Nanomaterials and Film Systems

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Contents of Talk

- **Materials**
  - ✓ Ceramics: Definition & Evolution
  - ✓ Functional Properties
- **Materials Synthesis**
  - ✓ Processing
  - ✓ Top Down *versus* Bottom Up Strategies
  - ✓ Nanocrystalline Ceramics
- **Summary**

Materials:

... substances with specific properties for an optimal use in modern industrial and consumer technology...

Chemistry

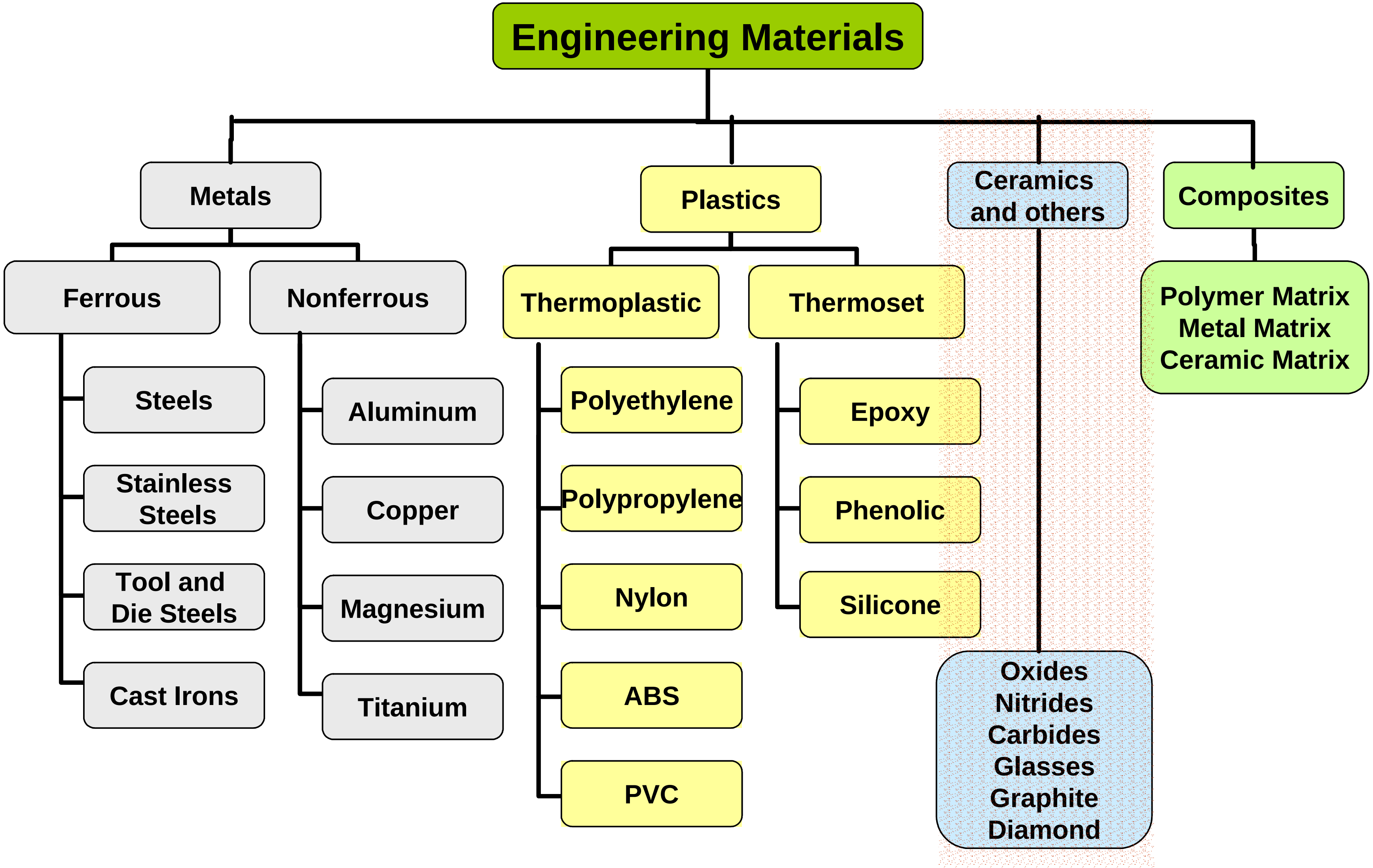
Physics

Materials Science

Engineering

... not of much value without any societal benefit ...

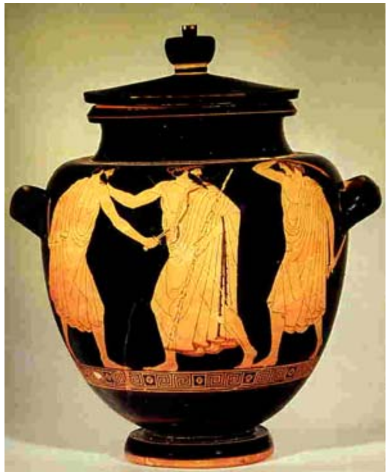
Materials: A Diverse World



Ceramics: Knowledge-based (R)Evolution

Ceramics

Origin of the word:



- Greek: *keramos*
- Significance: clay, brick

…. "the one who went through the fire“...

Definition:

- Primarily defined by the *texture and microstructure* of the material:
  heterogeneous ➡ amorphous + crystalline phases

- Modern ceramics are **high performance, high purity, inorganic non-metallic** materials with well defined microstructure and mainly *covalent* and *ionic* bonds

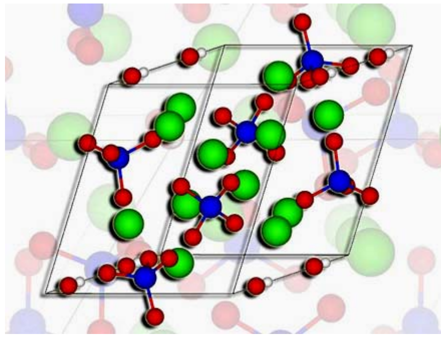
⬇

Ceramics ⟺ everything that is NOT polymer, metal, or grown

Examples

- Silica, SiO_2
  → main ingredient in glass
- Alumina, Al_2O_3
  → various applications (abrasives, … , artificial bones)
- Aluminium silicate, $Al_2Si_2O_5(OH)_4$
  → main ingredient in clay products

- Bio-ceramics



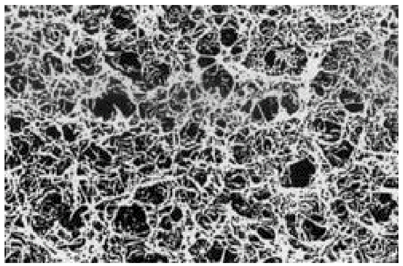
Crystal structure of HAP

➡ Calcium hydroxyapatite, $Ca_5(PO_4)OH$

⬇

Implants

Artificial bones



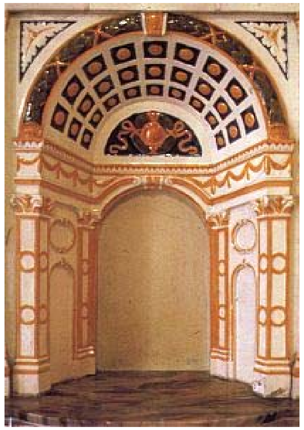
Tooth implants

Classification of Ceramics

Conventional Ceramics

Natural Raw Materials:
- Clay, Kaolin, Quartz, Feldspar, Mica

Biotite: $K_2(Mg,Fe)_3 AlSi_3O_{10}(OH,O,F_2)_2$



Silicate Ceramics

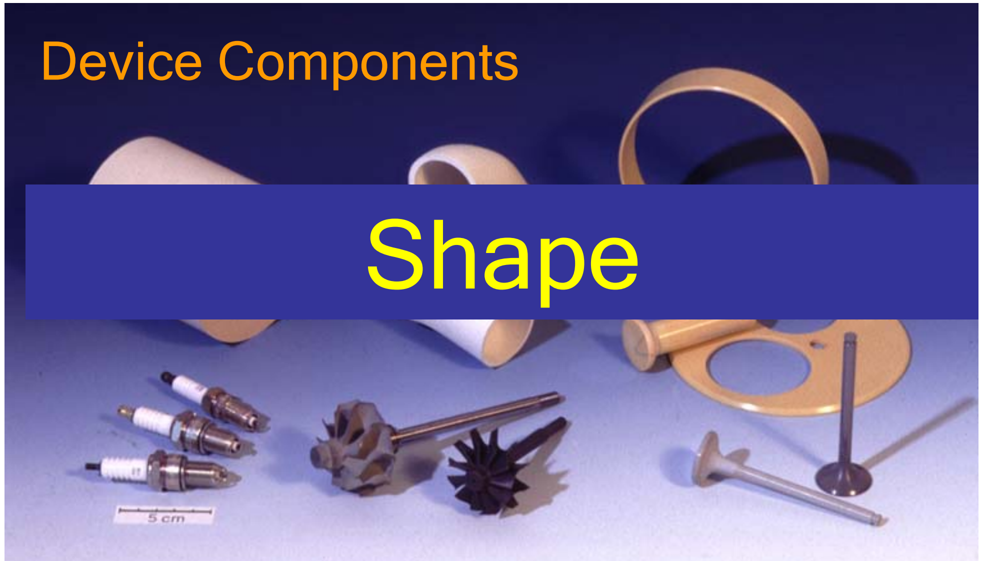
Refractory Materials

Advanced Ceramics

- Natural Raw Materials, but: chemically prepared
- Synthetic Raw Materials

Oxides	Non-oxides
Al_2O_3	SiC
ZrO_2	Si_3N_4
$MgAl_2O_4$	Graphite
BeO	Borides
ZnO	Silicides

Ceramics: Functional Materials



Advanced Ceramics

- Synthetically developed over the last several decades

  Through improvements in processing techniques

  - Control of microstructure
  - Tailored material properties

- Chemically simple when compared to natural materials

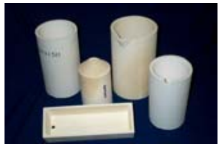
aluminium silicate

- oxides
- carbides
- nitrides
- borides

Examples: Advanced Ceramics

Oxides

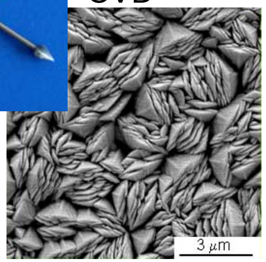
- high T resistant
- biocompatible



- alumina, Al_2O_3
  → refractory materials

- zirconia, ZrO_2
  → bio-materials

ZrO_2 films on dental drills deposited by CVD



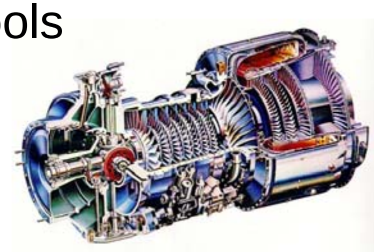
Carbides

- hard
- wear resistant

→ cutting tools

- SiC
- WC
- TiC
- TaC
- Cr_3C_2

+ metallic binder (Co, Ni)



Nitrides

- hard
- brittle
- high melting point
- semiconducting

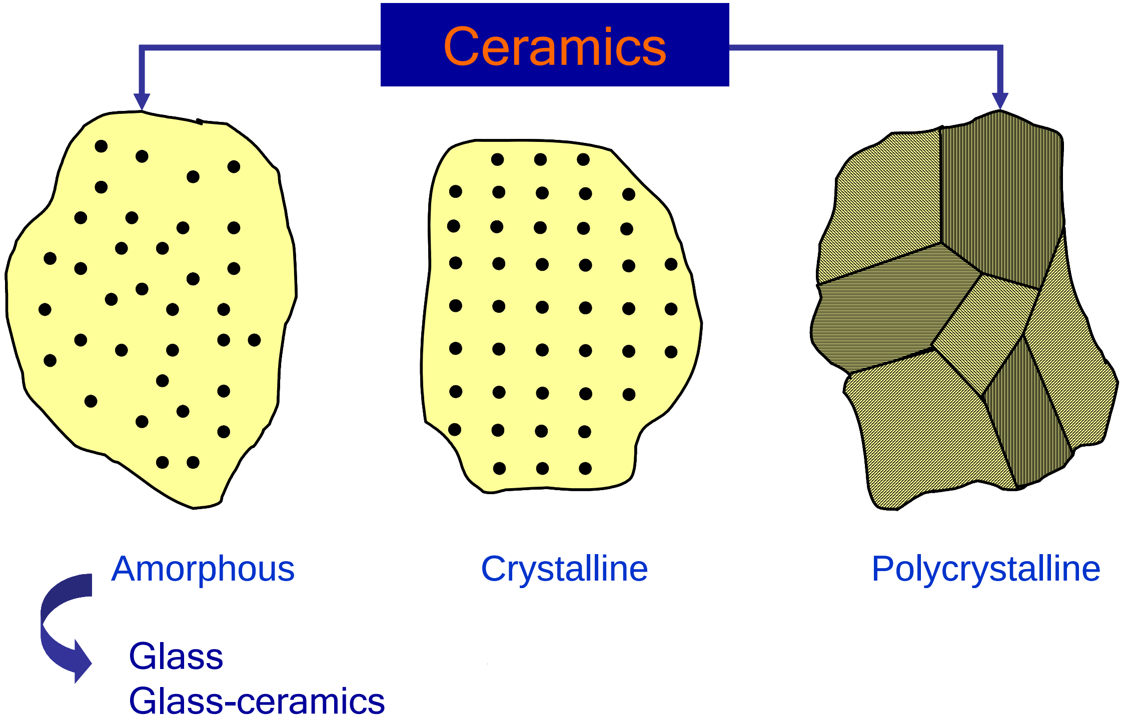
Silicon Nitride
→ gas turbines
→ rocket engines
→ melting crucibles

Boron Nitride / Titanium Nitride
→ cutting tools
→ coatings

Indium Gallium Nitride
→ LEDs, Displays
→Q-Dots

Ceramics:

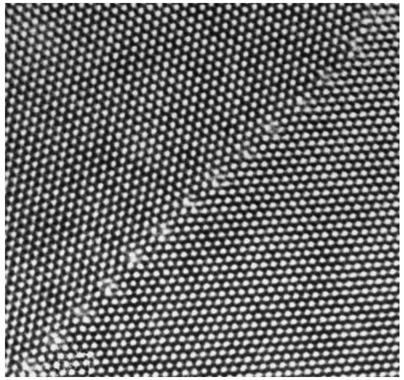
... poly(micro/nano)-crystalline materials whose properties are determined, besides chemical composition, by grain boundaries and microstructural defects ...



Careful control of synthesis and processing is important!

Grain Boundaries

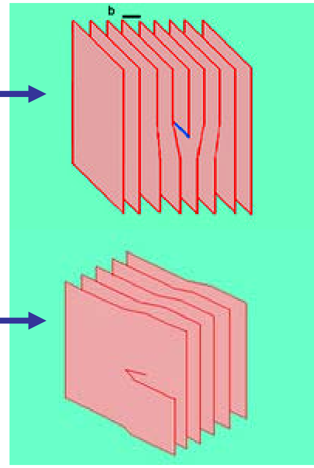
A *grain boundary* separates regions of the same crystal structure but of different crystal orientation.



Structure / Formation

Small-angle grain boundaries are formed by the periodic assembly of dislocations.

- small-angle-**tilt**-boundaries → periodic assembly of parallel **edge** dislocations →
- small-angle-**twist**-boundaries → periodic assembly of **screw** dislocations →



Edge dislocation

Screw dislocation

Influence on material properties:

grain size ↓ ➡ grain boundary surface ↑ ➡ influence ↑

Effects observed in *polycrystalline* material are not obligatorily observed in *single crystals*!

