Physical Bases of Dental Material science 5.

Crystallisation. Metals, alloys, ceramics.

E-book Chapters: 9-11

Homework: Chapter 3.: 3-5, 8, 10, 12, 14, 18

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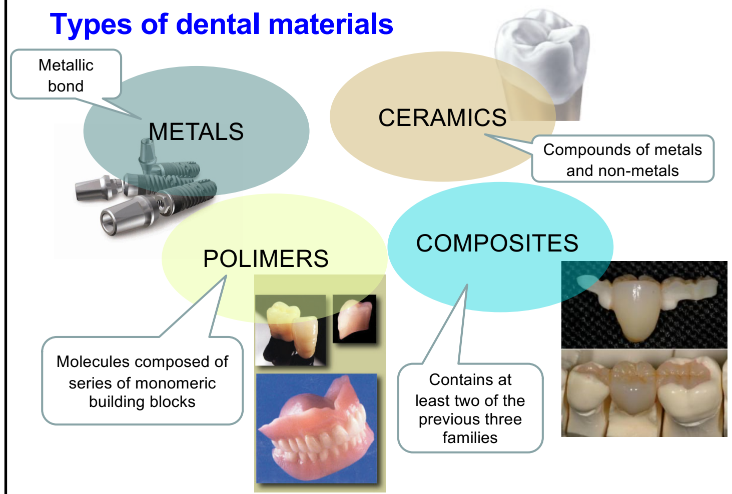
Types of dental materials



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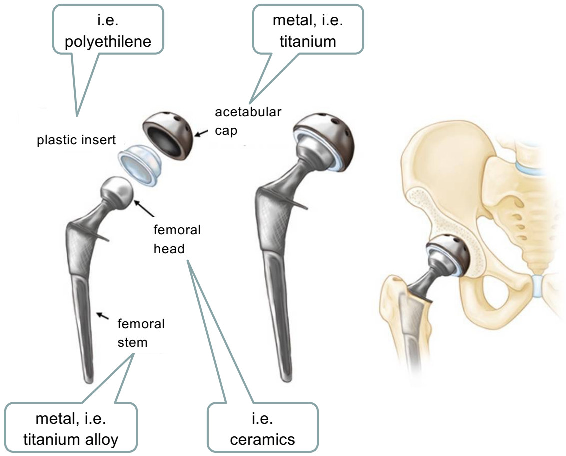
Medical examples



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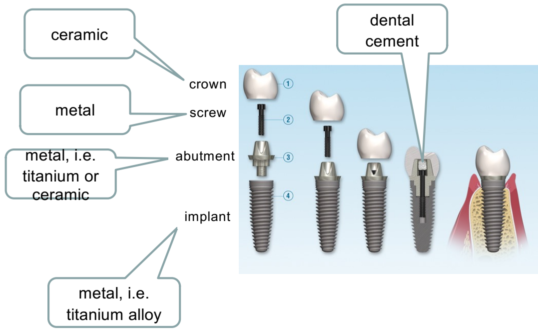
Dental examples



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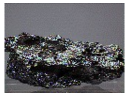
Metals

Properties:
- common material; diverse properties
- relatively large density
- solid at room temperature (except for Ga and Hg)
- relatively large toughness and strength
- relatively good deformability
- tendency to corrode (except for precious metals)
- properties can be influenced by alloying
- good heat and electric conductivity
- metallic color
- mostly not biocompatible


Structure:
- metallic bond
- Atoms with identical size in pure metals
- crystalline (typically hexagonal or cubic)*
- polycrystalline**

amorphous metallic glass!

examples for application:
- crown, bridge
- implants
- filling
- orthodontics

Production: melting, casting

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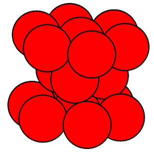
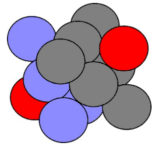
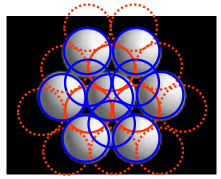
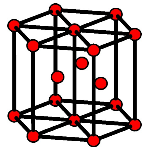
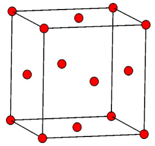
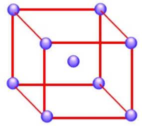
*Why is the hexagonal and cubic lattice common among metals?

close packing of equal spheres!

