Ceramics and Alloys

1. Structures of alloys
2. Structures of ceramics
3. Properties and applications for ceramics

Introduction
Who is who?

Characteristics of alloys and ceramics

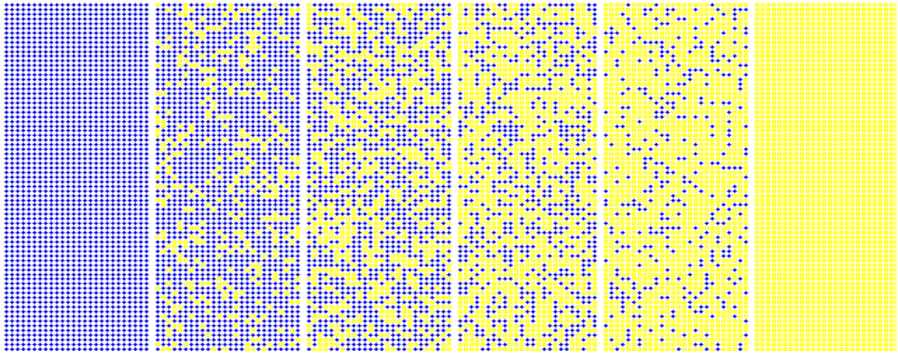
Alloys	Ceramics
Metallic or semi-metallic	Insulators
High electrical conductivity	Ionic conductors
Marginal charge separation	Ionic bonding
Structure description difficult	Polyhedral structures

1. Structures of alloys
Solid solutions

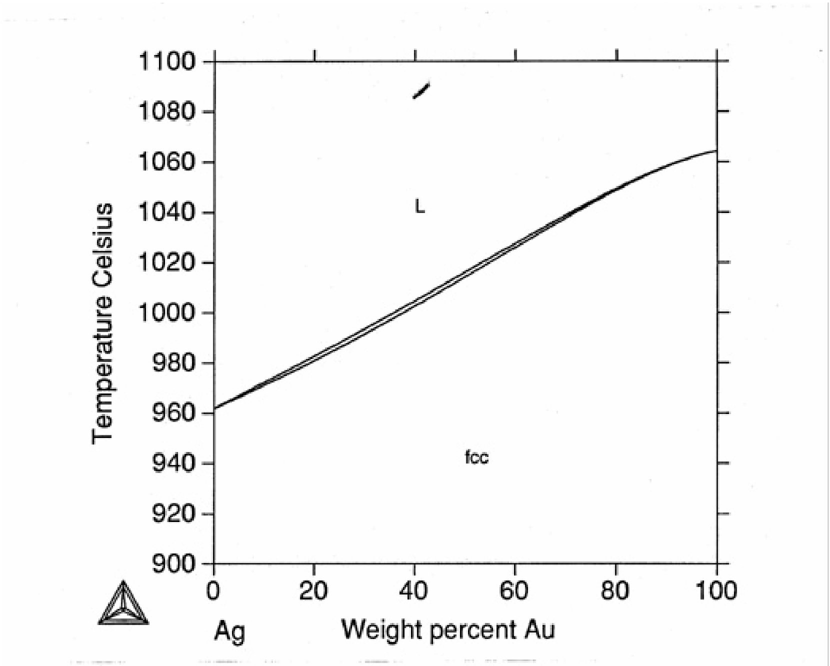
Random arrangement of species on the same position
Examples: Rb_xCs_{1-x} BCC, Ag_xAu_{1-x} CCP

The species must be related:

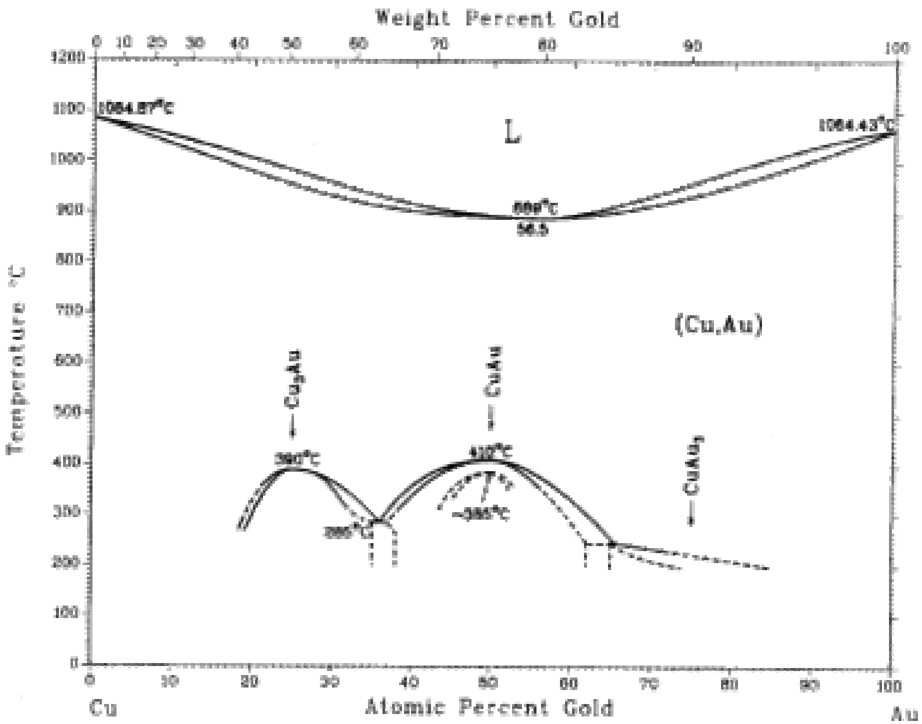
- **chemically related species**
- **small difference in electronegativity**
- **similar number of valence electrons**
- **similar atomic radius**
- **(high temperature)**



