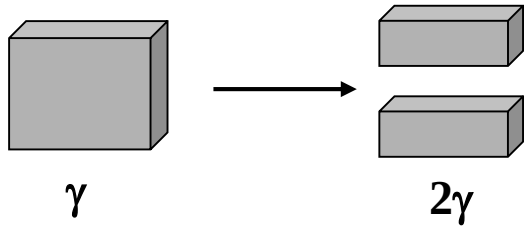
Real Crystals - 2-dim. Defects (Area Defects)

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 γ [J/cm²] → 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

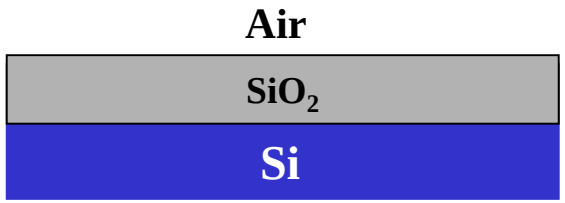
Material	γ [mJ/cm²]
Glass	300
Fe	700
W	1450



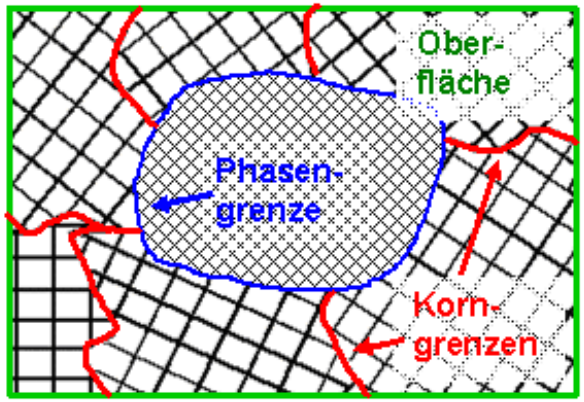
2. Structure of Solid State Materials

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



Grain boundaries: Most crystals are polycrystalline and therefore possess a large number of crystalline areas, that are divided by grain boundaries



<u>Stacking faults</u>
Occur in cubic face-centred structures for example

Normal stacking sequence:
ABCABCABCABC

With stacking fault:
ABCABCACABC

Leads to the formation of grain boundaries

2. Structure of Solid State Materials

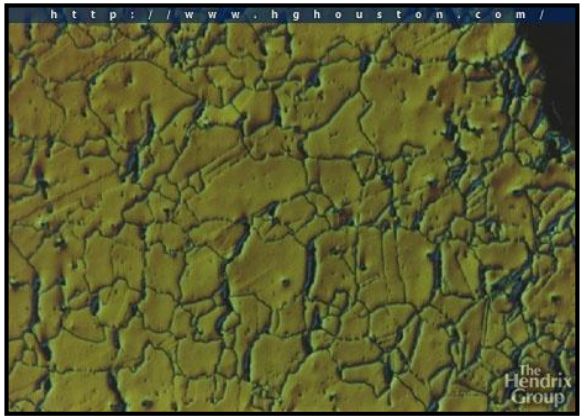
Real Crystals - 3-dim. Defects (Spatial Defects)

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

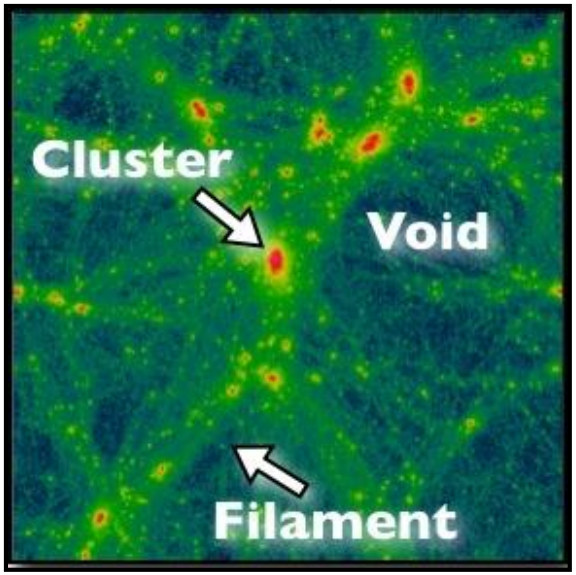
- **Micro cracks**
  - **Are treated as 2-dimensional defects**