hexagonal close packed (hcp)	face centered cubic (fcc)	less packed body centered cubic (bcc)
pl. Ti, Cd, Co, Zn, ...	pl. Ag, Au, Pt, Al, Cu, Ni, ...	pl. Fe, Cr, ...
space filling: 74 %	74 %	68 %

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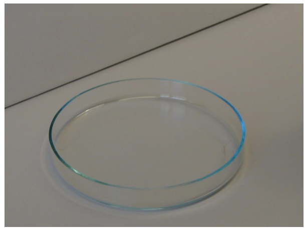
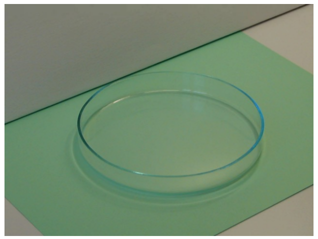

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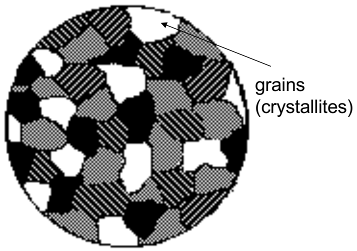
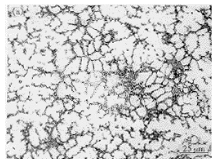
**Polycrystalline structure

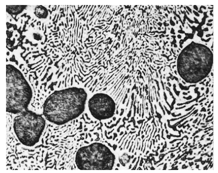
Microstructure:



homogenous microstructure



heterogeneous microstructure



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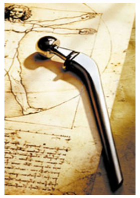
Metal alloys

Aim: to improove properties, for example:

- increase corrosion resistance, i.e. Fe, Ni, Co, …+Cr
- increase hardness, stiffness, i.e. Au+Cu
- to improve metal-ceramic adhesion, ie. precious metals +Fe, Sn, In

Classification:

- metal+metal, i.e. Fe+Cr
- metal+non-metal, i.e. Fe+C
- usage (i.e inlay, crown, ...)
- base element (gold or palladium based, ...)
- number of components (biner, terner, kvaterner,...)
- 3 main element (i.e. Au-Pd-Ag, Ni-Cr-Be, ...)
- type of phase diagram
  - solid solution
  - eutectic alloy
  - peritectic alloy
  - metal alloy



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Alloying ratios:

- mass% $c_{m,1} = \frac{m_1}{m_1 + m_2} (\cdot 100\%)$
- mole% $c_{v,1} = \frac{v_1}{v_1 + v_2} (\cdot 100\%)$ → properties!

(i.e. Ni-Cr-Mo-Be alloy: Be 1,8 mass% ↔ 11 mole%)

Conversion:

$$c_{v,1} = \frac{c_{m,1} \cdot M_2}{c_{m,1} \cdot M_2 + c_{m,2} \cdot M_1} (\cdot 100\%) \qquad c_{m,1} = \frac{c_{v,1} \cdot M_1}{c_{v,1} \cdot M_1 + c_{v,2} \cdot M_2} (\cdot 100\%)$$

Mean density: $\bar{\rho} = \frac{\rho_1 \cdot \rho_2}{c_{m,1} \cdot \rho_2 + c_{m,2} \cdot \rho_1}$

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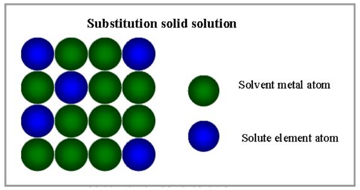
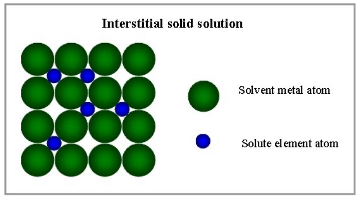
Solid solution

Good solubility in both liquid and **solid phases.**

homogenous microstructure



i.e. Cu-Ni, Pd-Ag, Au-Cu, ...



i.e. Fe-C, CP Ti (O, C, N, H), ...