Microstructure ⟺ Property Relationship

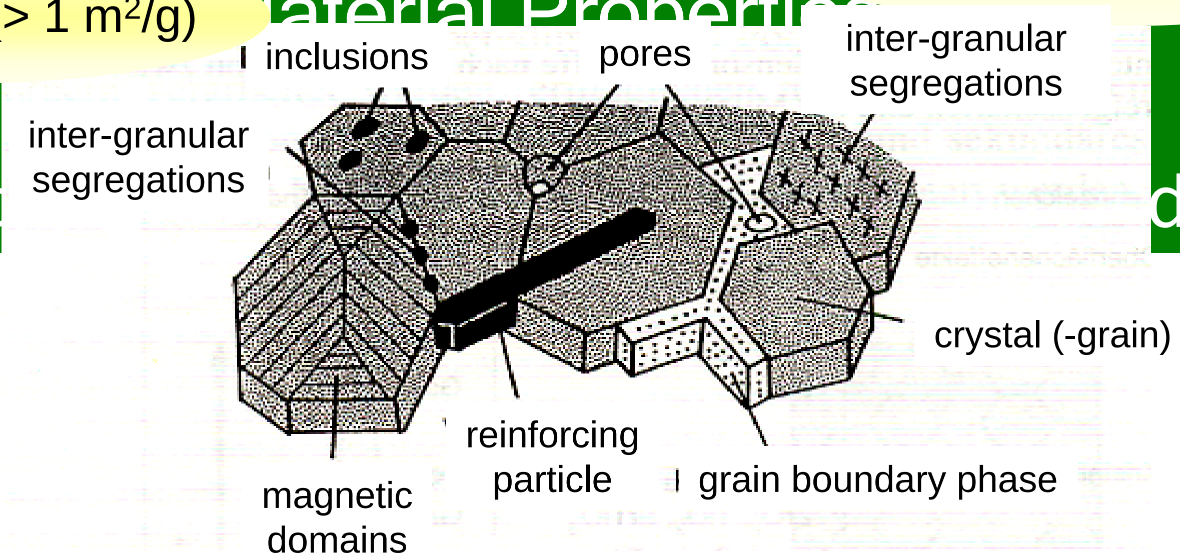
gradients in elemental, size and phase distribution

μm **dimension** nm

medium particle size

large surfaces (> 1 m^2/g)

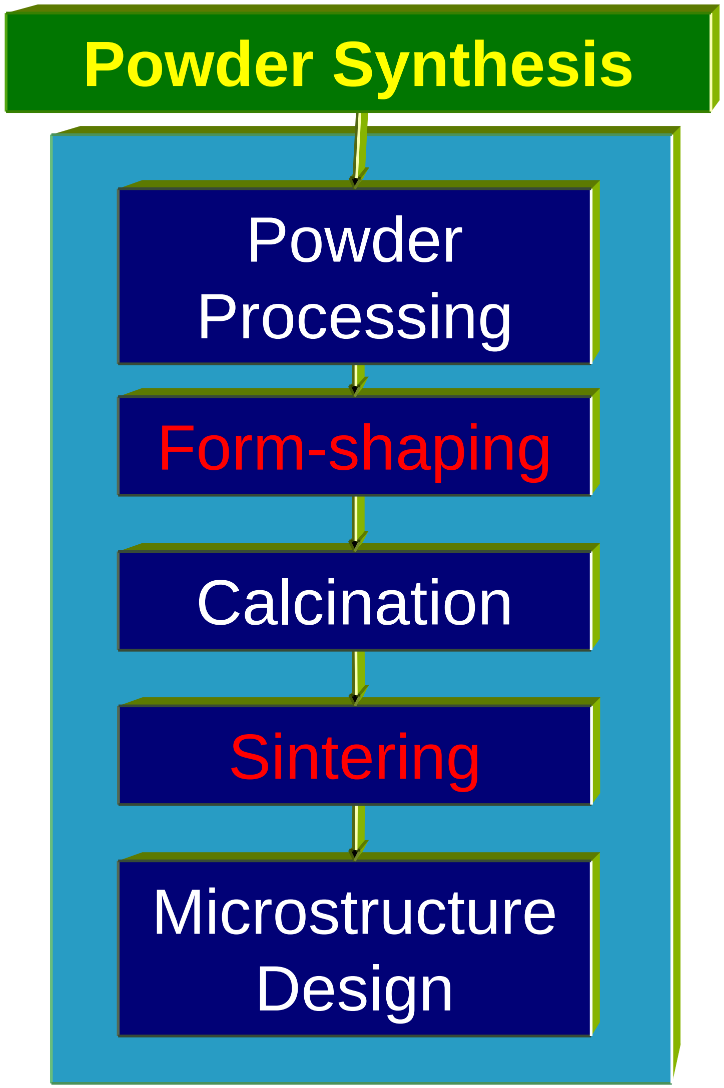
inter-granular segregations and grain boundary phases



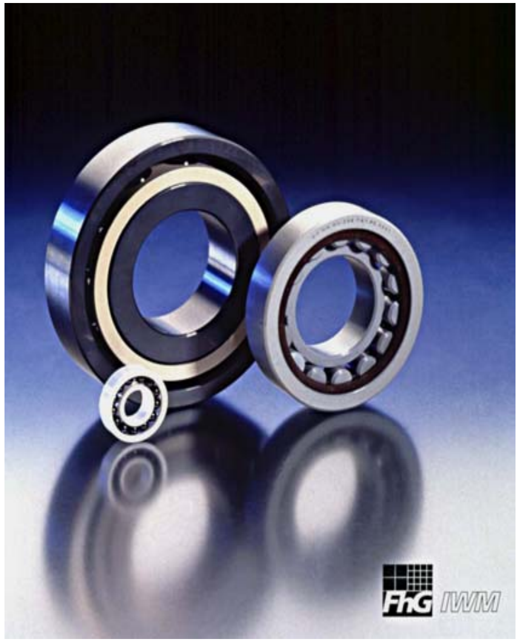
structural formation of **interfaces** and **grain boundaries**

Specific Properties

Ceramic Engineering: Synthesis & Processing

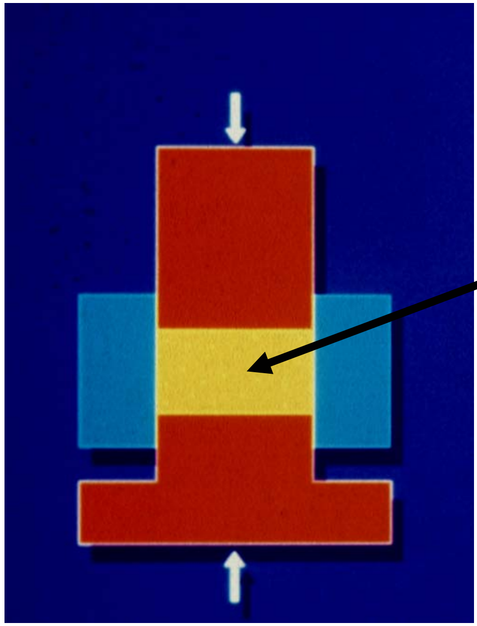


Ceramics: Processing



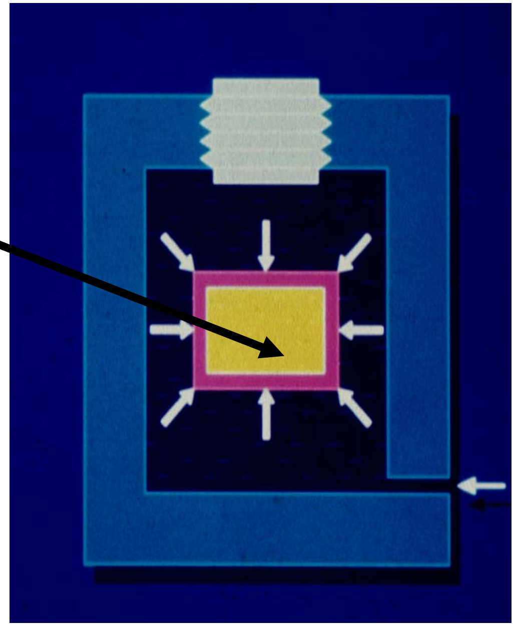
Ceramics: Powder Shape-Forming

Uni-axial Pressing



Green Body

Isostatic Pressing



<u>Limitations</u>

Density variation

Die wear/Contamination

Cracking

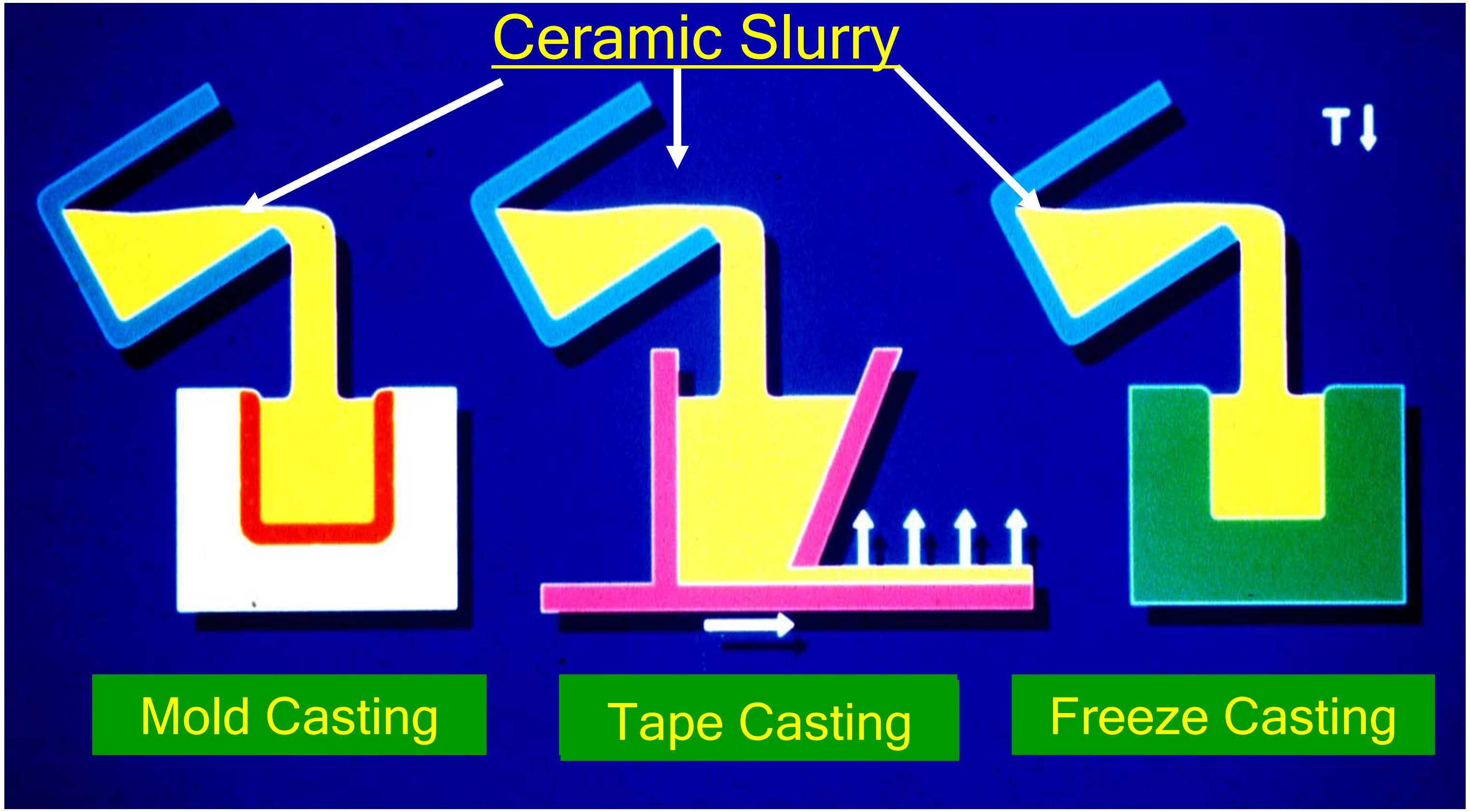
<u>Advantages</u>

Homogeneous pressure distribution

Compaction uniformity

Enhanced shape capability

Ceramics: Liquid Shape-Forming



Critical Factors

Slip (slurry) consistency, viscosity, entrapped air, chemical reactions, drain properties, shrinkage, release properties, strength of the cast-shape, etc.

Sintering

Green Body → **Densification** (ΔT) → Component

- Rearrangement of the powder particles
- Densification of the green body (decrease of porosity)
- Coarsening of the grains (grain growth)

Driving force = Reduction of the free surface energy

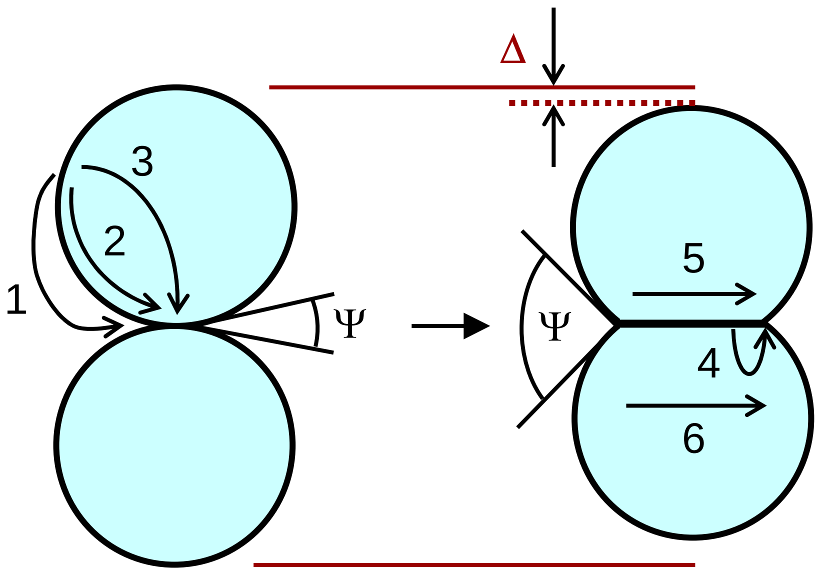
surface-E (powder system) > grain boundary-E (dense body)

I. Sintering Process

Sinter Temperature **<** Melting Temperatur (Eutectic T for composites)

Initial stage: → 40 – 75 % of theoretical density (TD)

- formation of sinter neck
- levelling of point of contact (→ neck growth)
- approach of grain centers (→ shrinkage Δ)