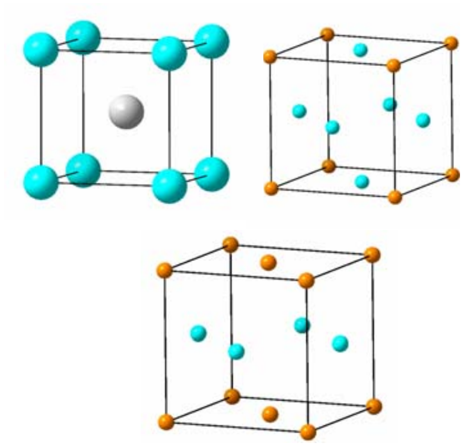
Au **Ag**



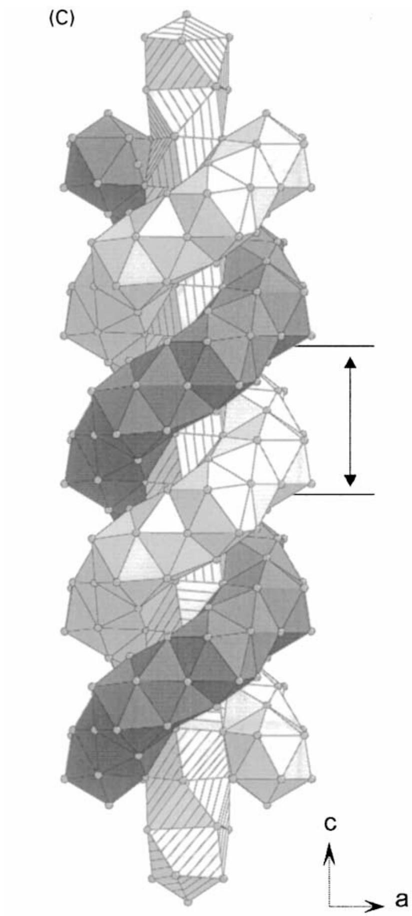
1. Structures of alloys
Intermetallics- fundamentals



Exception: simple structures



Rule:
complex structures

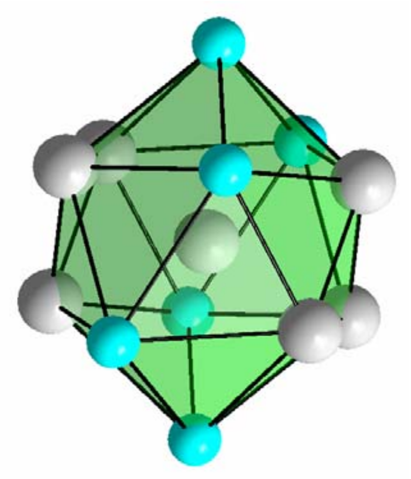


Co_2Zn_{15} (S. Lidin, JSSC 166, 53 (2002))

1. Structures of alloys
Intermetallics- Laves-phases

Intermetallics with a high space filling (71%)
Typical radius ratio: 1:1.225

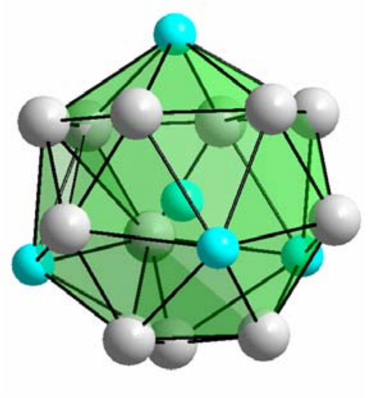
Structure	$MgCu_2$	$MgZn_2$	$MgNi_2$
Example	$TiCr_2$ $AgBe_2$ $CeAl_2$	$BaMg_2$ $FeBe_2$ WFe_2	FeB_2 $TaCo_2$ $ZrFe_2$



Structure description: mixed polyhedra

- Mg, CN: 12(Cu) + 4(Mg)
- Cu, CN: 6(Cu) + 6(Mg)

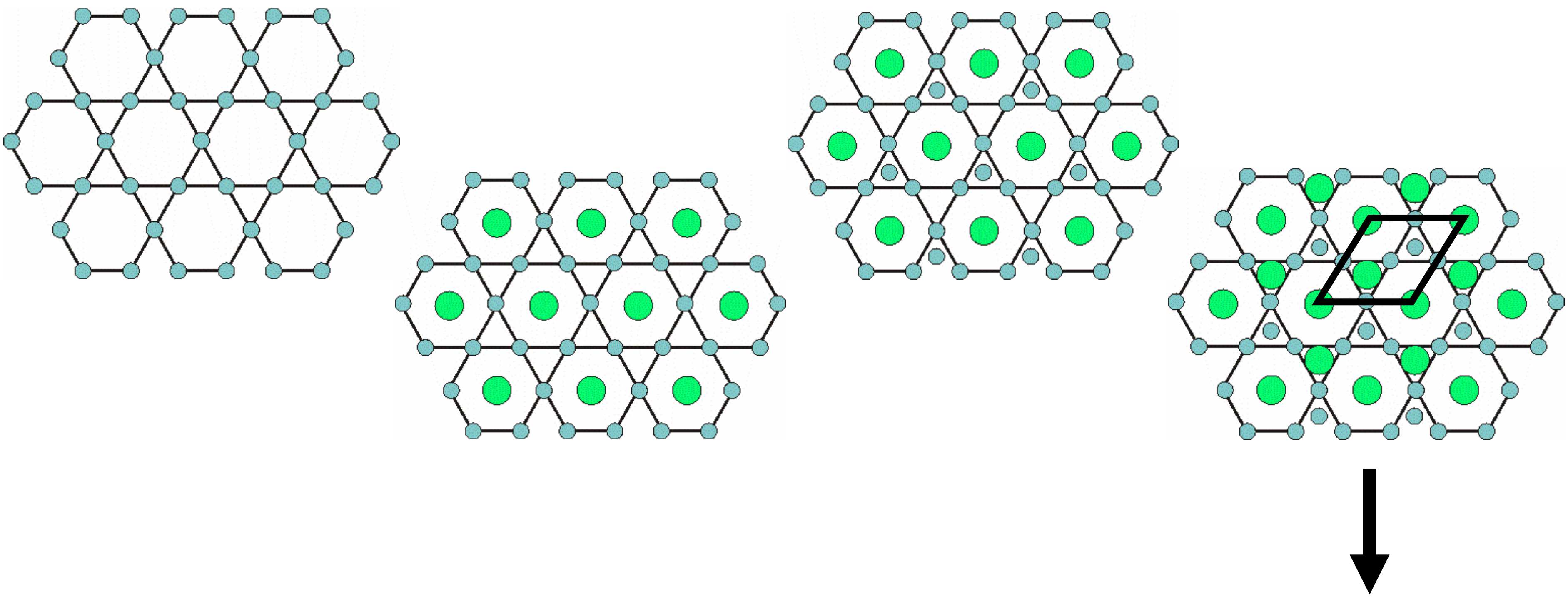
} Frank-Kasper-polyhedra



1. Structures of alloys
Intermetallics- Laves-phases (Kagome nets)

Description of the structure by separated elements: layers

Stacking sequences of Kagome-nets: $MgCu_2$: ABC, $MgZn_2$: AB, $MgNi_2$: ABAC

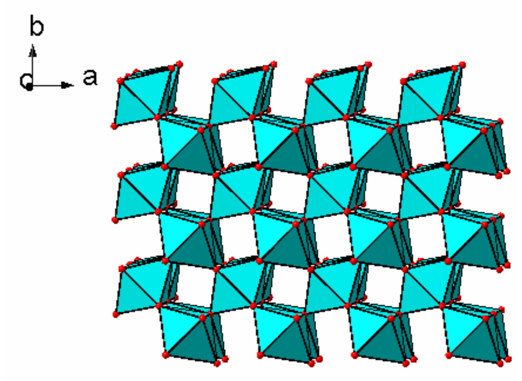


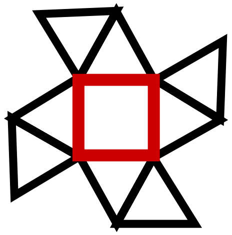
Exercise: Determine the composition of this multiple layer **A**