(CP: Commercial Purity)

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Criteria of solubility for substitution solid solutions:

- difference between size of atoms is small (< 15%)
- same crystal lattice type
- similar electronegativity
- same valence, or the valance of „solvent" is greater

metal	atomic diameter (nm)	lattice	electro-negativity
Au	0,2882	fcc	2,4
Pt	0,2775	fcc	2,2
Pd	0,2750	fcc	2,2
Ag	0,2888	fcc	1,9
Cu	0,2556	fcc	1,9
Ni	0,25	fcc	1,8
Sn	0,3016	tetragonal	1,8

Criteria of solubility for interstitial solid solutions:

- size of „solute" atom is much smaller
- amount of „solute" is low (< 10%)

Properties of solid solution:

elastic limit, strength, hardness increases

plasticity decreases, i.e. Au-Cu (5 mass%)

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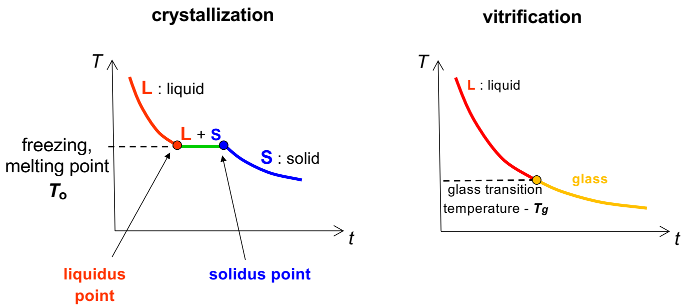
Cooling of pure melted metal



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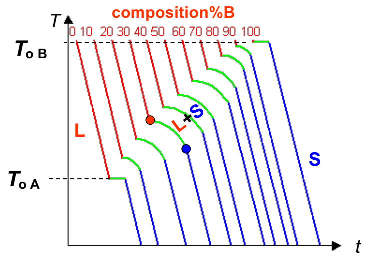
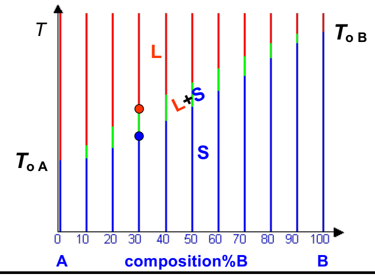
Cooling of solid solution



Phase diagram



Through equilibrium states! = infinitely slow cooling

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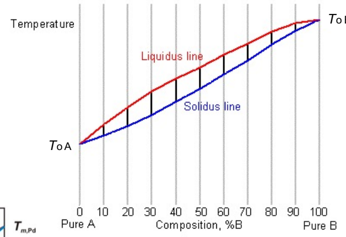
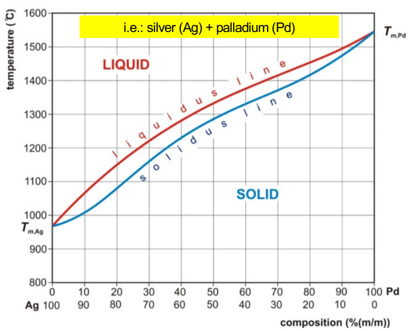
Equilibrium!





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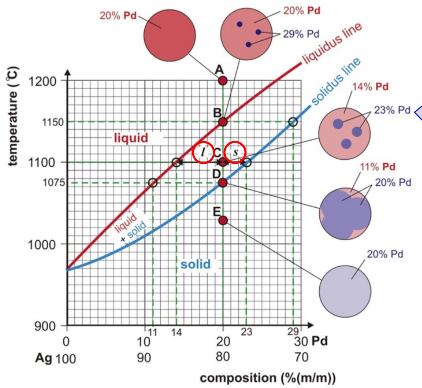
How to determine phase composition and ratio

Example: 80%(m/m) Ag + 20%(m/m) Pd



In point **C** :

- Liquid phase composition:

  14% Pd + 86% Ag

- Solid phase composition:

  23% Pd + 77% Ag

- Liquid phase ratio:

  $$\frac{s}{l+s} = \frac{23-20}{23-14} = \frac{3}{9} = 33{,}3\%$$

- Solid phase ratio: 66,6%

  $$\frac{l}{l+s} = \frac{20-14}{23-14} = \frac{6}{9} = 66{,}6\%$$

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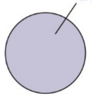
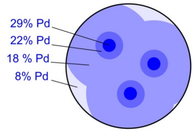
Through equilibrium states! = infinitely slow cooling



homogenous microstructure

Through non-equilibrium states = reasonable cooling



segregation!