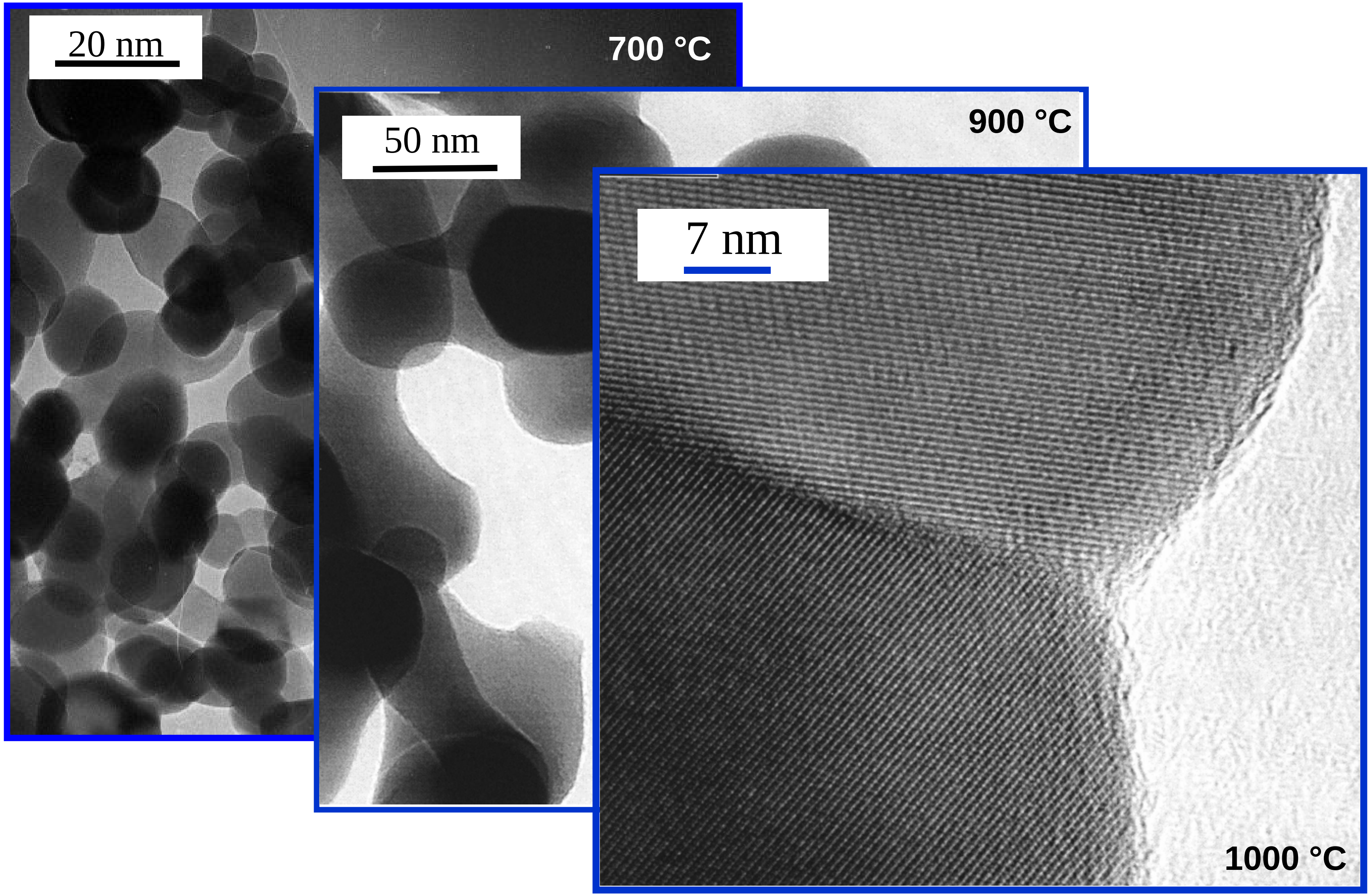
Without shrink:

1. Evaporation / Condensation
2. Surface Diffusion
3. Bulk Diffusion from the Surface

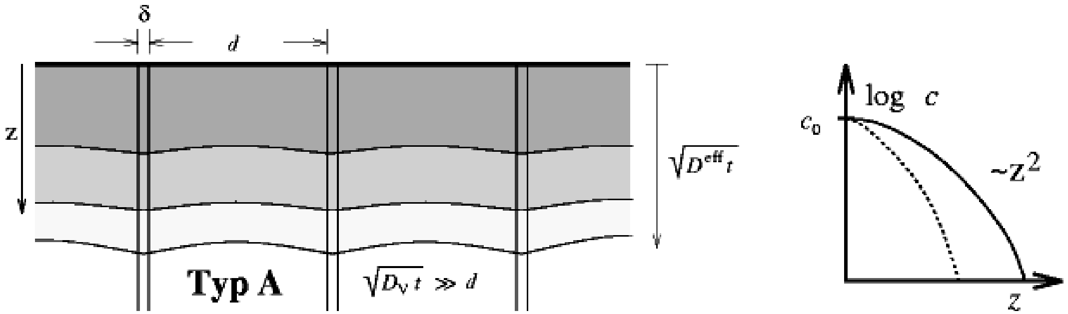
With shrink:

4. Bulk Diffusion from the Grain Boundary
5. Interface Diffusion at GB
6. Crystal-Plastic Creep

Sintering Process

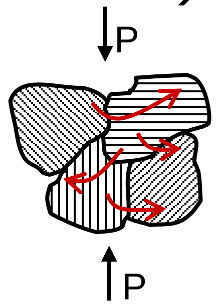


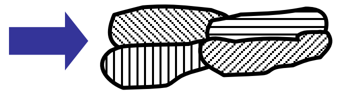
Grain Boundary Diffusion



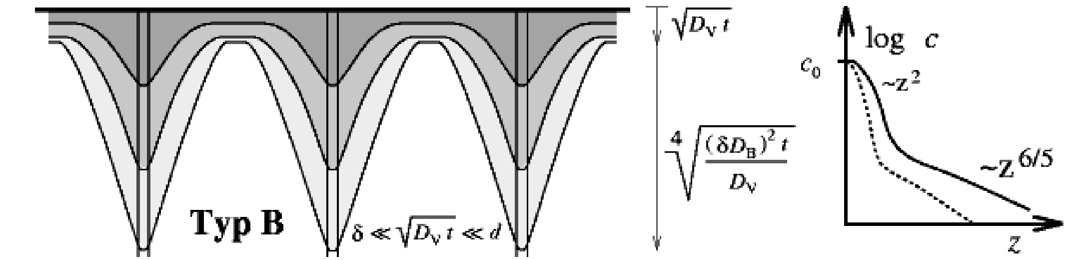
Diffusion depth >> Grain size

→ diffusion from different GBs overlaps in crystallites



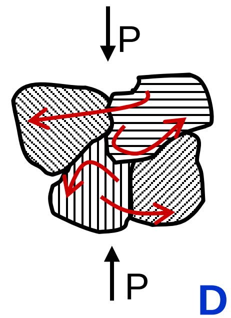


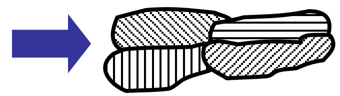
Deformed state



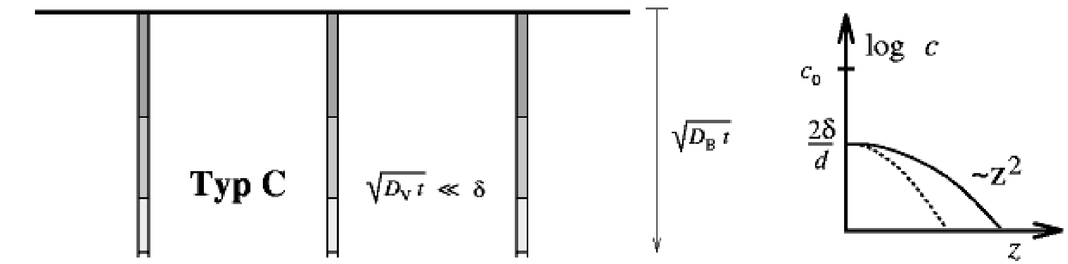
GB << Diffusion depth << grain size

→ diffusion takes place also into the crystallites



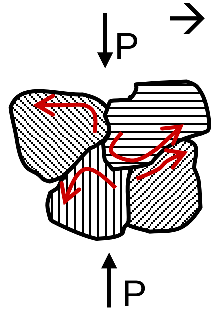


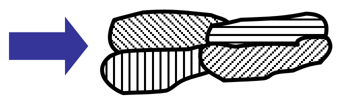
Deformed state



Diffusion depth << GB

→ diffusion only along GBs

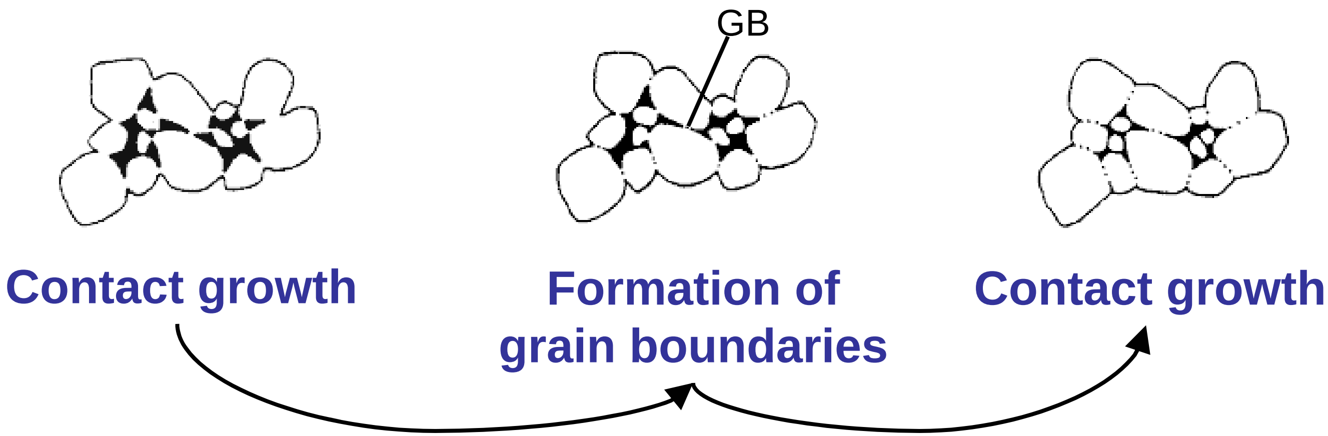


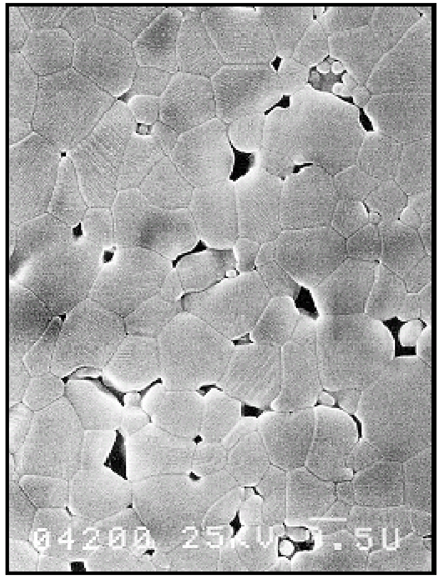


Deformed state

II. Sintering Process

Intermediate stage: → 90 – 95 % of TD





α-Al_2O_3 at the end of the intermediate stage

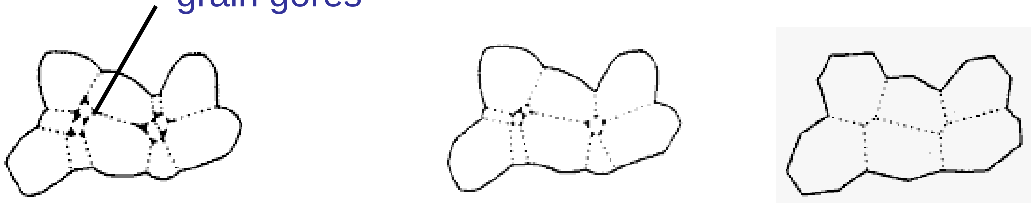
- Particles don't move any longer
- High coordination of the particles
- Mass transport by *volume- and GB-diffusion*
- 3-D *network of pores*

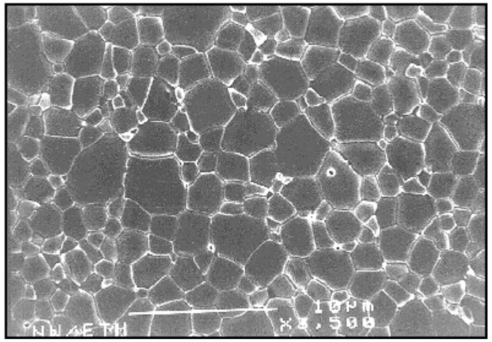
⇒ *Particle growth* begins
⇒ Pore volume decreases
⇒ Particle shape changes

→ •*Closed Porosity*

III. Sintering Process

Final stage: → 95 – 99.9 % of TD





α-Al_2O_3 after final densification

Grain growth **Healing of the pores and grain growth**

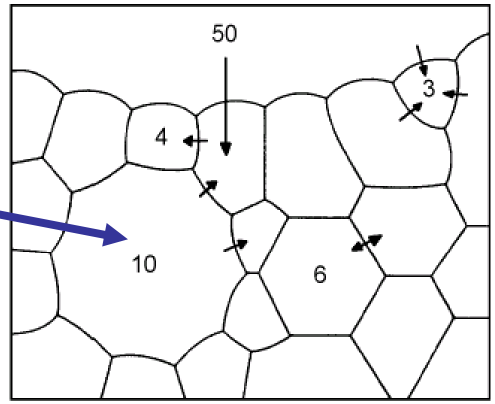
- Grain growth and elimination of the pores

Problems:

- Enclosed, entrapped, insoluble gas
- Coarsening of the grains / *growth of giant grains*

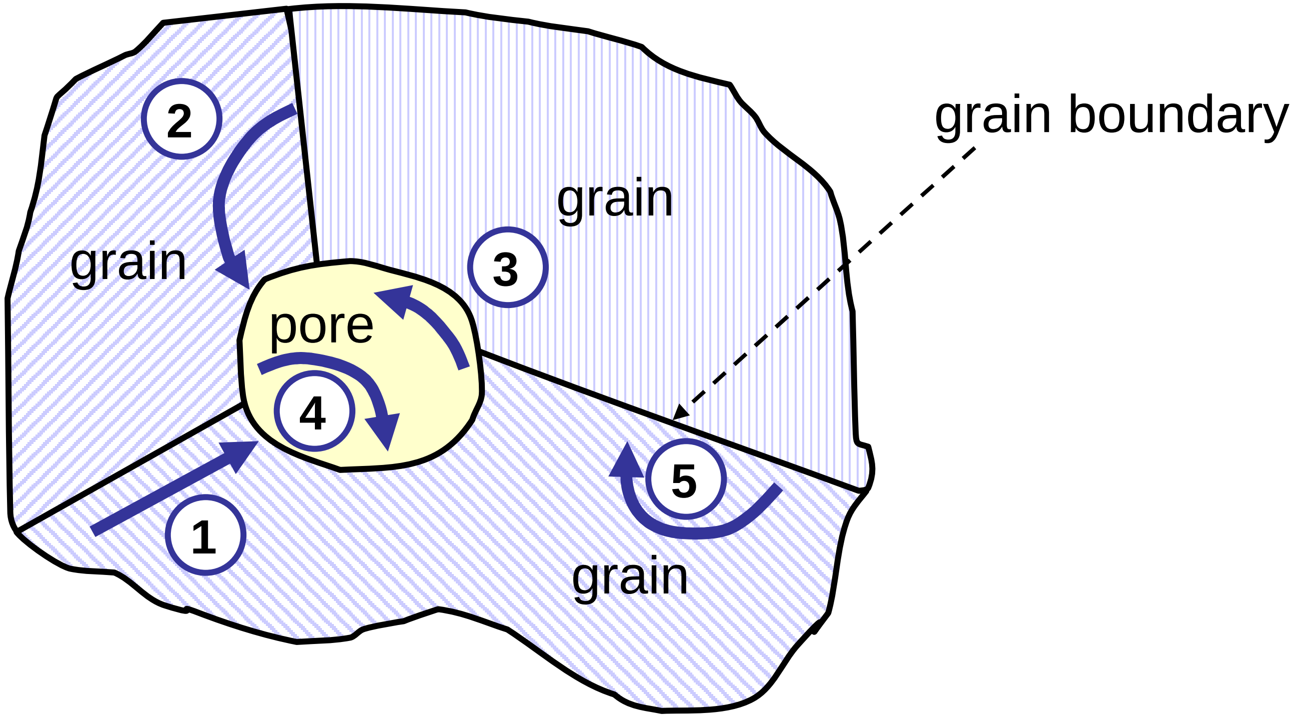
Driving force: reduction of the total surface area of all grain boundaries

Direction of GB movement



➡ Addition of *additives* to control microstructure

Sintering: Diffusion Mechanism

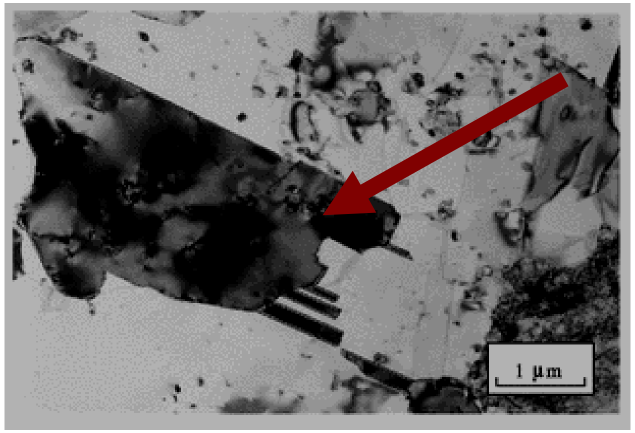


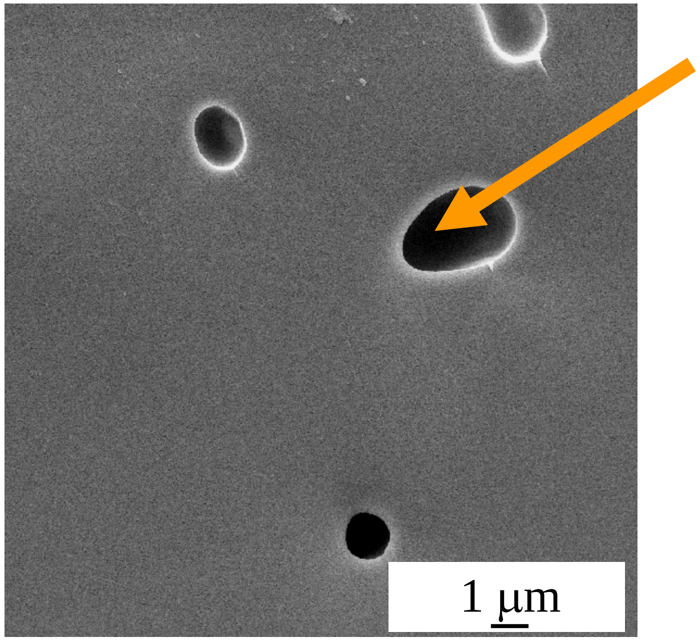
➢ *Grain boundary* and *bulk* diffusion (1, 2 and 5) to the neck contribute to densification.