2. Structures of ceramics
Oxides: Rutile (TiO_2)

Crystal data

Formula sum	TiO_2
Crystal system	tetragonal
Space group	*P* 4_2/m n m (no. 136)
Unit cell dimensions	*a* = 4.5937 Å, *c* = 2.9587 Å
Z	2





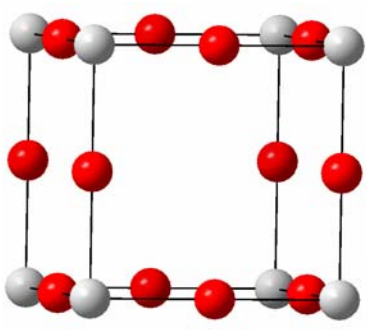
Atomic coordinates

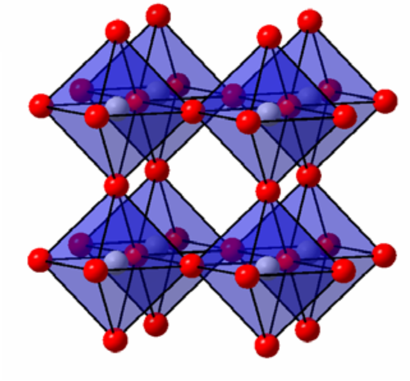
Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**
Ti1	+4	*2a*	0	0	0
O1	-2	*4f*	0.3047	x	0

Structural features:

- **no HCP arrangement of O (CN(O,O) = 11, tetragonal close packing)**
- **mixed corner and edge sharing of TiO_6-octahedra**
- **columns of trans edge sharing TiO_6-octahedra, connected by common corners**
- **many structural variants ($CaCl_2$, Markasite)**
- **application: pigment**

2. Structures of ceramics
Oxides: ReO_3





Crystal data

Formula sum	ReO_3
Crystal system	cubic
Space group	*P* m -3 m (no. 221)
Unit cell dimensions	*a* = 3.7504(1) Å
Z 1	

Atomic coordinates

Atom	Ox.	Wyck.	x	y	z
Re1	+6	1*a*	0	0	0
O1	-2	3*d*	1/2	0	0

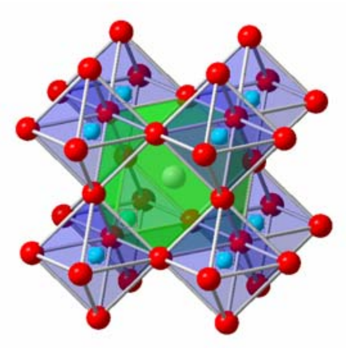
Structural features:

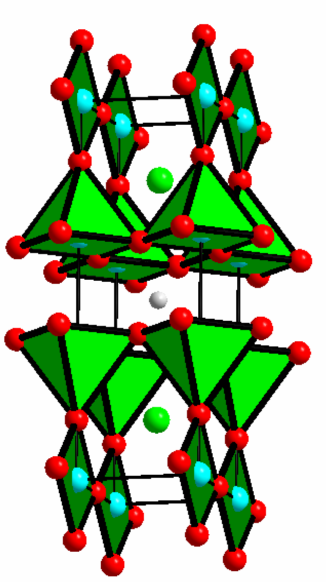
- primitive arrangement of Re, O on all centers of edges
- no close packing of O (CN (O,O) = 8)
- ReO_6 octahedra connected by six common corners
- large cavity in the center of the unit cell (CN = 12)
- filled phase (A_xWO_3 tungsten bronze)

2. Structures of ceramics
Oxides: undistorted perovskite ($SrTiO_3$)

Crystal data

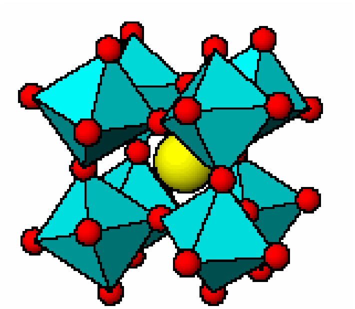
Formula sum	$SrTiO_3$
Crystal system	cubic
Space group	*P* m -3 m (no. 221)
Unit cell dimensions	*a* = 3.9034(5) Å
Z	1





Atomic coordinates

Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**
Sr1	+2	1*a*	1/2	1/2	1/2
Ti1	+4	1*b*	0	0	0
O1	-2	3*c*	0	0	1/2

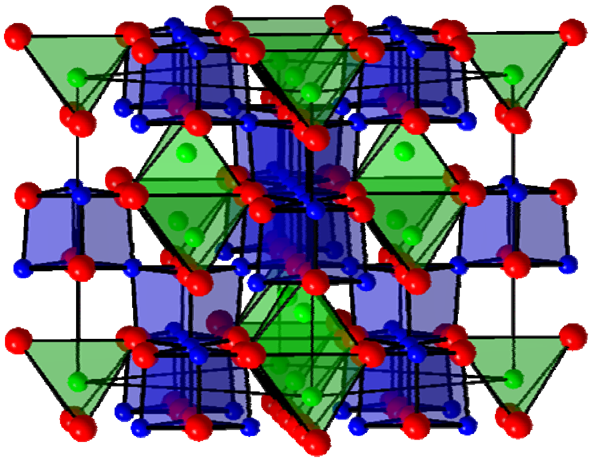


Structural features:
- filled ReO_3 phase, CN (Ca) = 12 (cuboctaehdron), CN (Ti) = 6 (octahedron)
- Ca and O forming CCP, Ti forms primitive arrangement
- many distorted variants ($BaTiO_3$, even the mineral $CaTiO_3$ is distorted!)
- many defect variants (HT-superconductors, $YBa_2Cu_3O_{7-x}$)
- hexagonal variants and polytypes