- **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 ↓ x 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)

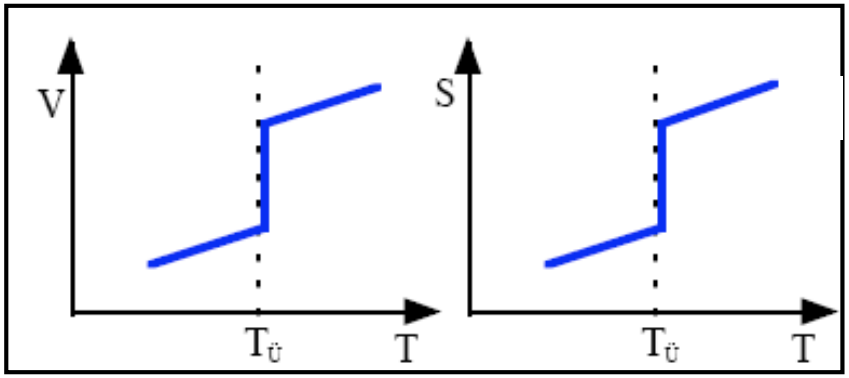
The phase state has a impact on dependent state variables (functions), such as V, U, H, S, F, G, polarisation, magnetisation, electrical resistance, ferroelectricity, etc.

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 °C**
- **Vaporisation of NH_3(l) at –33 °C**
- **Sublimation of CO_2(s) at -78 °C**

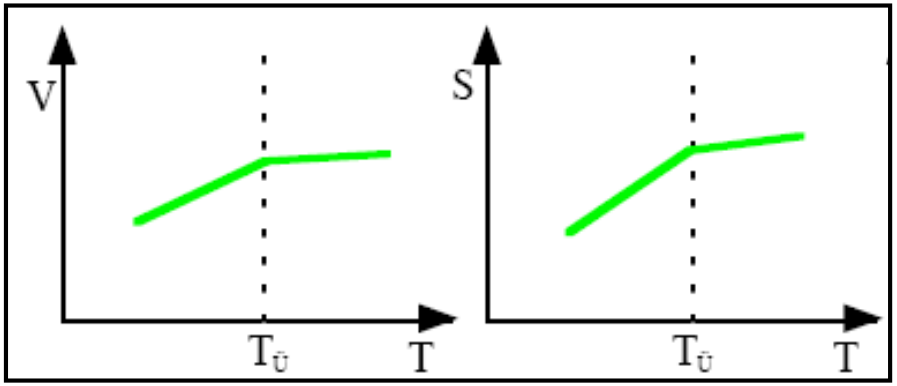
2. Structure of Solid State Materials

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)

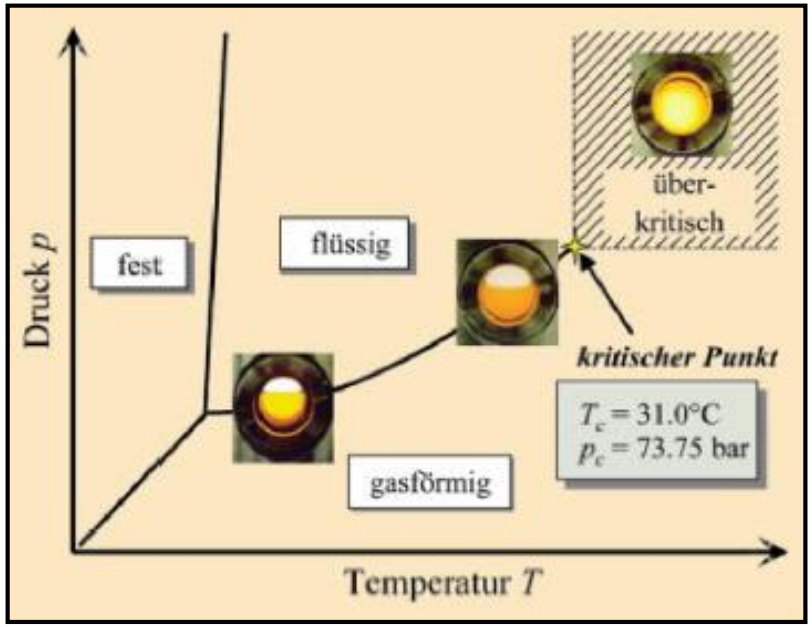
Phase transitions of the second order show a discontinuity in the second derivation of the state functions