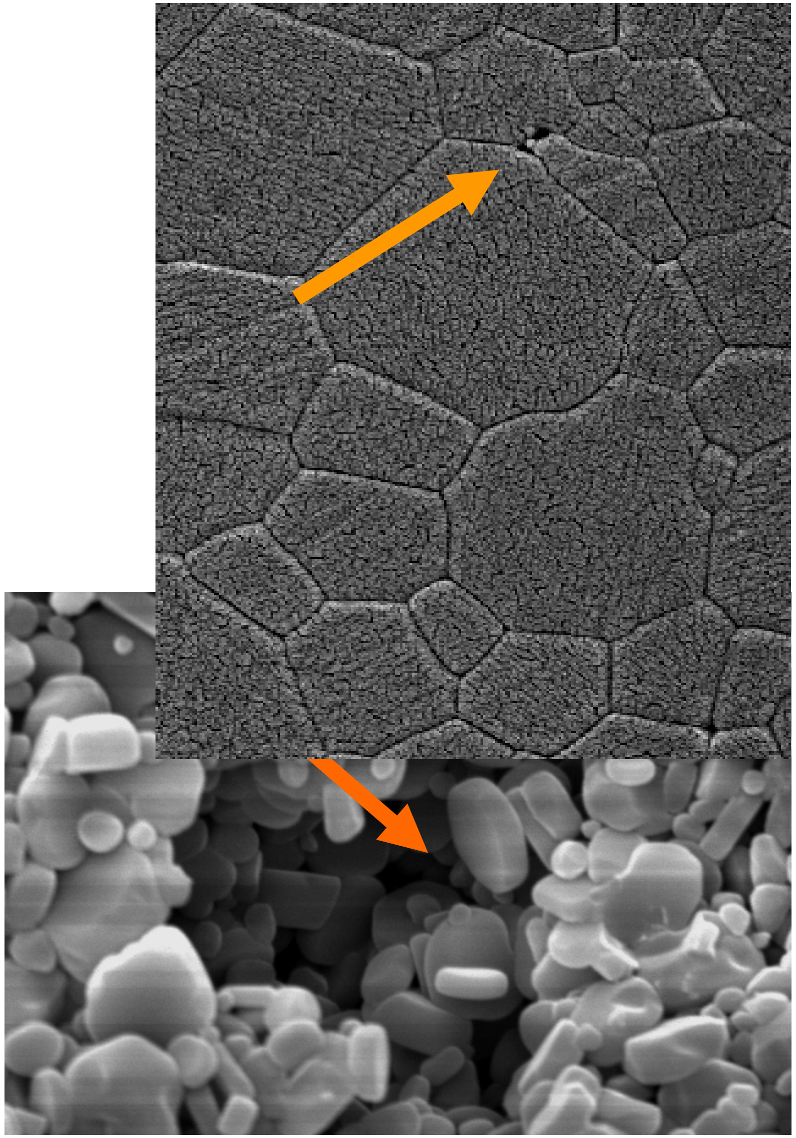
➢ *Evaporation – condensation* (4) and *surface* diffusion (3) do <u>not</u> contribute to densification.

(Adapted from: Principles for Ceramic Sience and Engineering: Y. M. Chang, D. Birnie and W. D. Kingery)

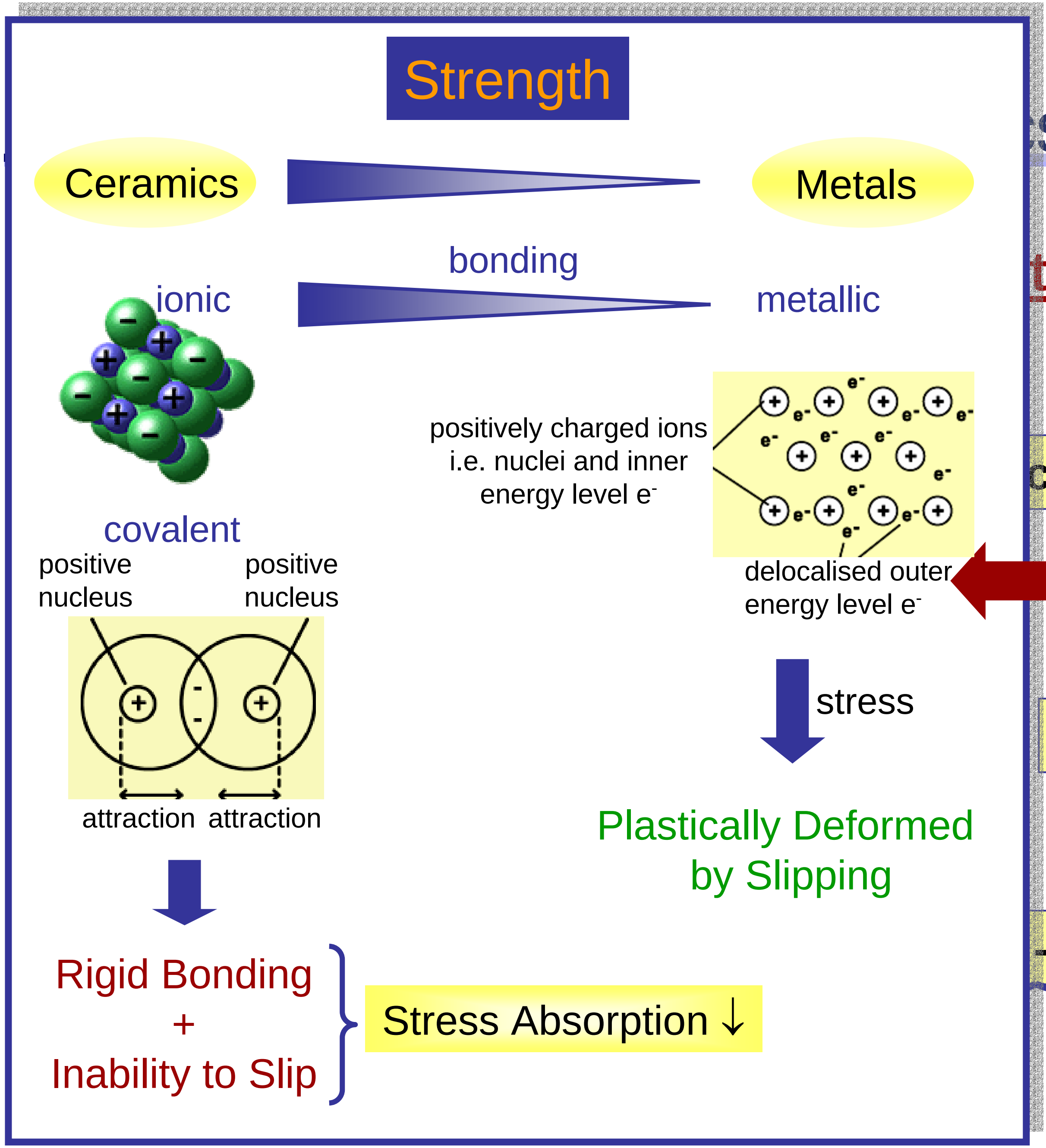
Micro-structural Defects







Properties



cs

terials

chanically Resistant

Problem: brittleness

➢ High Purity

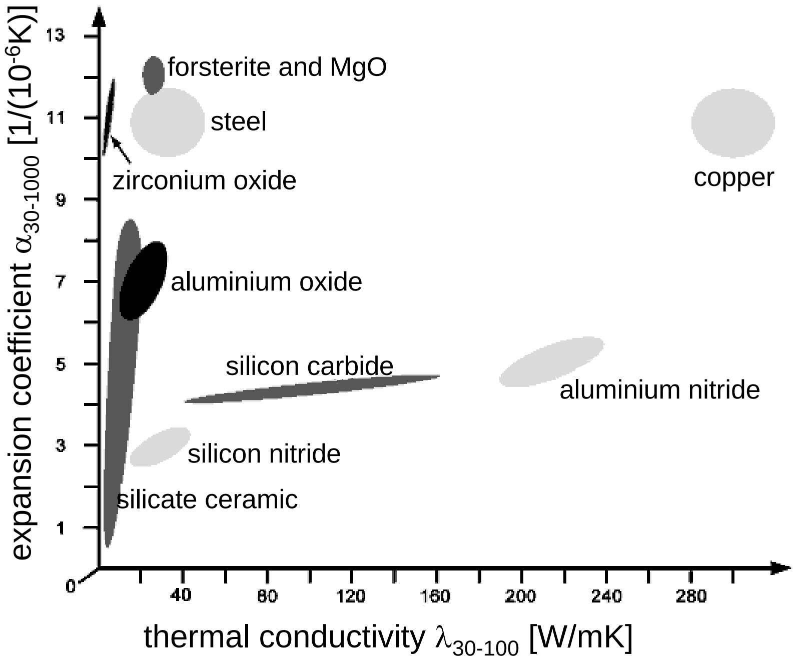
- Conducting

thermal

Thermal Properties

- Coefficient of thermal expansion:
  α (ceramics) $\lesssim$ α (metals) *
- Good heat conductivity

➡ use as **Refractory materials**



expansion coefficient and **thermal conductivity** of some materials

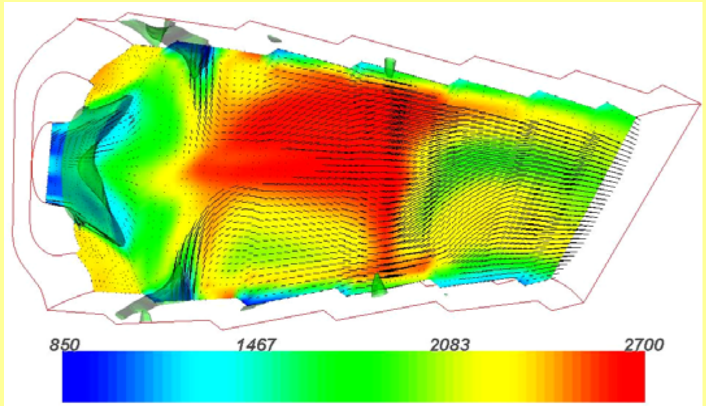
- Problem: Thermal shock resistance
  (internal stresses / brittleness)
  exceptions: quartz, cordierite

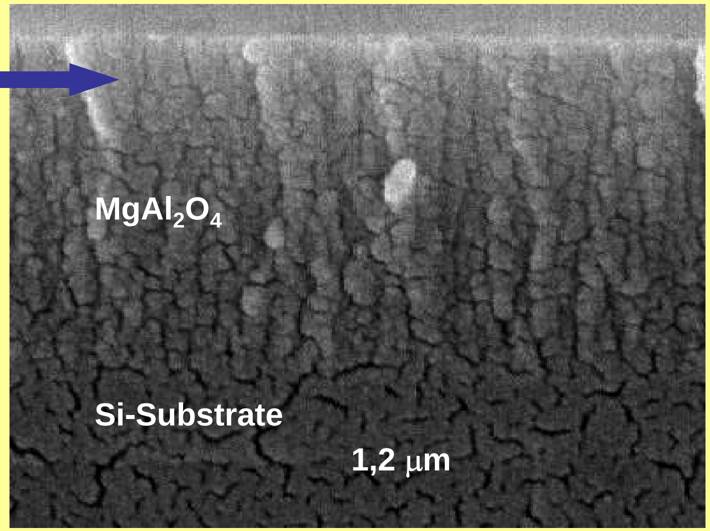
*** glass-ceramics: α ~ 0 K^{-1}**

Thermal Properties

Thermal Barrier Coatings

- *YSZ*
- *3 Al_2O_3 • 2 SiO_2 (Mullit)*
- *TiO_2*
- ***$MgAl_2O_4$*** → bond coats → CVD





columnar microstructure

Optical Properties

Transparency of Ceramics →

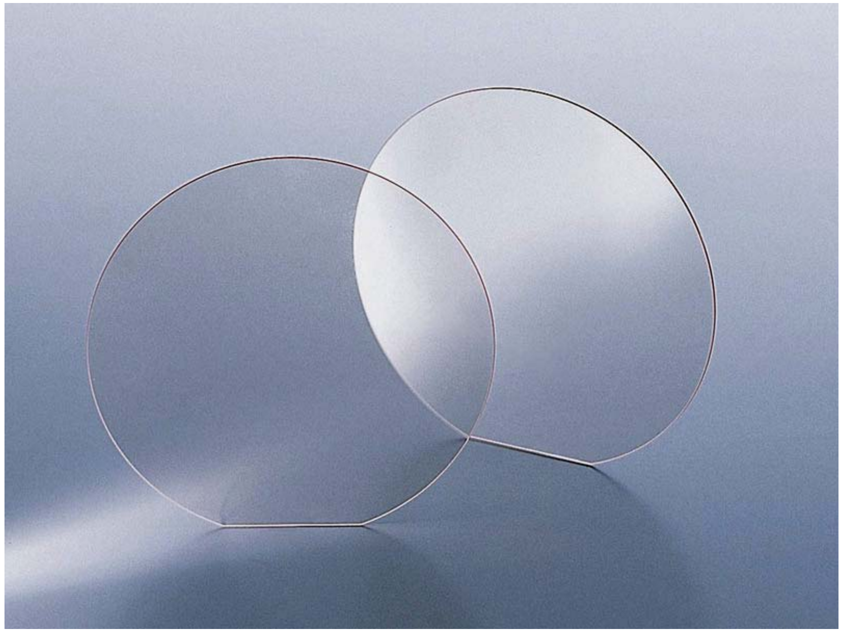
Opaque **Transparent**

<u>Requisites for Transparency:</u>

- Transparency and isotropy of the single grains
- Little contribution of the GBs to diffraction and diffusion
- No pores and voids (→ sinter techniques)

↓

Improved Synthesis



LUMICERA by CASIO: Ceramic lenses for digital cameras
- transparency ~ optical glass
- refractive index: n_d = 2,08 > optical glass (n_d = 1,5-1,85)
- excellent stability