2. Structures of ceramics
Oxides: Spinel ($MgAl_2O_4$)

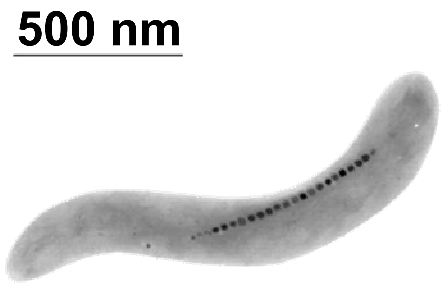
Crystal data

Formula sum	$MgAl_2O_4$
Crystal system	cubic
Space group	*F* d -3 m (no. 227)
Unit cell dimensions	*a* = 8.0625(7) Å
Z	8



Atomic coordinates

Atom	**Ox.**	**Wyck.**	**x**	**y**	**z**
Mg1	+2	8*a*	0	0	0
Al1	+3	16*d*	5/8	5/8	5/8
O1	-2	32*e*	0.38672	0.38672	0.38672



Structural features:
- **distorted CCP of O**
- **Mg in tetrahedral holes (12.5%), no connection of tetrahedra**
- **Al in octahedral holes (50%), common edges/corners**
- **Inverse spinel structures $Mg_{TH}Al_{2OH}O_4 \rightarrow In_{TH}(Mg, In)_{OH}O_4$**
- **Application: ferrites (magnetic materials)**

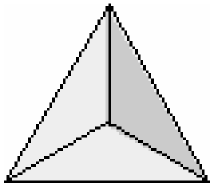
2. Structures of ceramics
Oxides: Silicates- overview 1

From simple building units to complex structures

Structural features:
- fundamental building unit (b.u.): SiO_4 tetrahedron
- isolated tetrahedra and/or tetrahedra connected via common corners
- MO_6 octahedra , MO_4 tetrahedra (M = Fe, Al, Co, Ni…)

Composition of characteristic b.u.:
Determine the composition and relative number of different b.u.

SiO_4

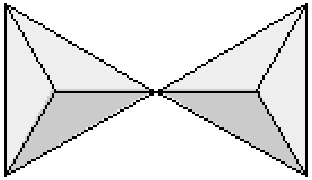


common corners (c.c): 0

Nesosilicates

SiO_4^{4-}
Olivine: $(Mg,Fe)_2SiO_4$

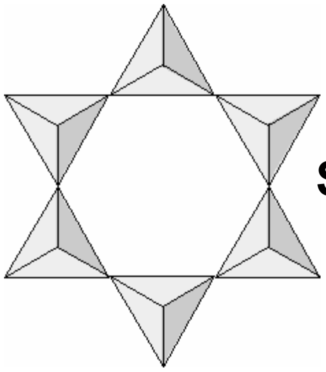
$SiO_3O_{0.5}$



c.c: 1

Sorosilicates

$Si_2O_7^{6-}$
Thortveitite: $(Sc,Y)_2Si_2O_7$



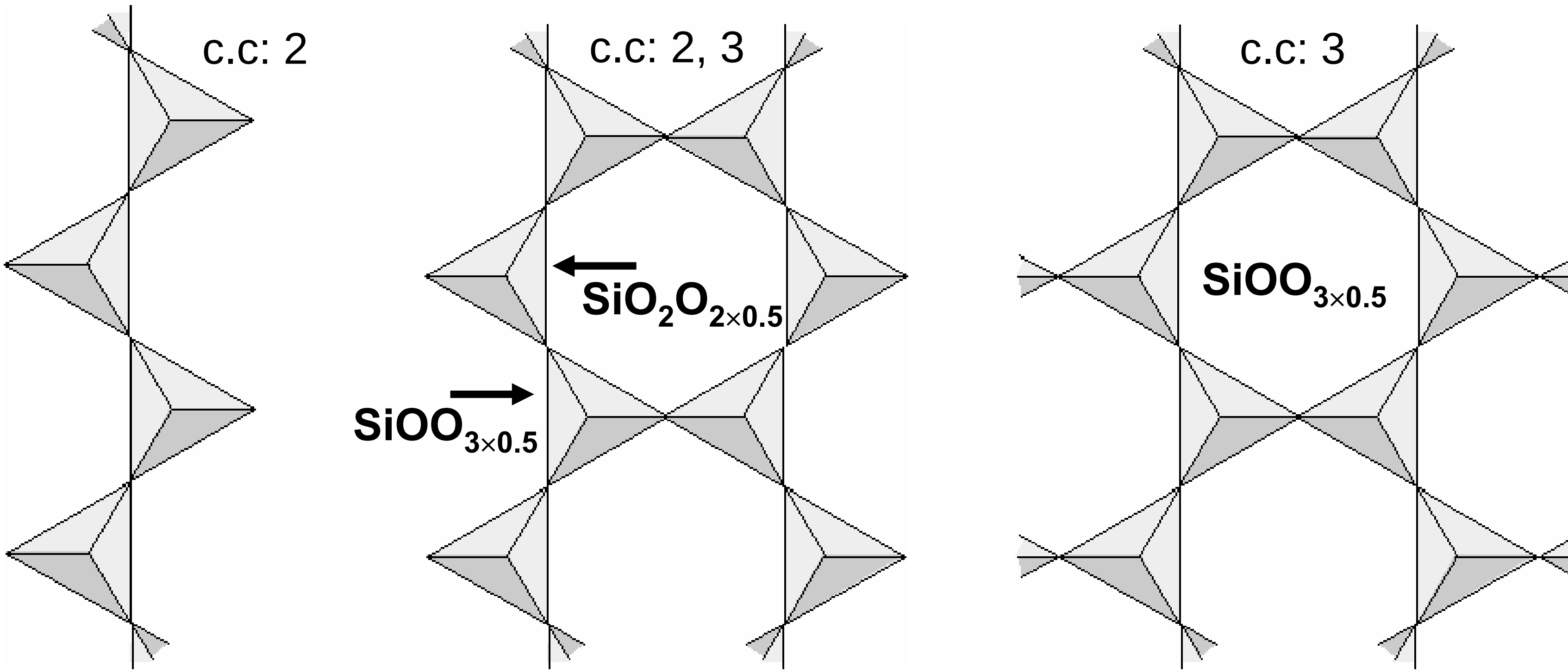
$SiO_2O_{2\times0.5}$

c.c: 2

Cyclosilicates

SiO_3^{2-}
Beryl: $Be_3Si_6O_{18}$

2. Structures of ceramics
Oxides: Silicates- overview 2



$SiO_2O_{2\times0.5}$

Inosilicates

Phyllosilicates

single chain: SiO_3^{2-}
Pyroxene: $(Mg,Fe)SiO_3$

double chain: $Si_4O_{11}^{6-}$
Tremolite:
$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$