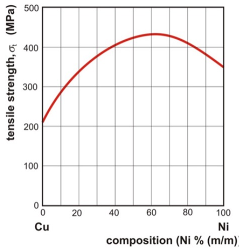
„cored" structure

heterogeneous microstructure

➡ **homogenization**

Alloying determines the properties

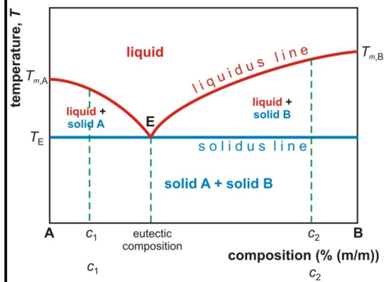
example: Cu-Ni

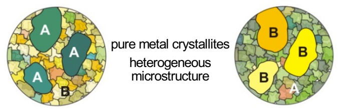


Eutectic alloys

Components do not dissolve in solid phase

The alloys melting temperature is lower than the pure component's.





Example:

0°C

800°C

$77\%H_2O+23\%NaCl$:

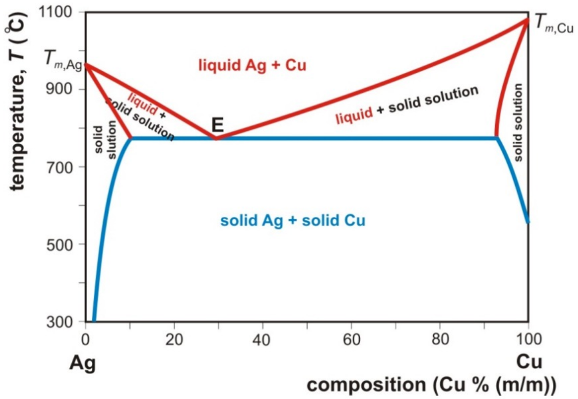
$T_E = -21°C$

Wood's metal (Bi-Pb-Cd-Sn):

$T_E = 68°C$

>230°C

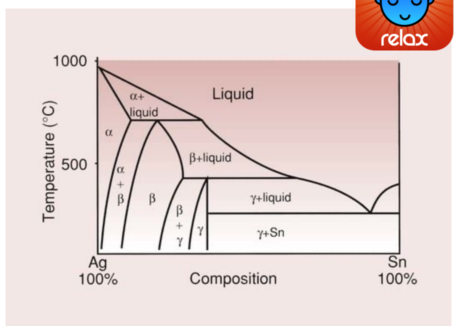
Ag-Cu



Amalgam

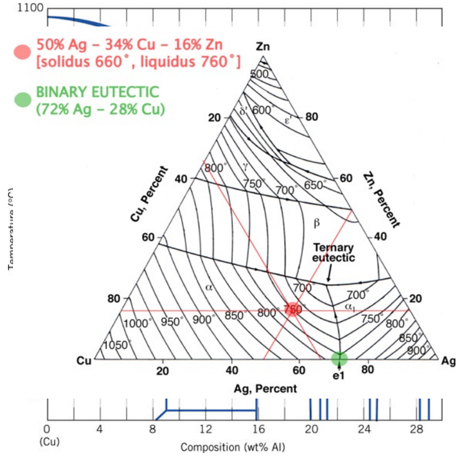
typical composition	
metal	**%(m/m)**
Hg	50
Ag	34
Sn	13
Cu	2
Zn	1

Ag-Sn phase diagram

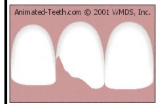


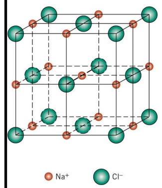
γ phase: Ag_3Sn

Eutectic phase diagram can be a nightmare!



Ceramics



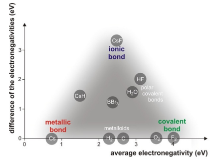


NaCl

Definition: mixture of metallic and non-metallic elements (there are exemptions!)

Properties:

- medium density
- solid at room temperature
- large stiffness, hard, not deformable, brittle
- great heat- and corrosion resistance
- heat shock sensitive
- bed heat- and electric conduction
- diverse optical properties
- biocompatible



Production:

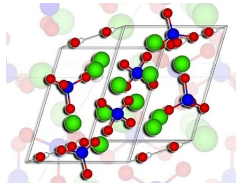
- melting
- sintering*

Structure:

- mainly ionic bond, less covalent
- ions of different sizes
- crystalline or amorphous or mixed**

Applications:

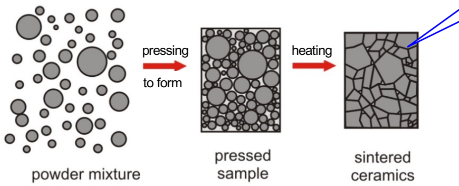
- crowns, bridges
- implants
- cements
- polishing materials

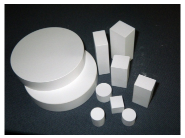


● P^{5+} ● O^{2-} ● Ca^{2+} ○ H^{+}

apatite

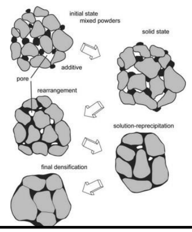
***Sintering**





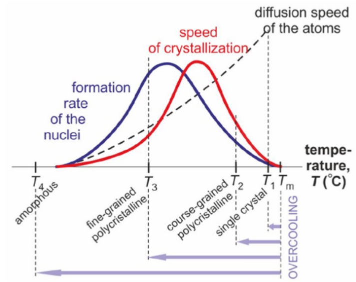
Practical problem: **porosity!**

Liquid phase sintering: one component melts

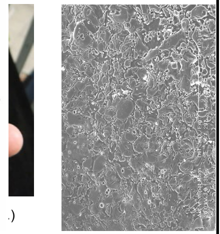


****Structure**

amorphous



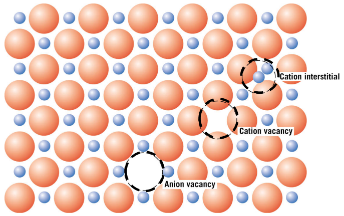
mixed

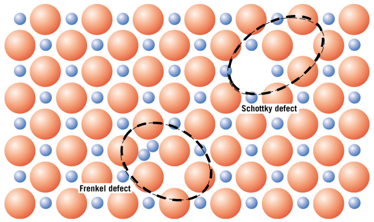


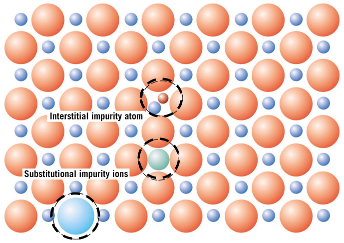
Glass-ceramics:

molten ceramics or heated ceramics quickly cooled → amorphous glass → heating up to high temperature, but below melting point. → crystallization → cooling → **polycrystalline material with very fine grains**

Lattice defects:







Limitations:
- **electroneutrality**
- **diffusion in „pairs"**

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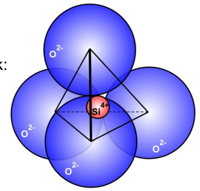
I. Silicates

Main elements: Si and O

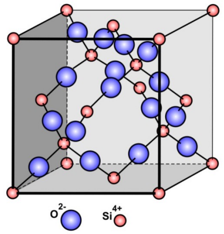
Building block: SiO_4^{4-}



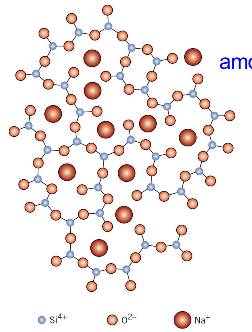
- **I./1. Silicon-dioxide (SiO_2)**

crystal

(i.e. cristobalite)



amorphous/glass



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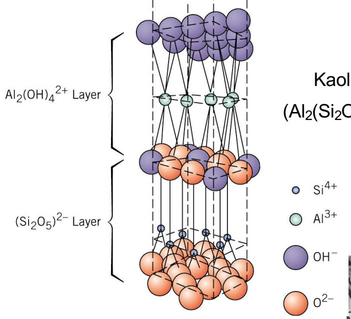
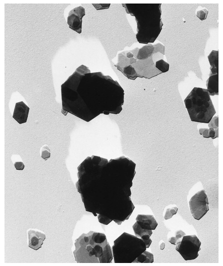
- **I./2. Porcelain** (traditional)