Electrical Properties

electrical conductivity κ [S/m]

- a measure of the ease with which electrical carriers flow in a material (reciprocal of the **resistivity)**
- the ability of a material to allow the flow of electrical current

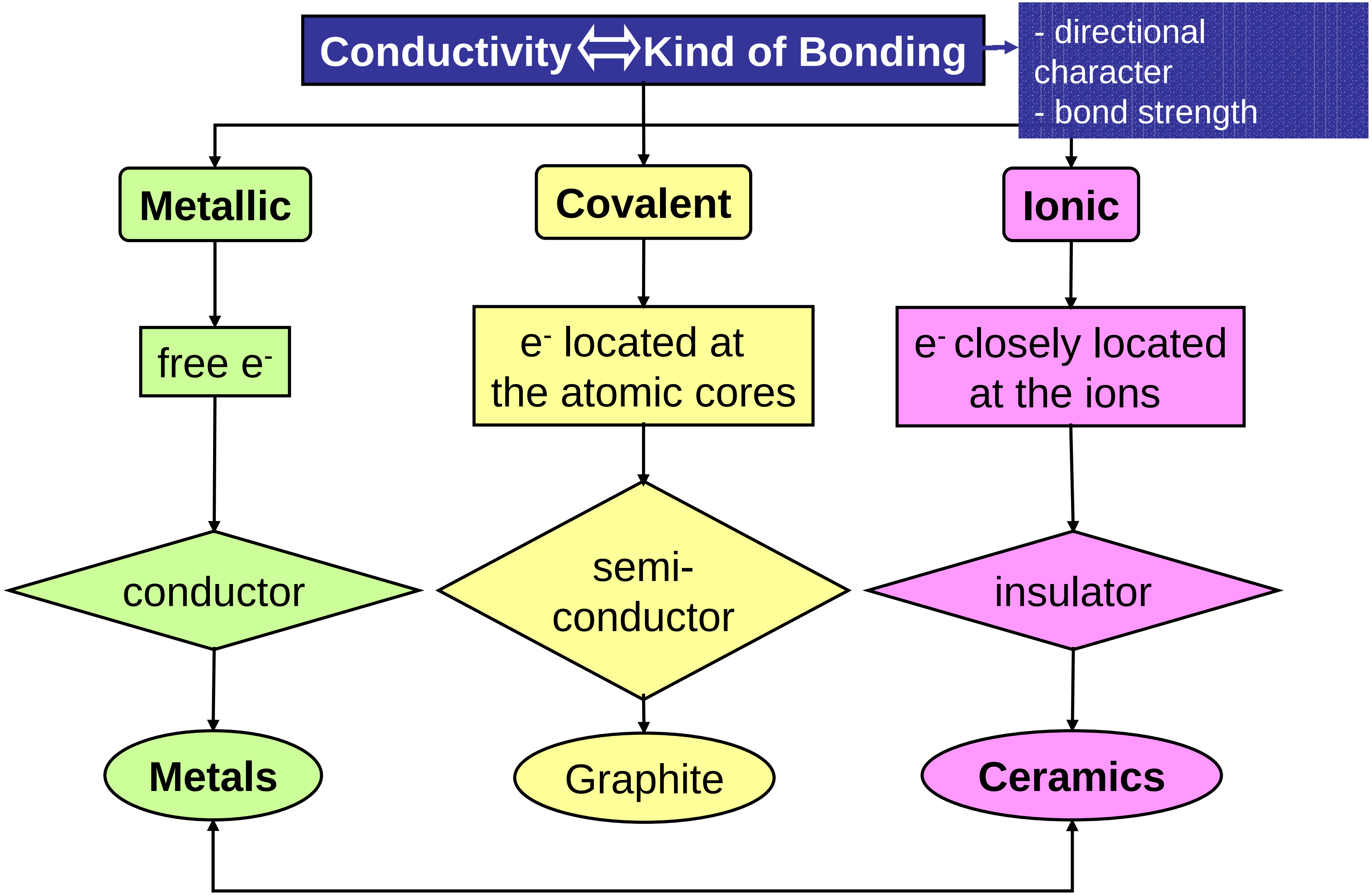
• free electrons

- metals
- organic molecules (delocalised e^-)

• ions

- electrolytes (salts)

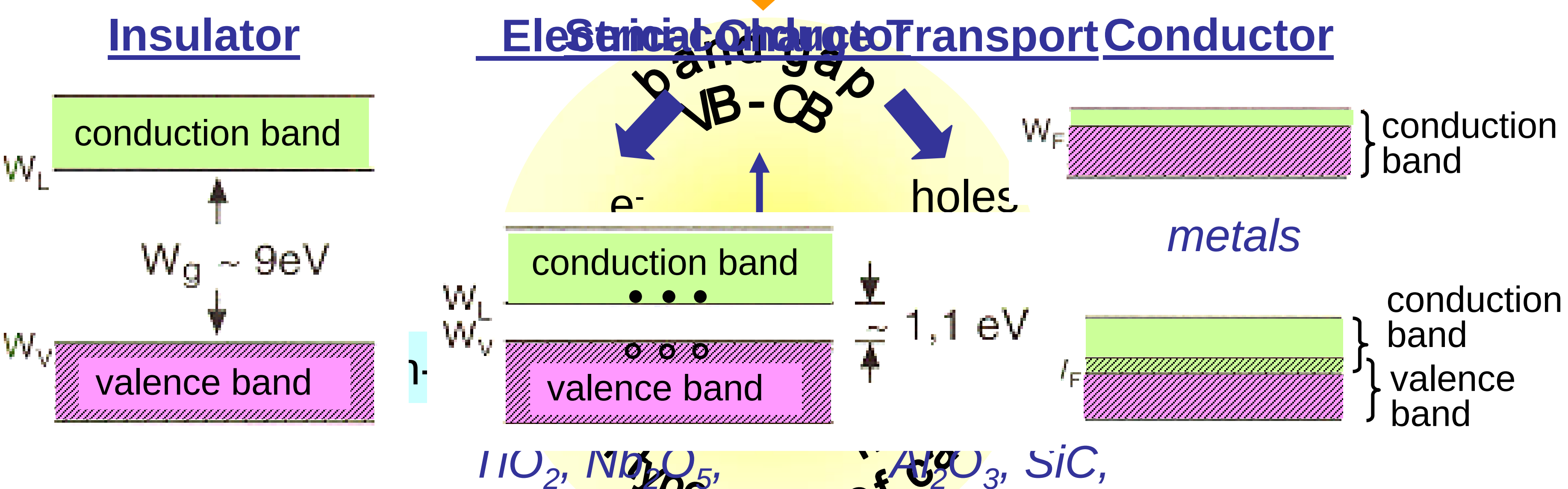
Conductive Behaviour



Advanced Ceramics: Tuneable Conductivity

Conductivity of Ceramics

Insulator	Semi-conductor	(Super) conductor
Al_2O_3	SnO_2	$YBa_2Cu_3O_{7-x}$

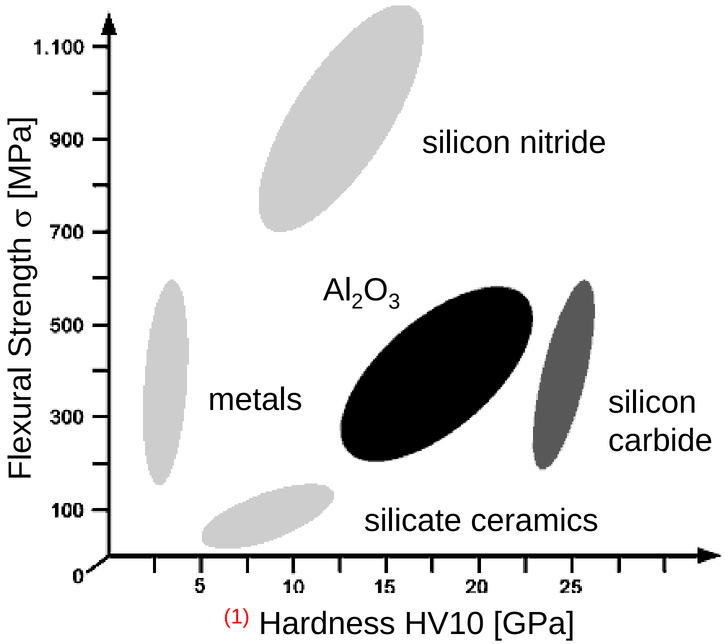


SiO₂ *SnO₂, BaTiO₃* *Co₃O₄, Mn₃O₄* *SiC*

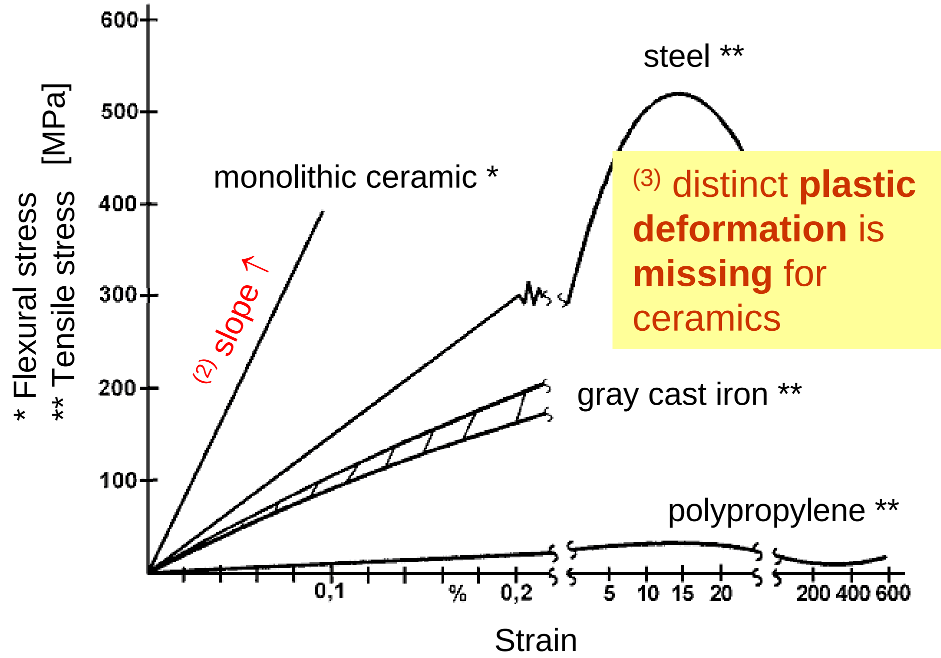
Mechanical Properties

☺ 👍
- Hardness [1]
- Young's modulus [2]
- Stiffness

☹ 👎
- Poor plastic deformation [3] via GB diffusion + diffusion creep
- Brittle / low fracture toughness



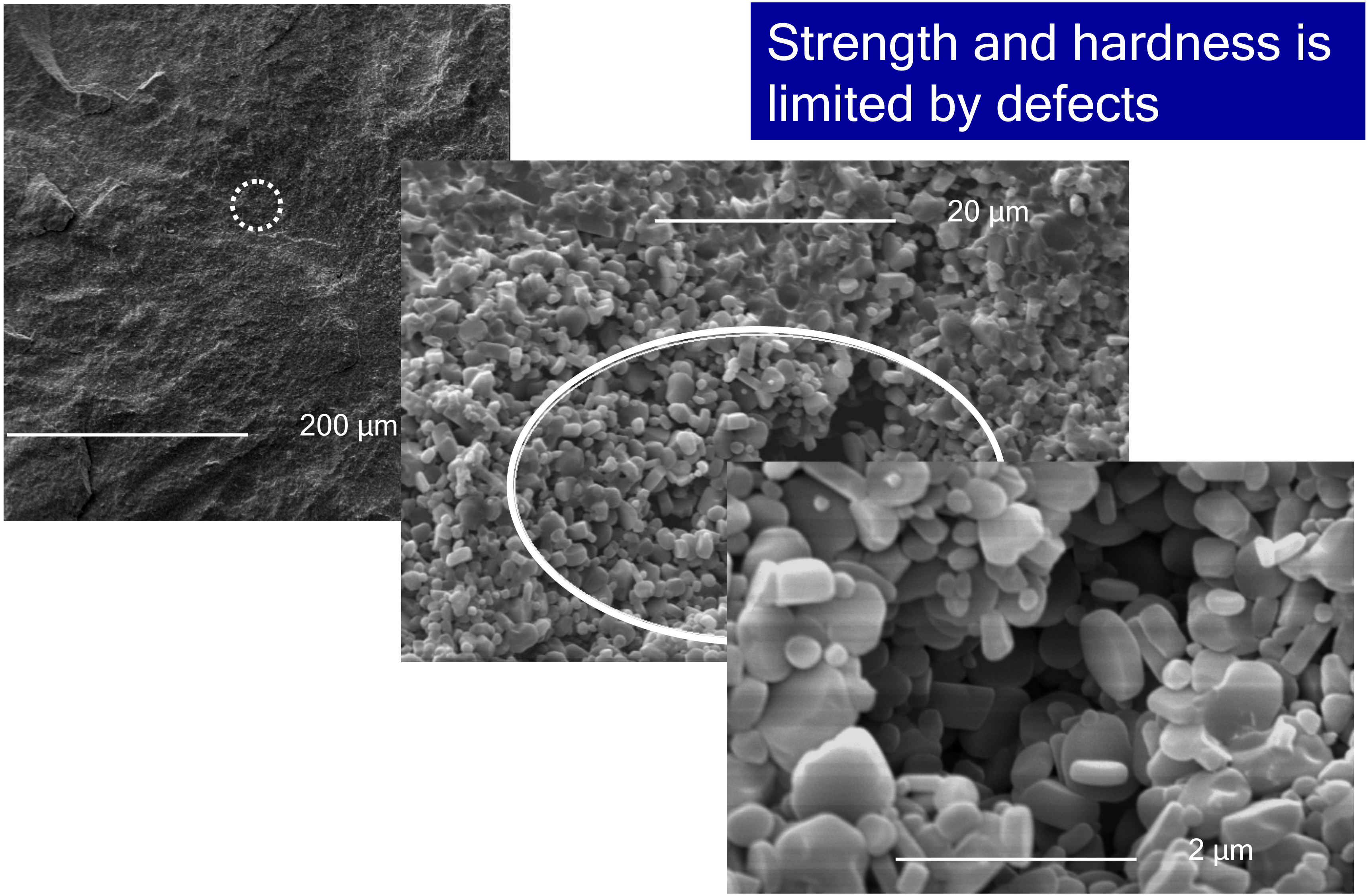
flexural strength and **hardness** of some materials



stress-strain-behaviour of ceramics in comparison with metals and polymers

Microstructural Defects

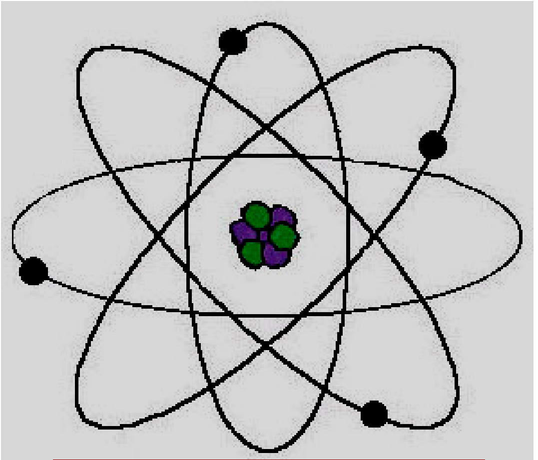
Strength and hardness is limited by defects



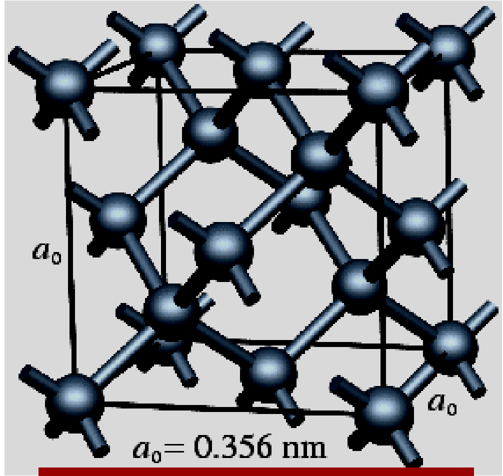
Control of chemical composition,
particle size, and particle size distribution is
required to achieve the optimum properties …

… (Better) Optimized Synthesis of Matter

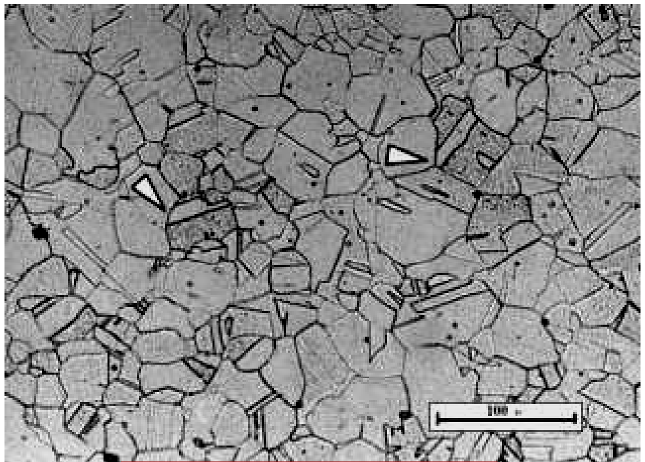
Control over ?