$Si_2O_5^{2-}$
Biotite: $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$

2. Structures of ceramics
Oxides: Silicates- overview 3

Tectosilicates, c.c: 4, SiO_2,
Faujasite: $Ca_{28.5}Al_{57}Si_{135}O_{384}$

Zeolites can be considered as crystalline 3D alumosilicates with open channels or cages (d < 2 nm, "boiling stones")

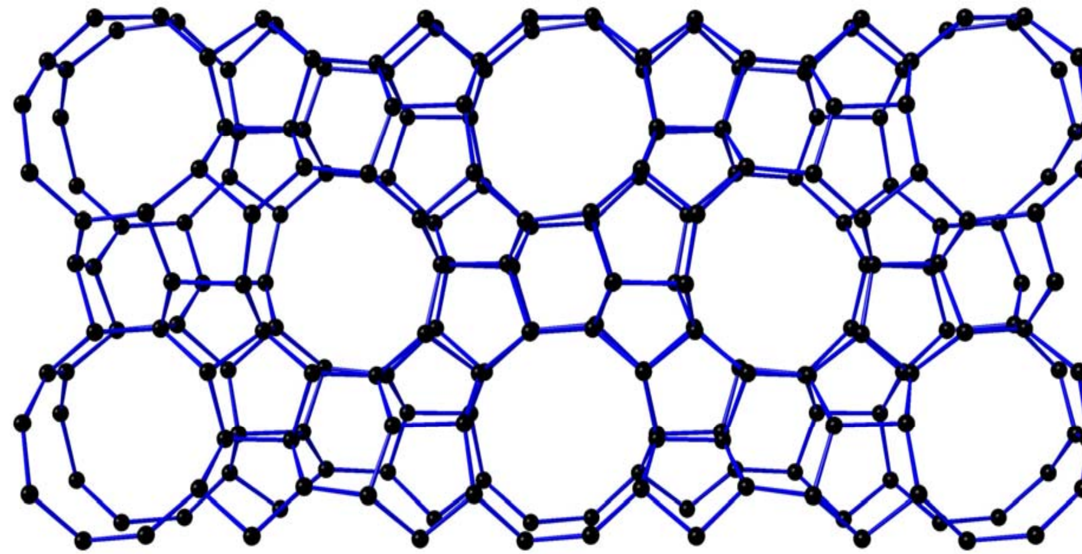
Pores → $A_{x/n}[Si_{1-x}Al_xO_2]\cdot mH_2O$ ← **Pores**

T (= Si, Al)O_4-Tetrahedra sharing all corners, isomorphous exchange of Si^{4+}, charge compensation

x: Al content, charge of microporous framework
n: charge of A

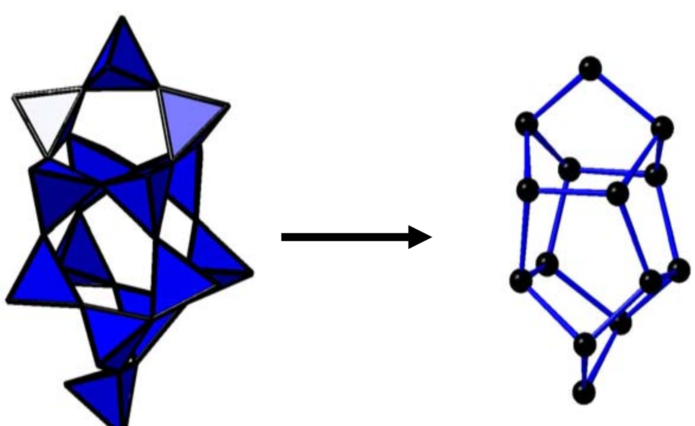
2. Structures of ceramics
Zeolites – Visualization 1

primary building unit
(TO_4 tetrahedron)



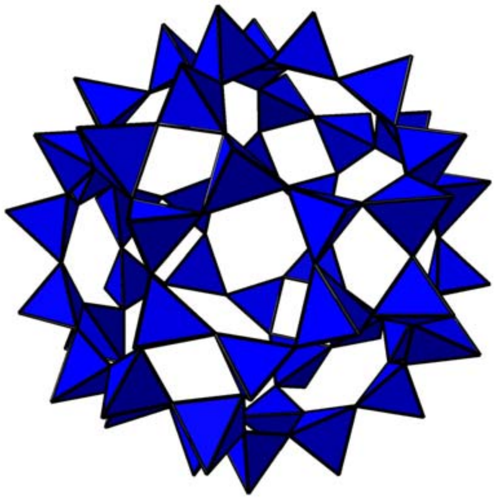
ZSM-5

secondary building unit
(pentasil-unit)

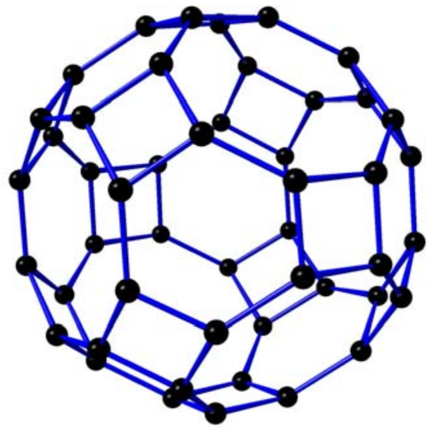


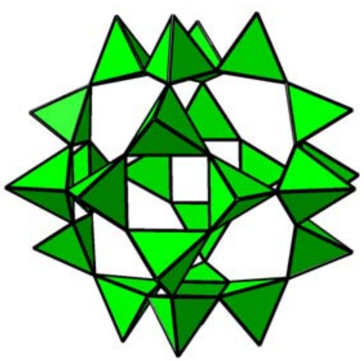
T-atom representation:
- **omitting all O atoms**
- **interconnections between T-atoms (no chemical bond!)**

2. Structures of ceramics
Structure of zeolites 1

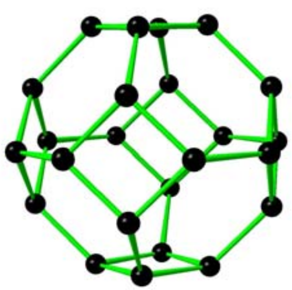


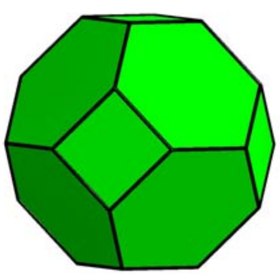
α-cage (Faujasite)





β-cage (Sodalite)