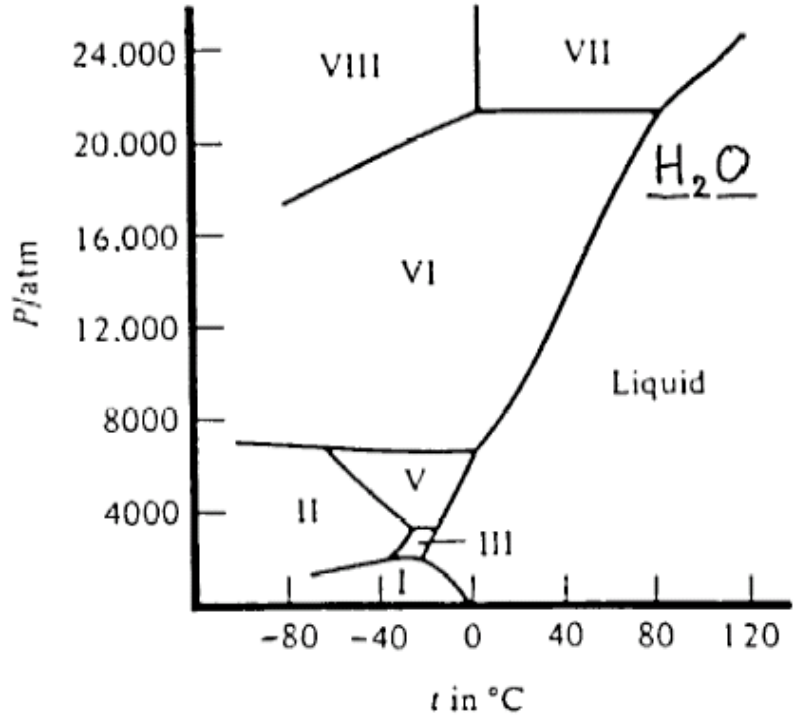
- **Glass transition of polystyrene at ca. 100 °C**
- **Transition to superconducting solid phase of metals (4.15 K for Hg)**

Phase Diagrams of Aggregate States: pT-Diagrams

Phase diagram of CO_2



Phase diagram of H_2O



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2. Structure of Solid State Materials

Phase Diagrams – Solid Solutions

Complete miscibility in solid state

Prerequisites

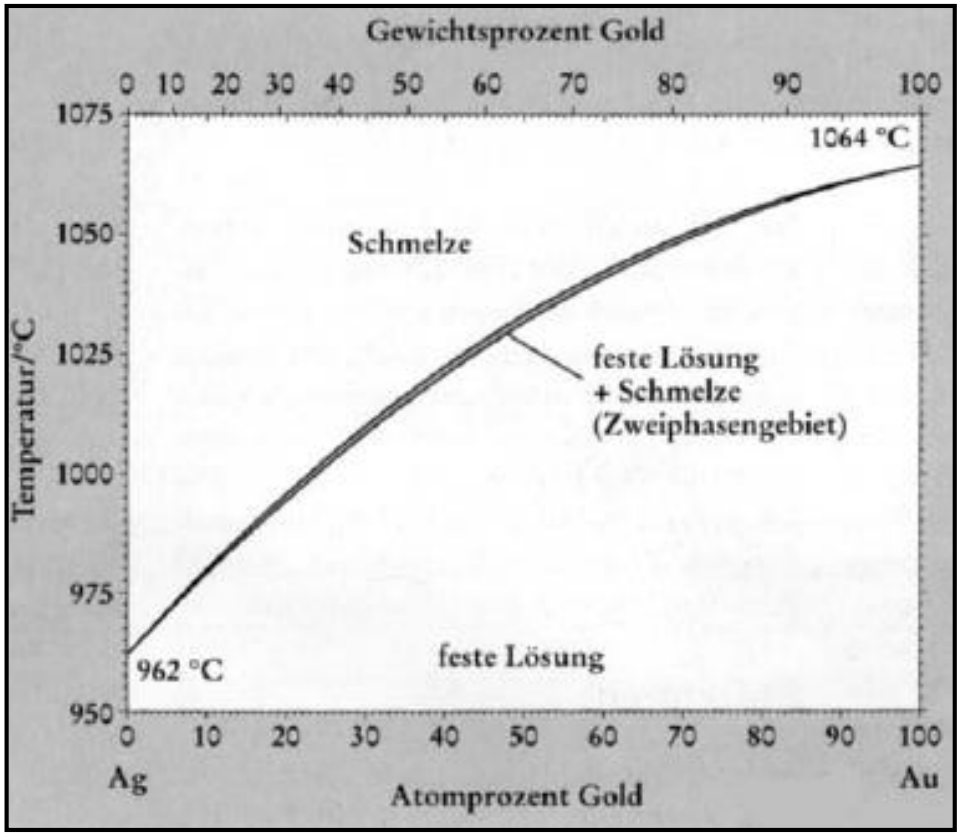
1. The pure materials must crystallise in the same crystal structure (isotypic)