Atomic Structure



Crystal Structure



Microstructure

Phase Composition

Synthesis of Ceramics

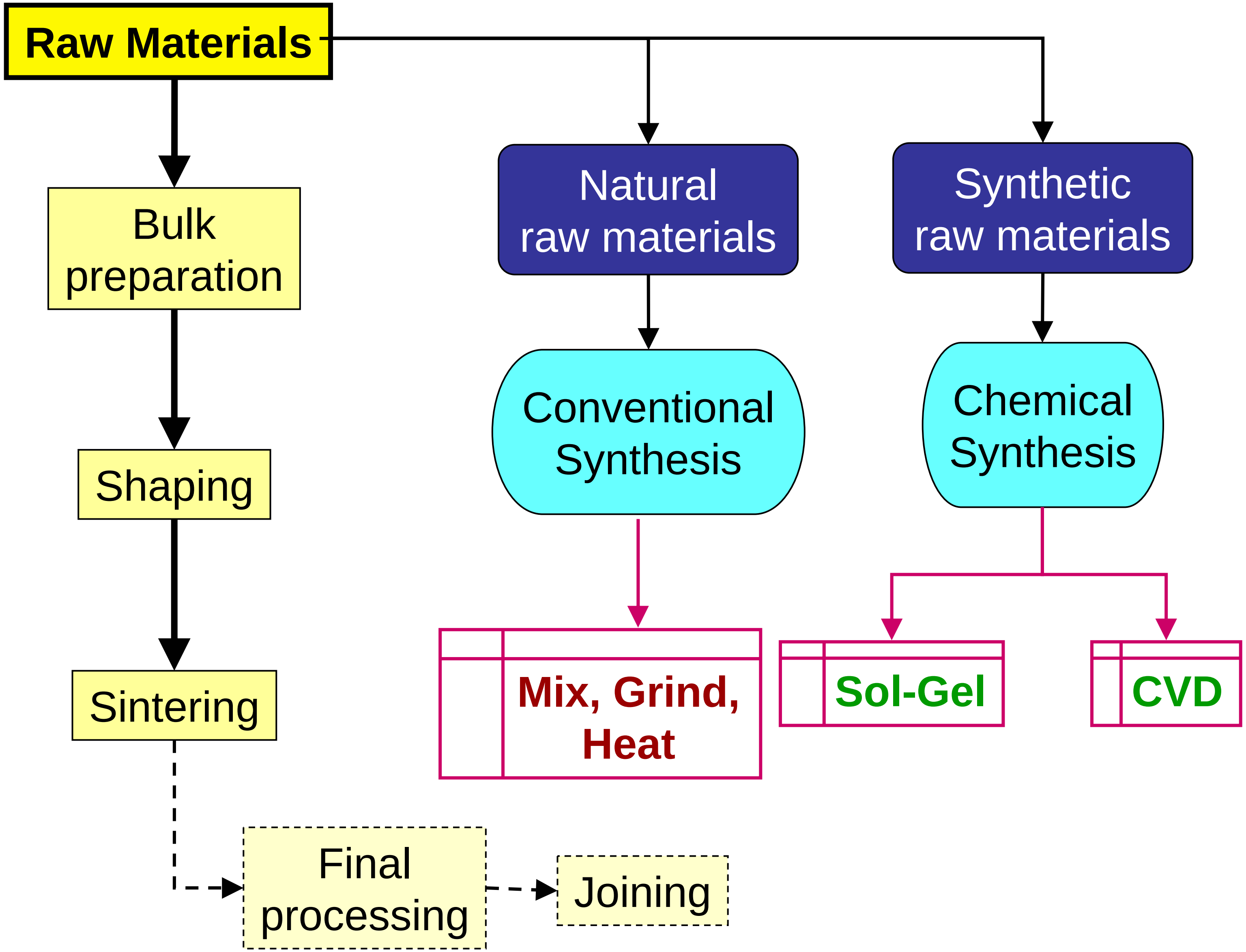
Key Issues:

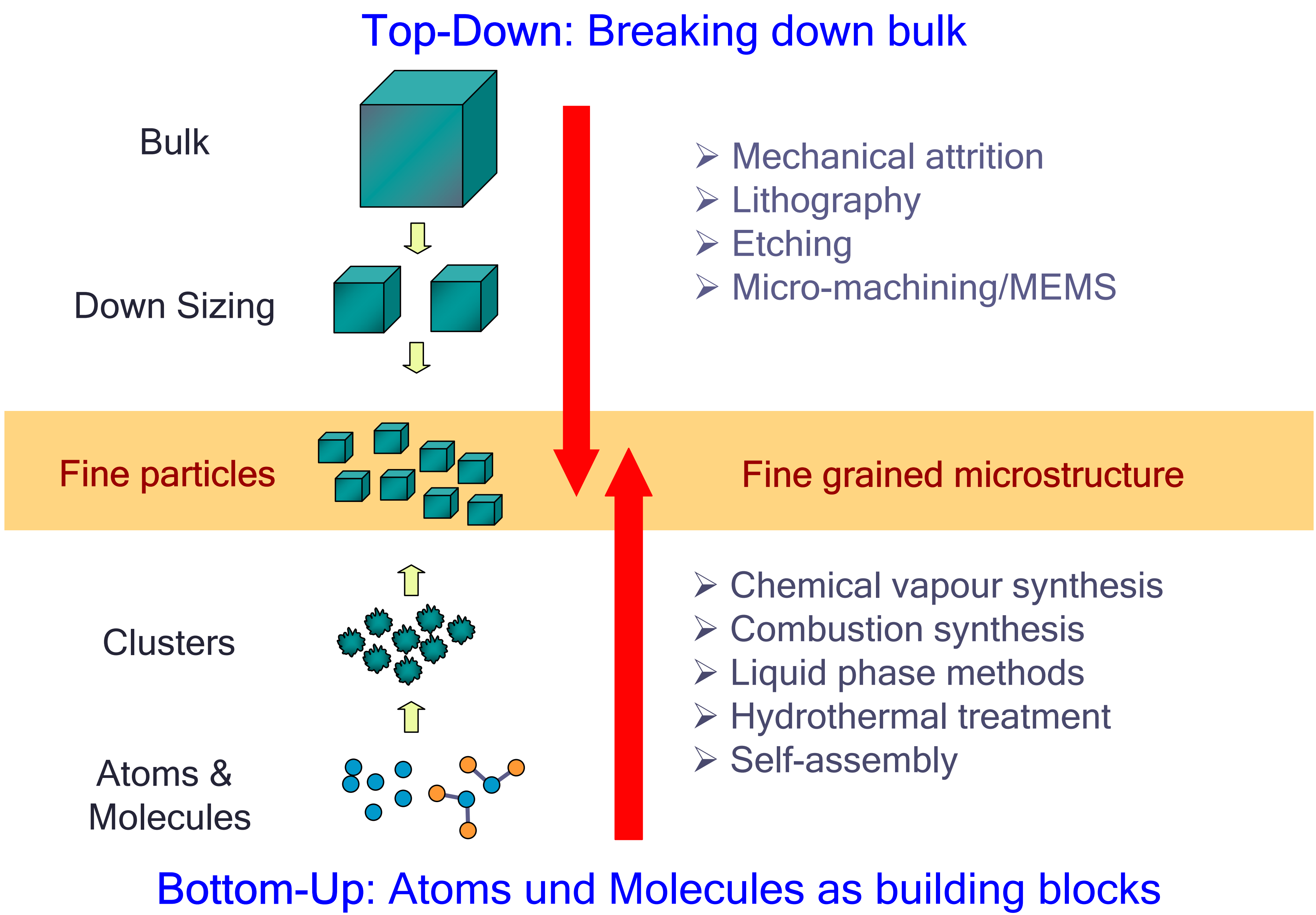
- Compositional homogeneity
- Phase purity
- Morphology
- Particle size and distribution
- Synthesis temperatures → Grain growth

Limitations:

- Elemental Segregation
- Co-existence of metastable or intermediate phases
- Abnormal grain growth
- Marginal control over particle size/ morphology

Ceramics: Synthesis and Processing

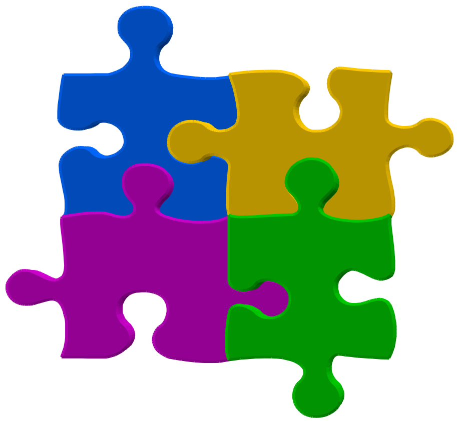



Top-Down: Breaking down bulk
Bulk
Down Sizing
Fine particles
Clusters
Atoms &
Molecules
Mechanical attrition
Lithography
Etching
Micro-machining/MEMS
Fine grained microstructure
Chemical vapour synthesis
Combustion synthesis
Liquid phase methods
Hydrothermal treatment
Self-assembly
Bottom-Up: Atoms und Molecules as building blocks

Chemical Synthesis of Ceramics

Atomic scale mixing

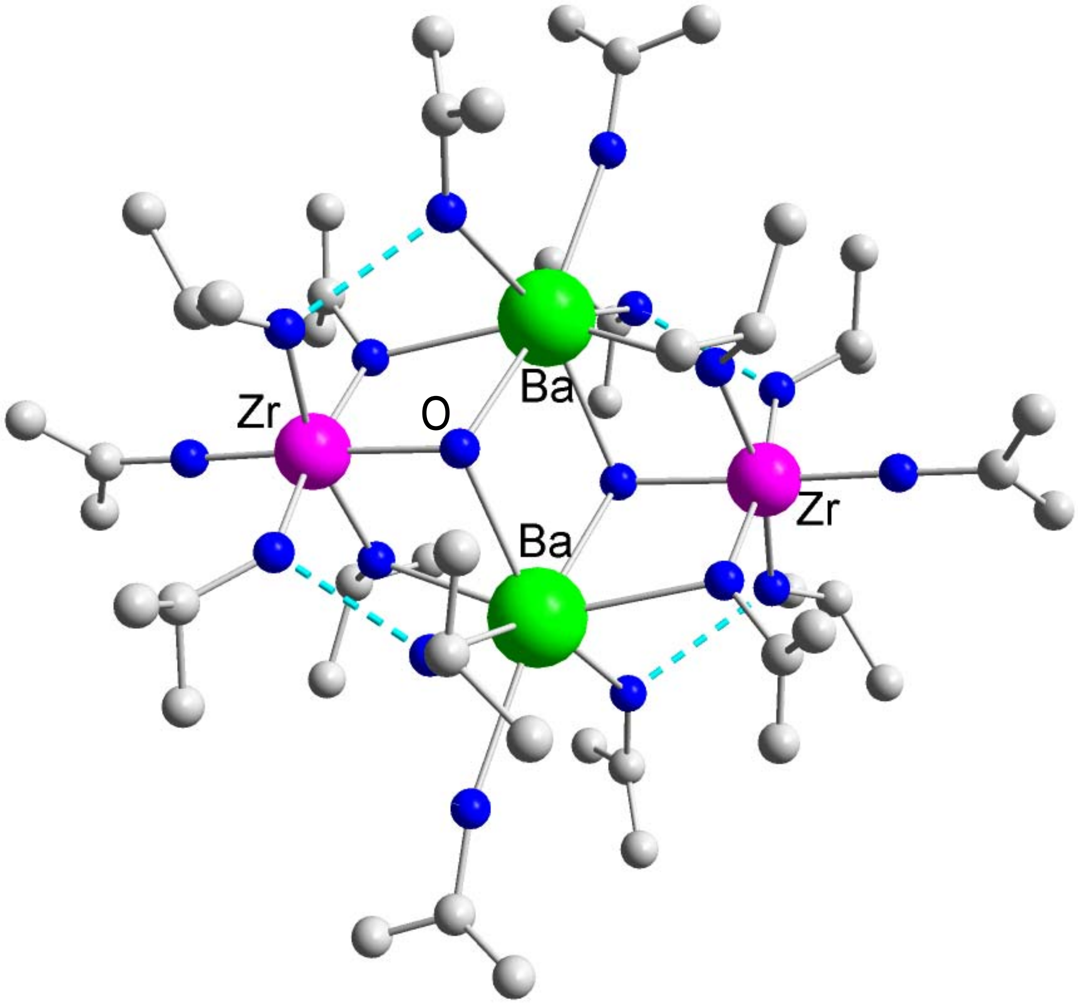
(Nano)Crystalline material at low temperature