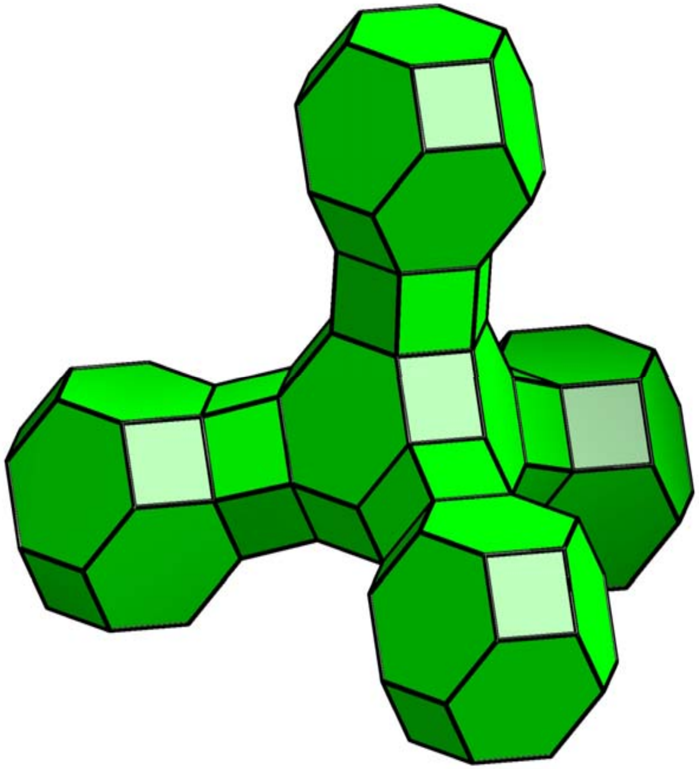




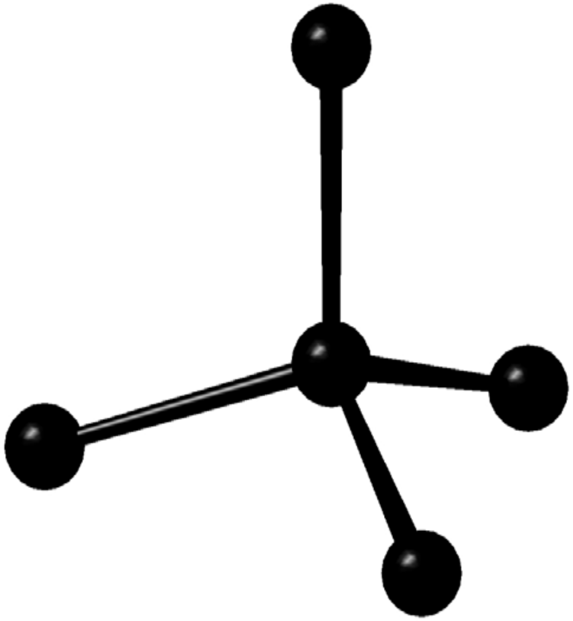
2. Structures of ceramics
Structure of zeolites 2

Visualization of topology

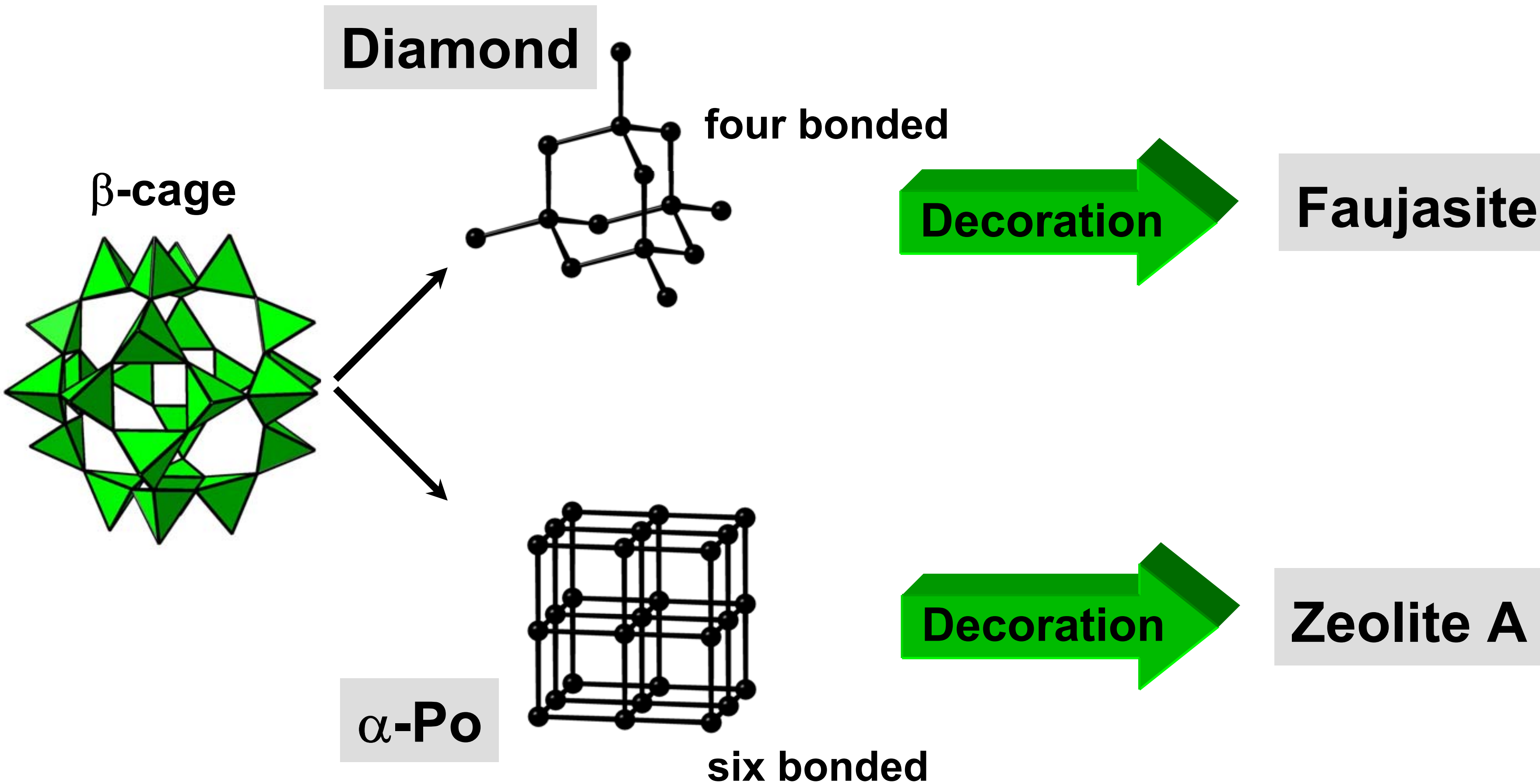
T-Atom representation



3D-Nets: edge + vertex



2. Structures of ceramics
Structure of zeolites 3



Trend in microporous structures: based on basic structure types

2. Structures of ceramics
Zeotypes – introduction

Zeotype: compounds with structures and properties related to zeolites - but no alumosilicates