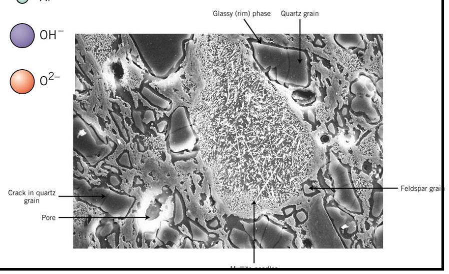
Kaolinite

$(Al_2(Si_2O_5)(OH)_4$



+ quartz

+ feldspar



drying, heating

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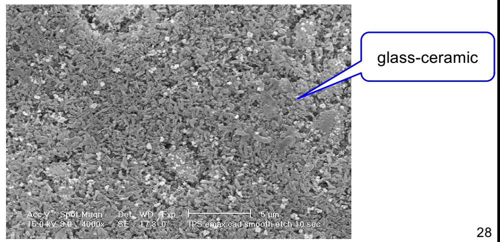
- **I./3. Dental silicate ceramics** (dental porcelain)
  - amorphous glass (alkali feldspars - $NaAlSi_3O_8$, $KAlSi_3O_8$, SiO_2, Al_2O_3, …)
  - amorphous glass with crystalline regions
    - amorphous feldspar glass + few leucite crystals ($KAlSi_2O_6$)
    - amorphous feldspar glass + 50% leucite crystals ($KAlSi_2O_6$)
    - Li-silicate glass + 70% Li-disilicate crystals ($Li_2Si_2O_5$)



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II. Oxide ceramics

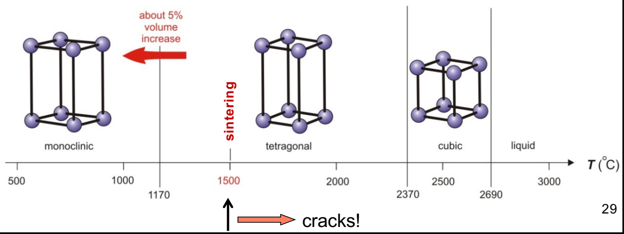
- **II./1. Zirconium-dioxide (ZrO_2 , zirconia)**

Properties (when sintered to compact state):

- white
- density approx. 6 g/cm^3
- great strength, toughness, stiffness, hardness (see later)

Production:

- from $ZrSiO_4$
- expensive purification steps
- cold or hot extrusion, sintering



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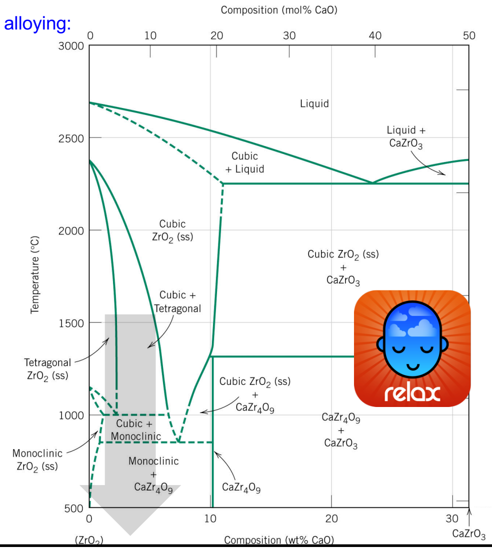
Stabilizing zirconia with alloying:

ZrO_2–MgO

ZrO_2–Y_2O_3

ZrO_2–CaO



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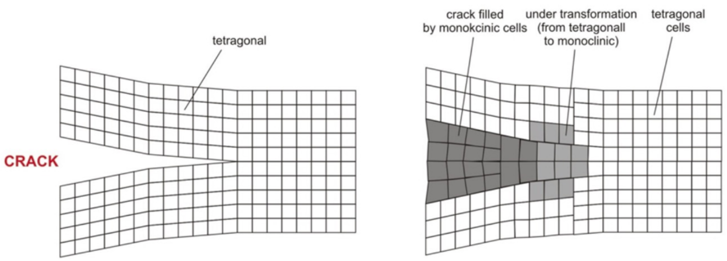
„Self-healing" property of zirconia:



Upon adding zirconia, other ceramics will become more resistant against cracks !

I. Ceramics toughened by phase transition!

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- **II./2. Aluminium-oxide (Al_2O_3)**

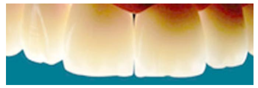
Properties:

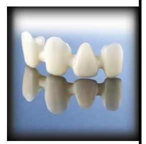
- colorless, white
- melting point 2700°C
- density approx. 4 g/cm^3
- very hard (see later)

Crystalline forms: corundum

$Al_2O_3 + CrO_2 \rightarrow$ ruby

$Al_2O_3 + CoO_2 \rightarrow$ sapphire





- **II./3. Oxide ceramics crystal + glass**

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