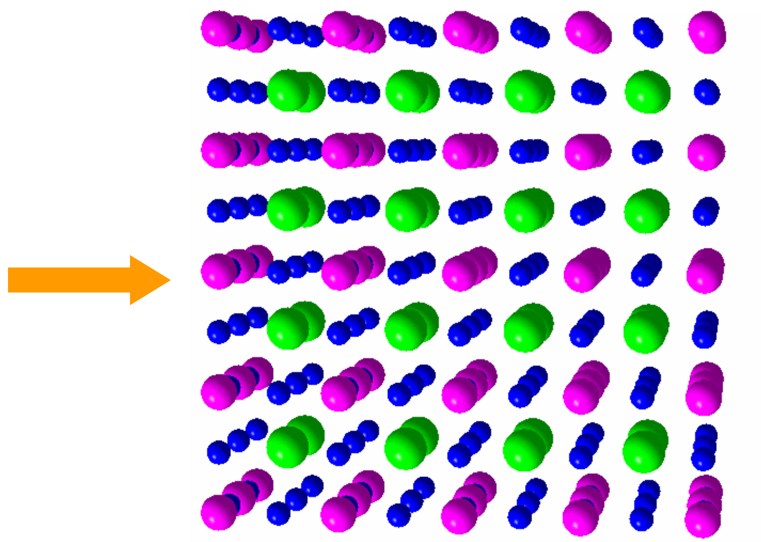
Phase purity and selectivity

Pre-defined reaction chemistry and single-step synthesis

Molecule Derived Materials



$[BaZr(OH)(OPr^i)_5(Pr^iOH)_3]_2$



$BaZrO_3$

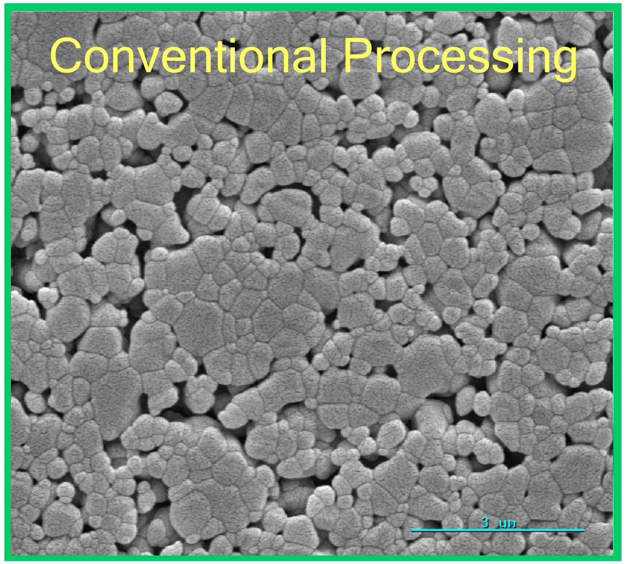
$BaZrO_3$ Ceramics

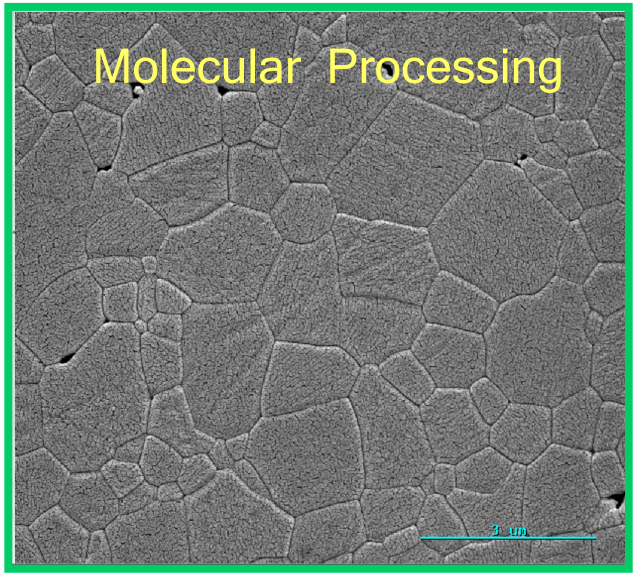
Powders Treated Identically

Cold Isostatic Pressing (14 kN)
Sintered: 1400 °C

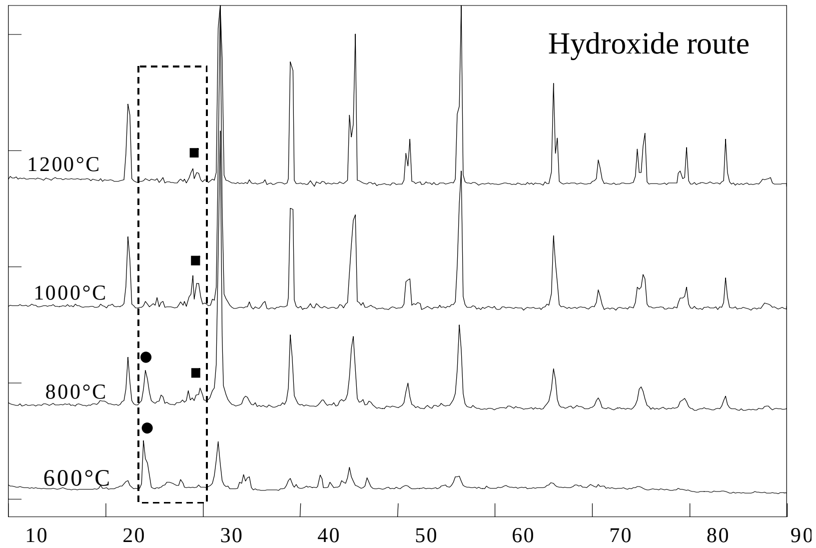
Density of Pellets

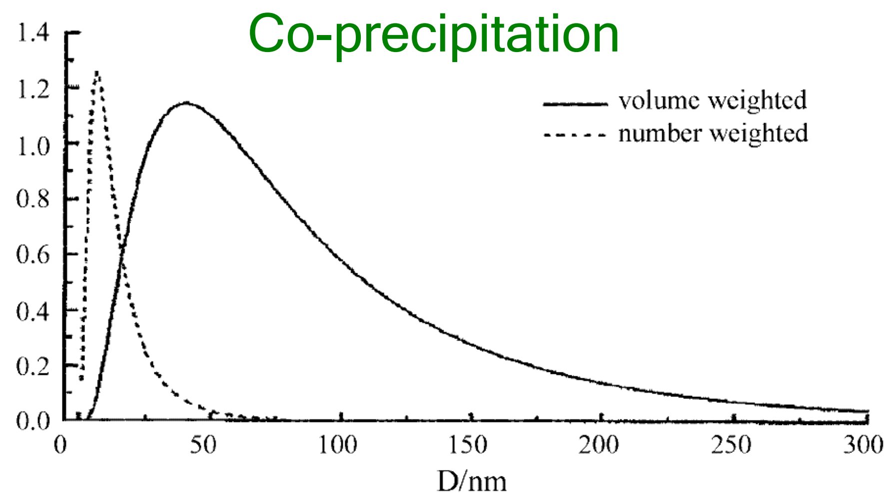
Alkoxide: 93-95 %
Non-alkoxide: 65-70 %

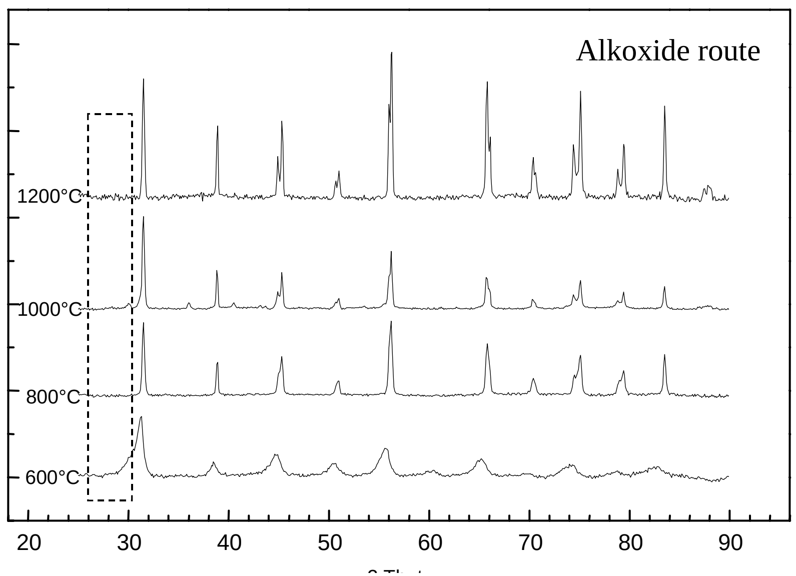


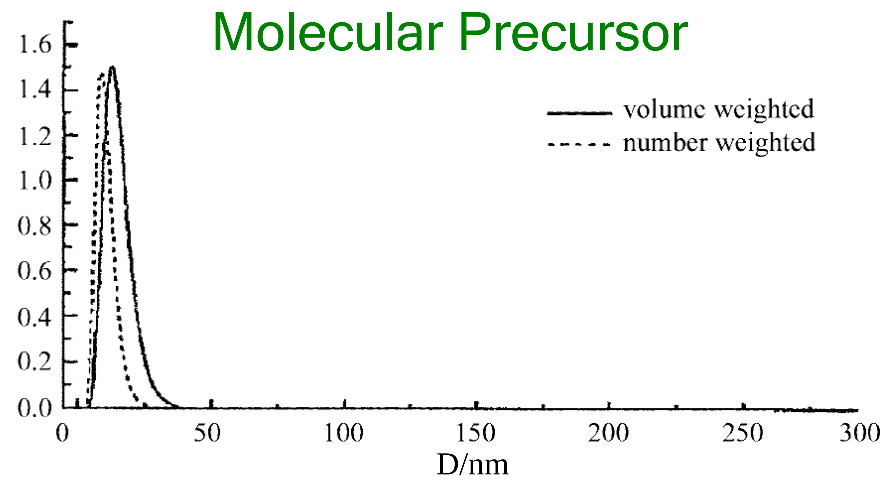


Phase Purity and Particle Size Distribution





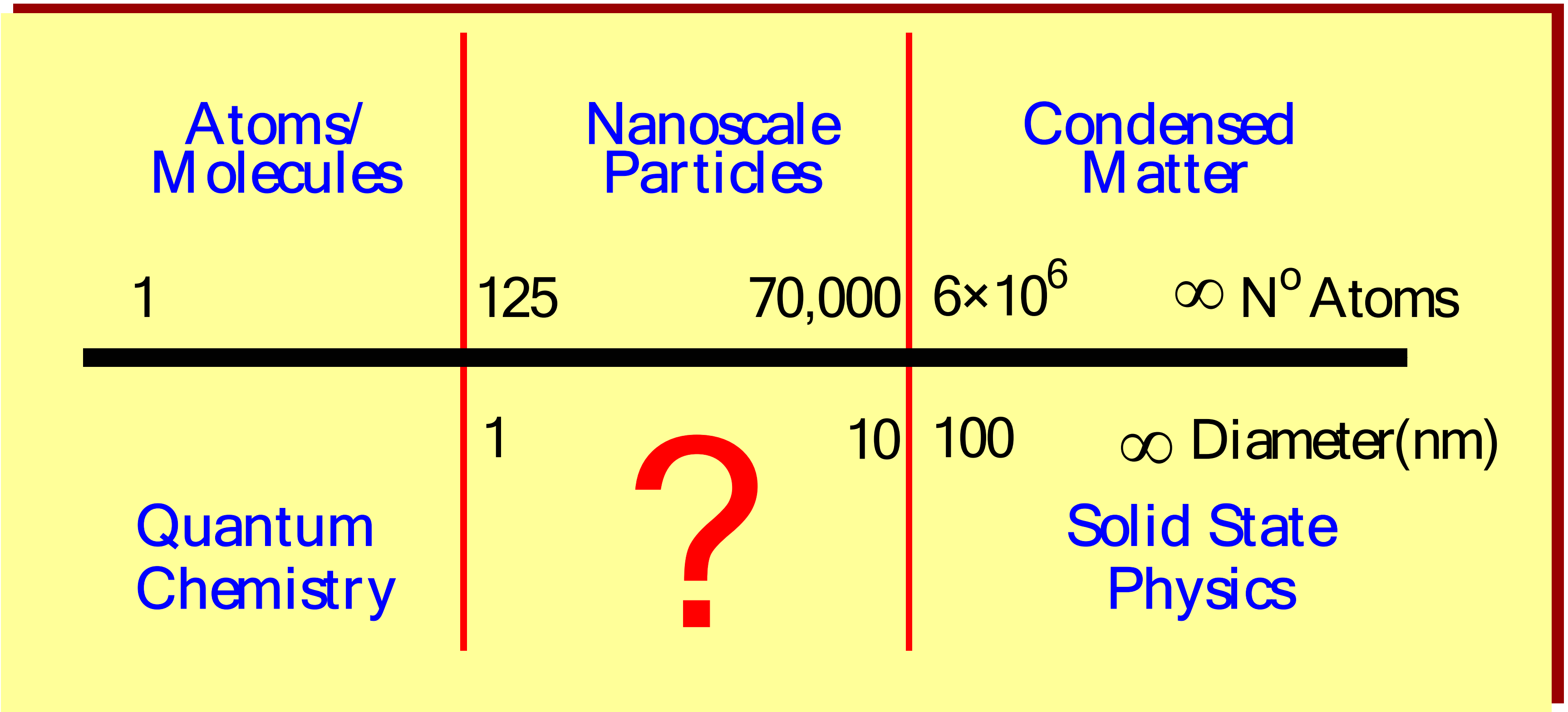




Nanocrystalline Materials

Nanometer

“A magical point on the length scale, for this is the point where the smallest man-made devices meet the atoms and molecules of the natural world”



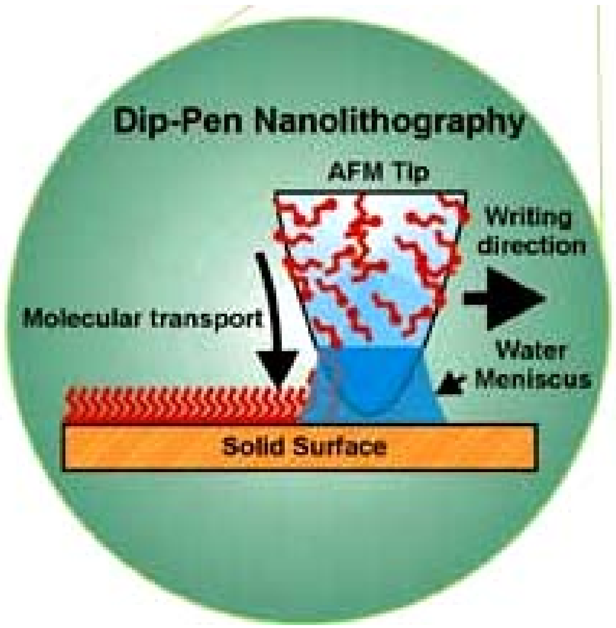
Room at the Bottom

What I want to talk about is the problem of manipulating and controlling things on a small scale …

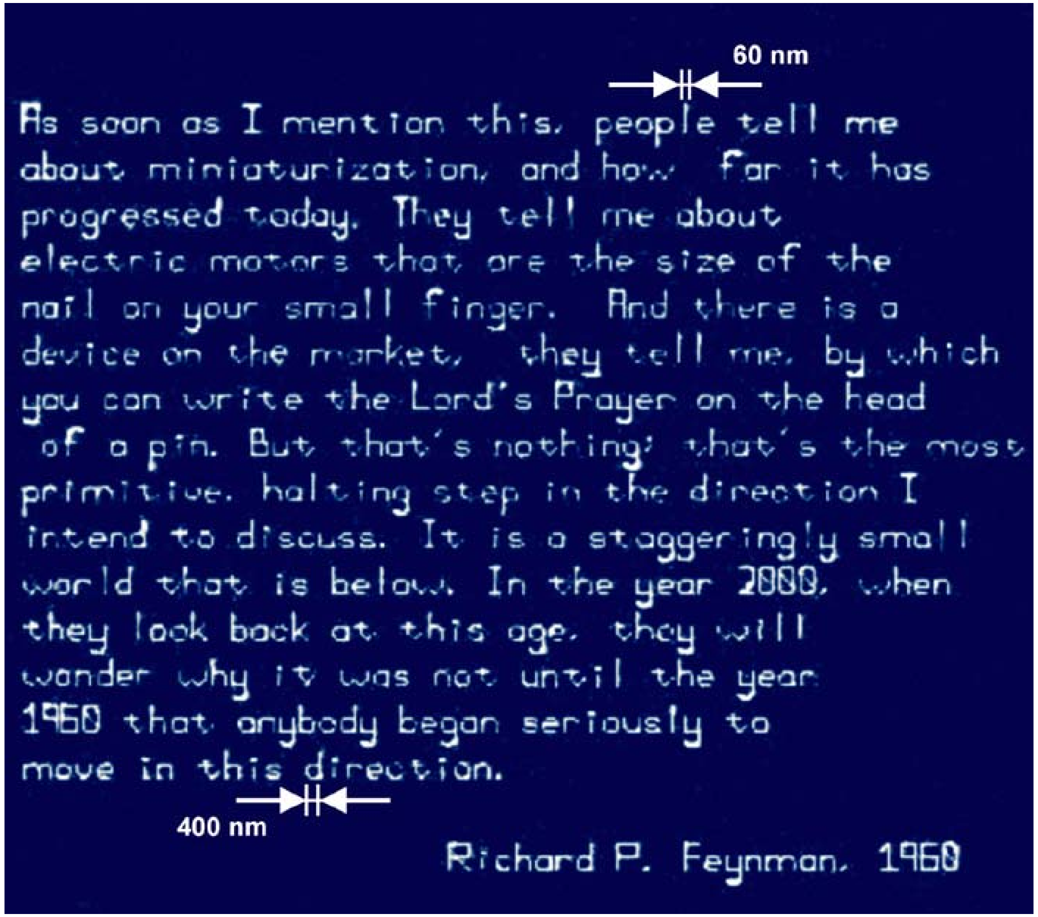
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It's a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction……

Prof. Richard Feynman in "There's plenty of room at the bottom", lecture delivered at the annual meeting of the APS, Caltech, 29 December, 1959.