Analogy to Zeolites:

1) Zeotypes originate from a compound related to SiO_2
   - Isoelectronic: $SiO_2 \leftrightarrow AlPO_4$
   - Structure: SiO_4 tetrahedra $\leftrightarrow$ AlO_4 and PO_4 tetrahedra (Quartz, Tridymite, Cristobalite)

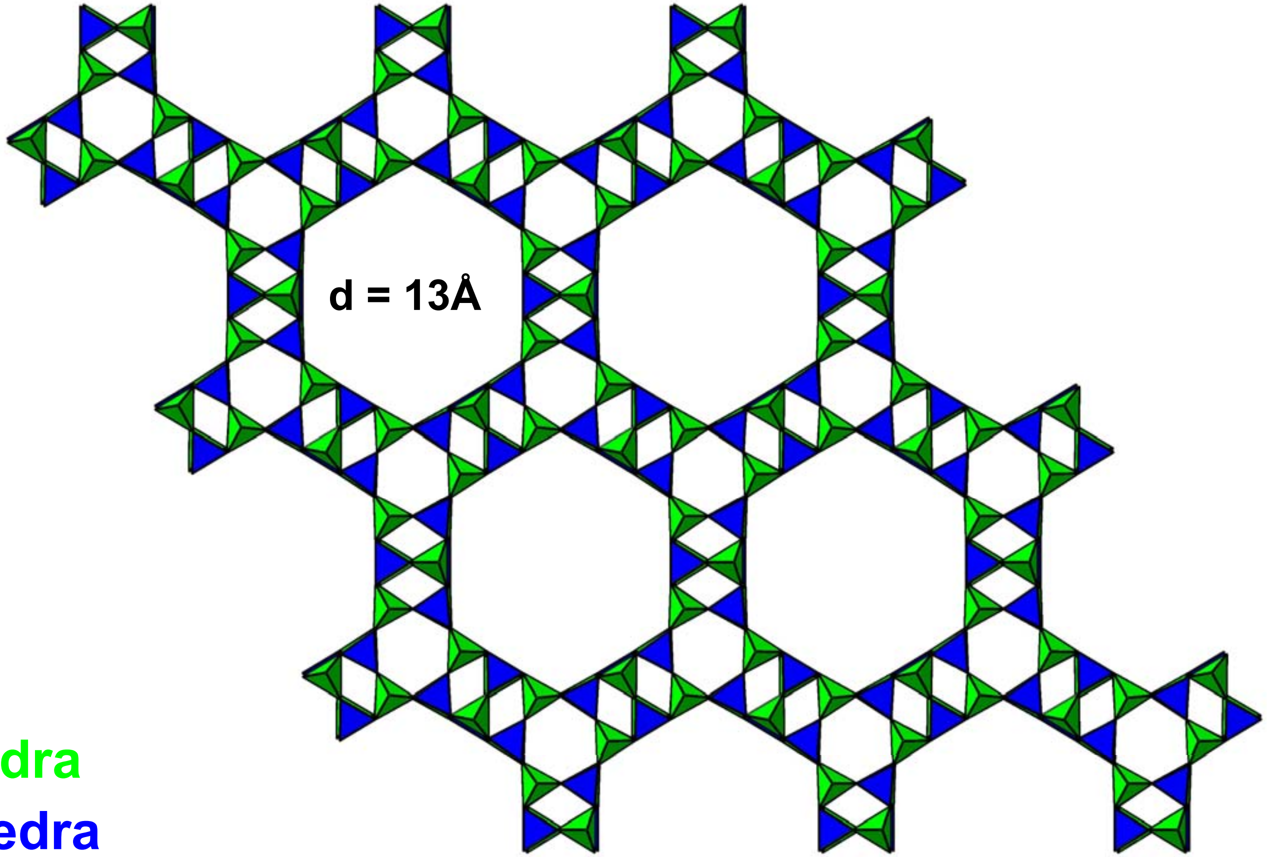
2) Related syntheses (Hydrothermal synthesis, template)

3) Isomorphous exchange: $Si^{4+} \rightarrow P^{5+}$ und $M^{2+} \rightarrow Al^{3+}$

2. Structures of ceramics
Zeotypes – $AlPO_4$ phases

New frameworks

***VPI-5**



PO_4-tetrahedra
AlO_4-tetrahedra

***Virginia Polytechnical Institute**

3. Properties and applications
Zeolites - applications

Catalysis
Cracking

Exchange
Washing powder

Special
Cosmetics

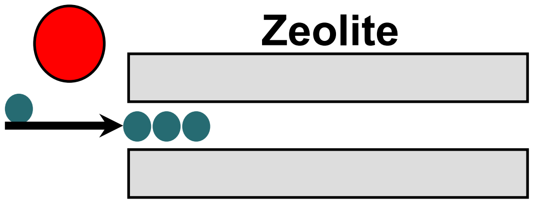
Separation
Gas separation

Structure property relations:

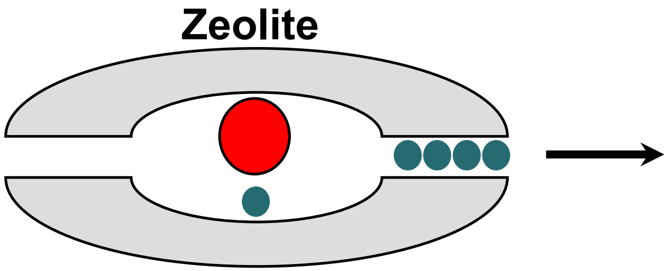
- different framework: different d (0.3 – 1 nm)
- same framework: Si/Al-ratio for tuning of stability, acidity...