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

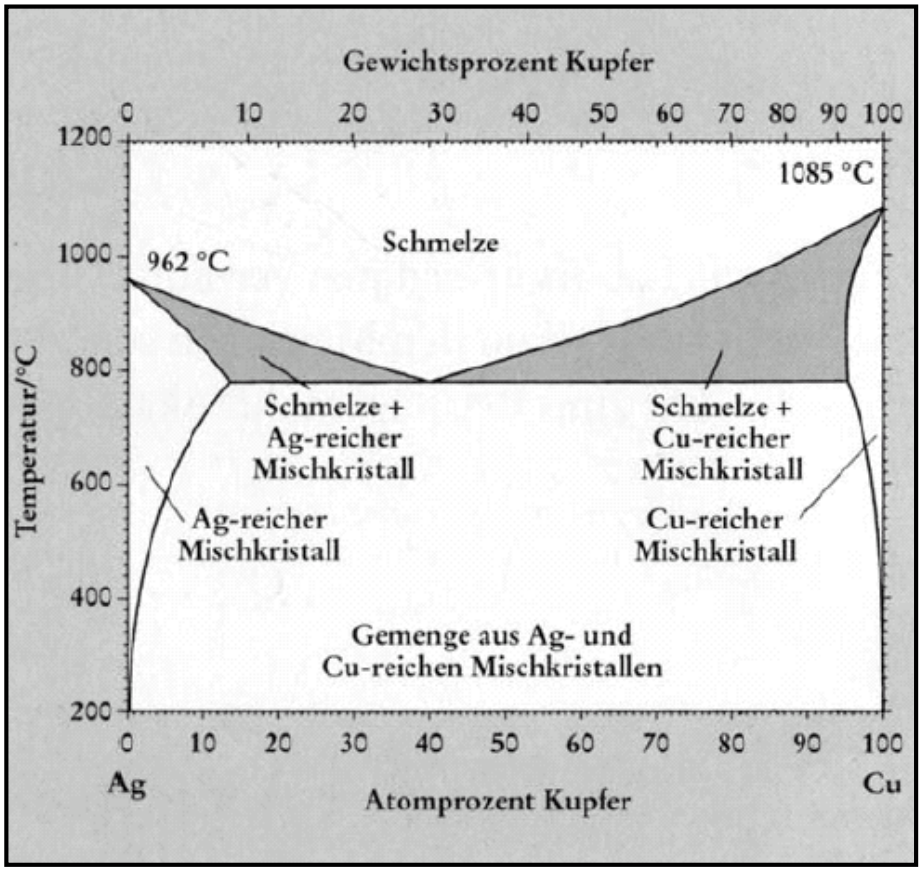
Limited miscibility in solid state

Example

System Cu-Ag

Solubility

- **15 atom percent Cu in Ag**
- **5 atom percent Ag in Cu**



2. Structure of Solid State Materials

Phase Diagrams – Solid Solutions

No miscibility

Example

System Al_2O_3-CaO

(important for concrete)

Formation of following compounds

Al_2O_3	cubic
$CaAl_{12}O_{19}$	hexagonal
$CaAl_4O_7$	monoclinic
$CaAl_2O_4$	monoclinic
$Ca_{12}Al_{14}O_{33}$	cubic
$Ca_3Al_2O_6$	cubic
CaO	cubic

Alkalinity ↓