Nanoscale Writing



Nanoscale writing with an AFM (Mirkin et al.)



Size as Innovation Motor

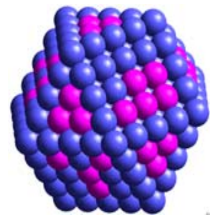
How big is nano?

~ 10 million times

smaller

~ 10 million times

smaller



d = 1- 10 nm

What Changes?

√ Small → Negligible light scattering → New optics

√ Quantum size effects → Information technology, Storage media

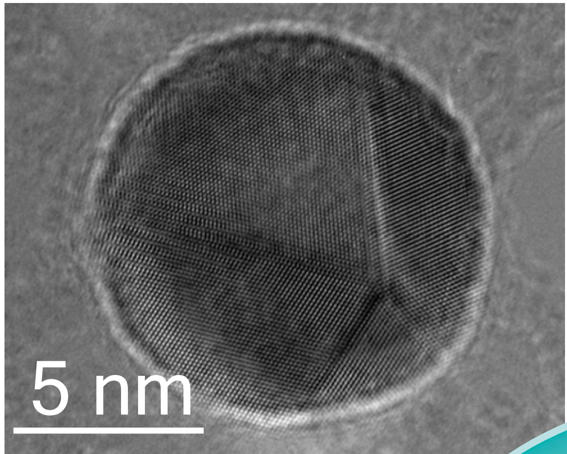
√ High surface area → Catalysts, Adsorbents

√ Large Interfacial area → New composites

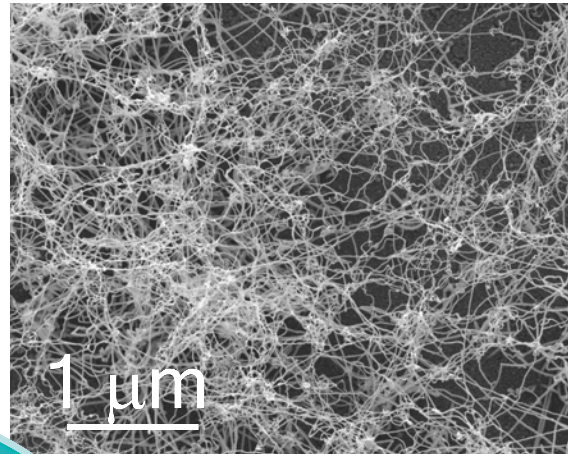
√ Surface modifications → Targeted Drug Delivery

The Nano-family

Nanoparticles



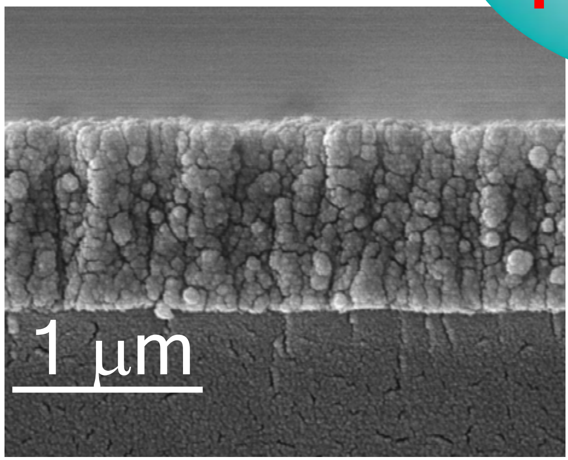
Nanowires



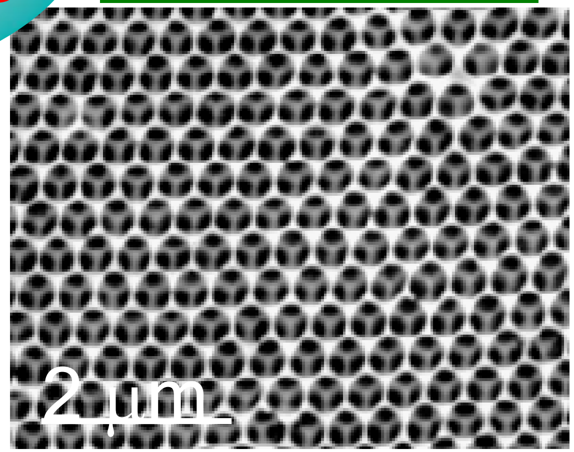
Form of

Nanomaterials

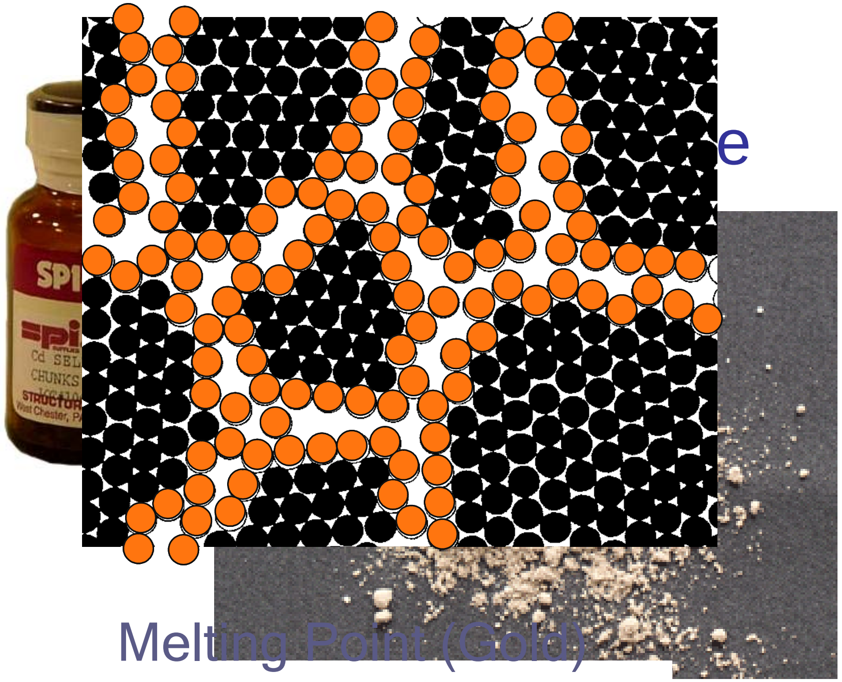
Thin Films

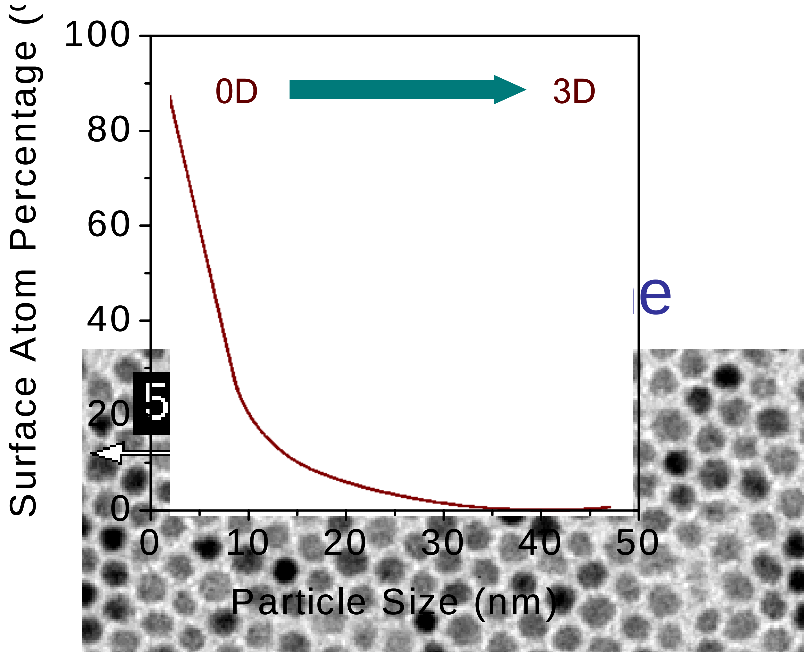


Porous Materials

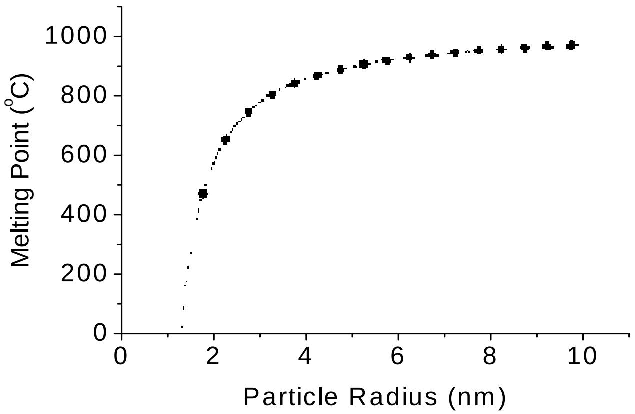


Macro *vs.* Nano: The Size Effect





Melting Point (Gold)



Size

Nanomaterials – no buzz word!

Soot and silicon carbide nanoparticles in tyres reduce abrasion (ca. 50%)

www.nanoproducts.com

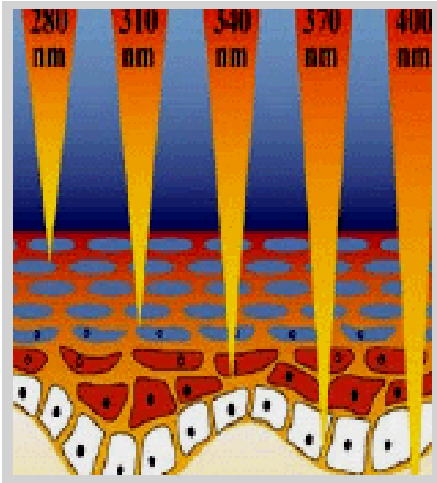
www.nucelle.com

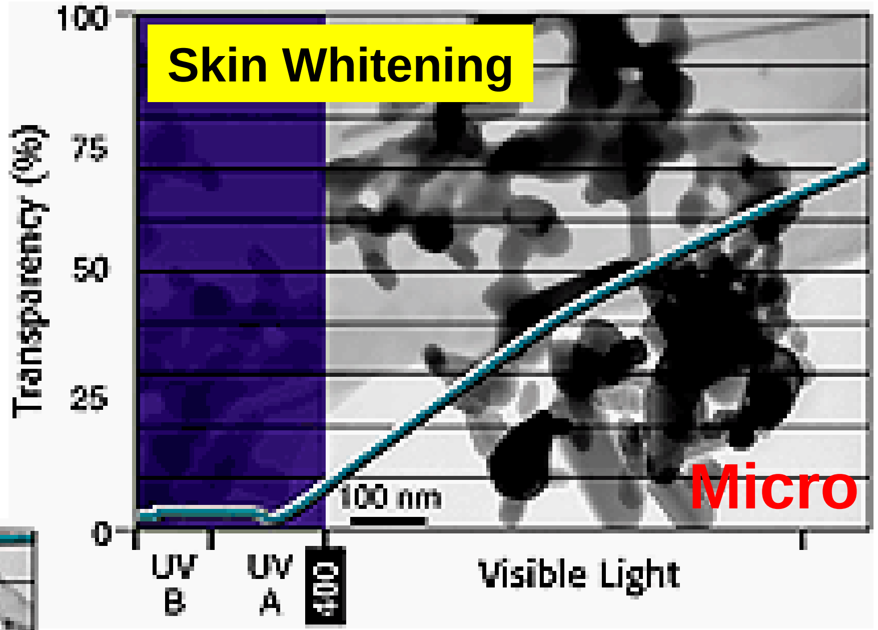
TiO_2 and ZnO in sunscreen lotions
Enhanced prevention from of UV radiation

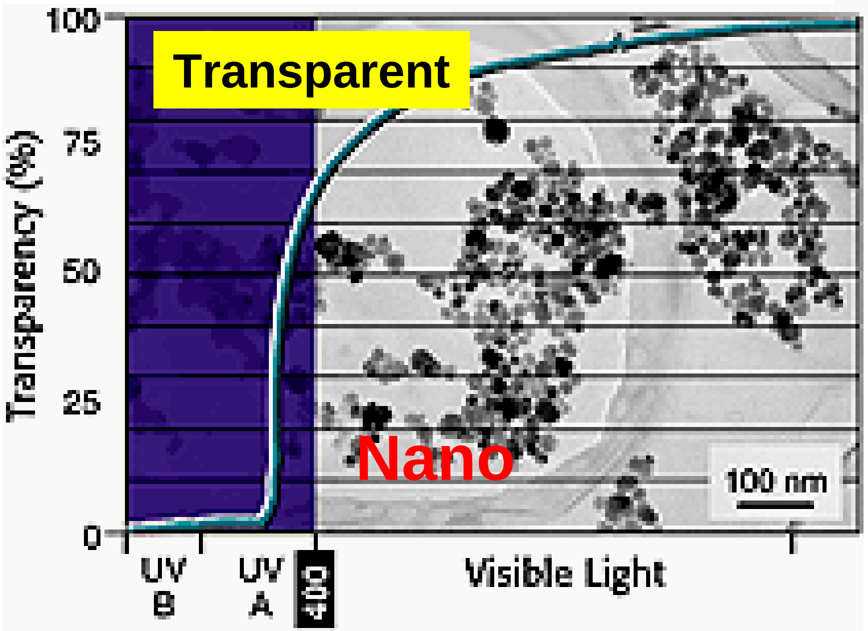
Nanometric polymer capsules with incorporated vitamin A - Better absorbance in the skin

www.lorealparis.co.uk

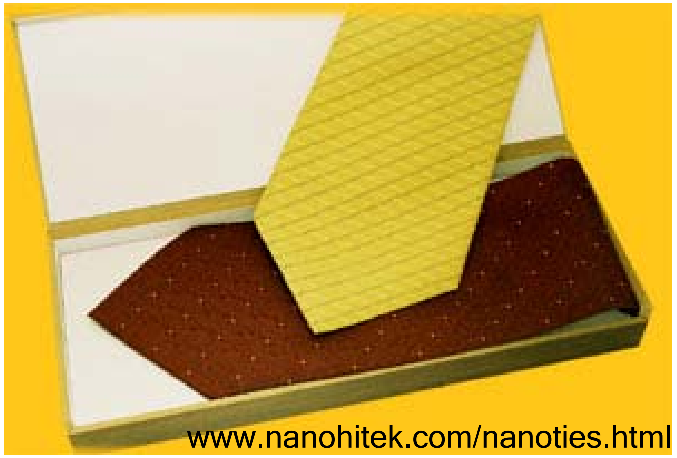
Nano ZnO: UV-Blocker







Nanotechnology on the Market

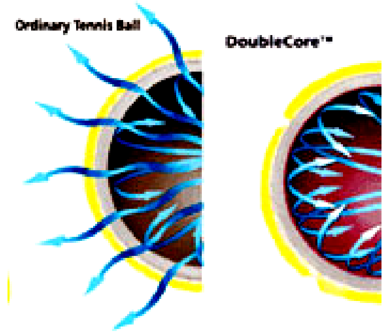

www.nanohitek.com/nanoties.html

Ties with nano-coatings repel water and greasy food and fluids

3-5% Carbon nanotubes in the front bumper increases shape stability and strength

www.ahwahneetech.com/technology/carbon_nanotube.htm

Wilson: nanocomposite coatings of tennis balls doubles life time and restricts airflow from escaping the core



www.wilson.com