3. Properties and applications
Zeolites - catalysis

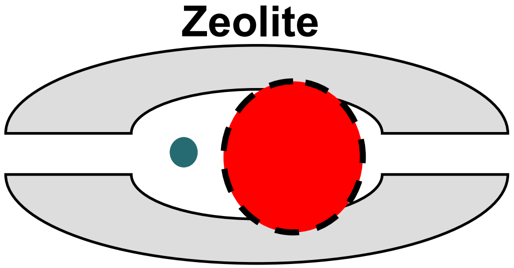
Educt-Shape-Selectivity
(before the reaction)



Product-Shape-Selectivity
(after the reaction)

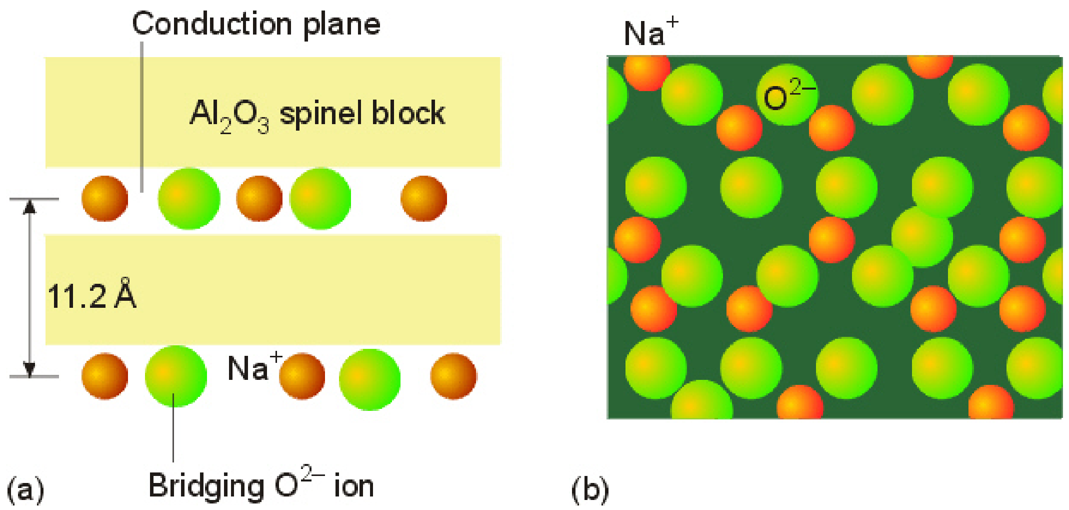


Transition State-Shape-Selectivity
(during the reaction)



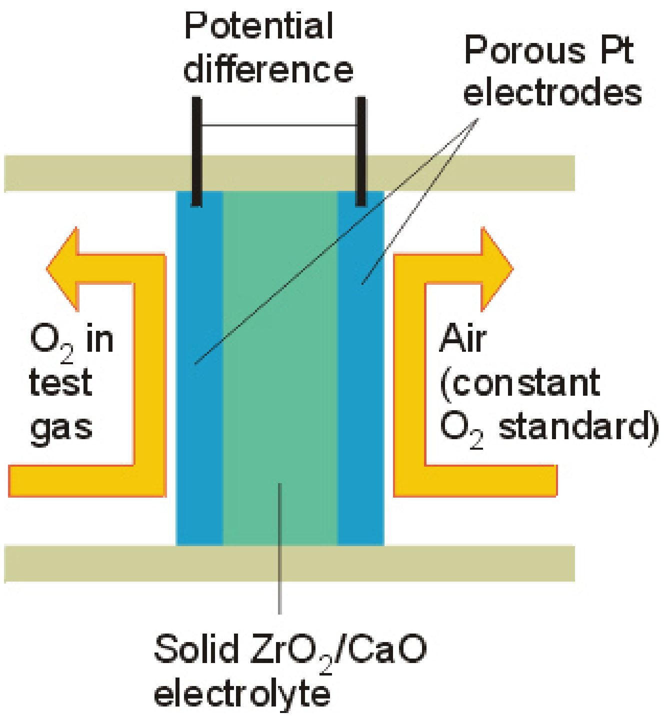
3. Properties and applications
Ionic conductivity- β-alumina

" β-alumina " ~ e.g. $Na_2O \cdot 11Al_2O_3$



3. Properties and applications
Ionic conductivity- YSZ

Oxygen sensor in exhaust systems



A Ca^{2+} (or Y^{3+}) doped ZrO_2 electrolyte is used as electrochemical sensor for the oxygen partial pressure in automobile exhaust systems.

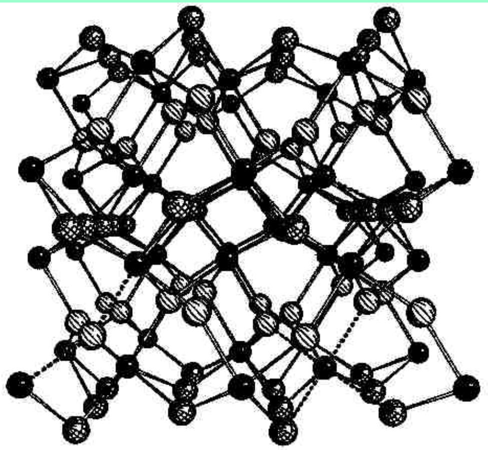
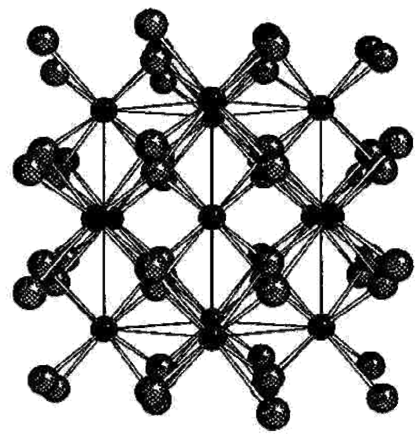
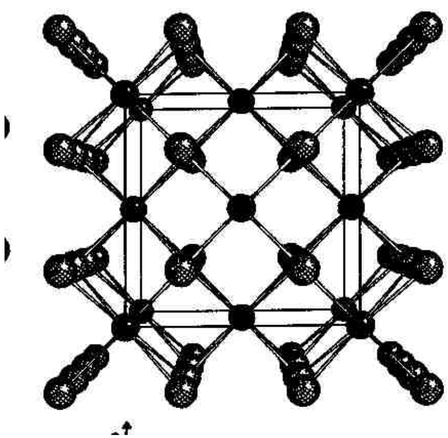
- Pt electrode absorbs O, in case of different O_2 partial pressure O^{2-} is migrating through the electrode:

$O_2(g) + Pt(s) \rightarrow 2O$ (at Pt surface)
O (at Pt surface) + $2e^- \rightarrow O^{2-}$ (ZrO_2)

O^{2-} (ZrO_2) $\rightarrow$ O (at Pt surface) + 2 e^-
2O (at Pt surface) $\rightarrow O_2(g) + Pt(s)$

3. Properties and applications
YSZ- high-performance ceramics

O < T <1170 ºC	1170 < T < 2370 ºC	2370 < T < 2950 ºC

ZrO_2(monoclinic) (baddeleyite) **ZrO_2(tetragonal)** **ZrO_2 (cubic)**

(distorted CaF_2-structure) **(CaF_2 – undistorted)**