# Inorganic Materials Chemistry C7780

Jiri Pinkas Office A12/224 Phone 549496493

Email: jpinkas@chemi.muni.cz

#### Course grading:

- 3 graded homeworks during semester
- Short presentations on a selected topic concerning materials chemistry
- Written final exam (100 pts, minimum 50 pts to pass)

Grading weights: final test 75%, homeworks 15%, presentation 10%.

#### Recommended Literature

SCHUBERT, U. a N. HÜSING. Synthesis of Inorganic Materials. Weinheim: Wiley-VCH

CALLISTER, W.D.J. Materials Science and Engineering, An Introduction. John Wiley and Sons

SMART, L. a E. MOORE. Solid state chemistry: an introduction. 2nd ed. London: Chapman & Hall

Plinio Innocenzi, The Sol to Gel Transition, Springer International Publishing

Mary Anne White, Physical Properties of Materials, 2nd Edition, CRC Press

Ulrich Muller, Inorganic Structural Chemistry, 2nd Edition, Wiley

## **Materials in Human History**

**Historical perspective:** 

New materials bring advancement to societies

- Stone age
- Bronze age
- Iron age
- Silicon age



Crescent Axes. The top Syrian, the bottom Egyptian. about 1900 BC

## **Materials in Human History**

50 000 B.C. Iron oxide pigments Lascaux, Altamira

24 000 B.C. Ceramics – fat, bone ash, clay

3 500 B.C. Cu metallurgy

**Glass, Egypt and Mesopotamia** 

3 200 B.C. Bronze

1 600 B.C. Iron metallurgy, Hittites

1 300 B.C. Steel

1 000 B.C. Glass production, Greece, Syria

105 B.C. Paper, China

590 A.D. Gun powder, China

700 A.D. Porcelain, China

This is a Hittite dagger-sword made of

iron about 1100 B.C. Much of it has turned to rust over the

past three thousand years.

## Materials in Human History - Metals

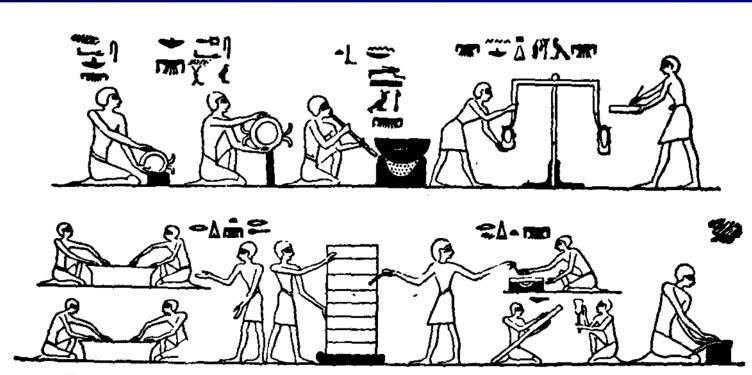


FIG. 11.—EGYPTIAN GOLDSMITHS WASHING, MELTING AND WEIGHING GOLD.

Beni Hasan, 1900 B.C.

## Materials in Human History - Ceramics

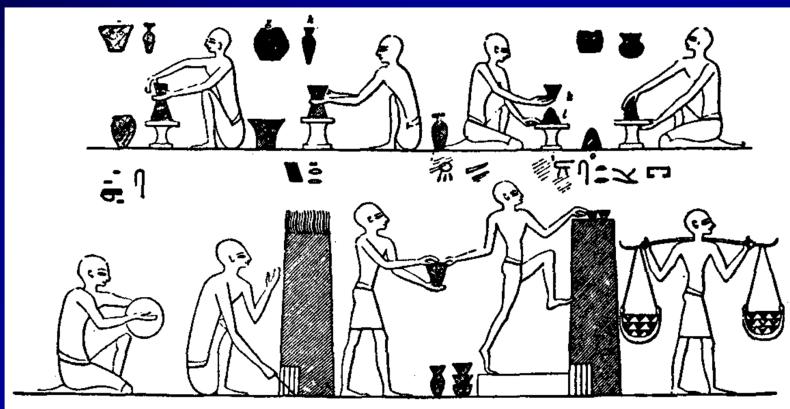
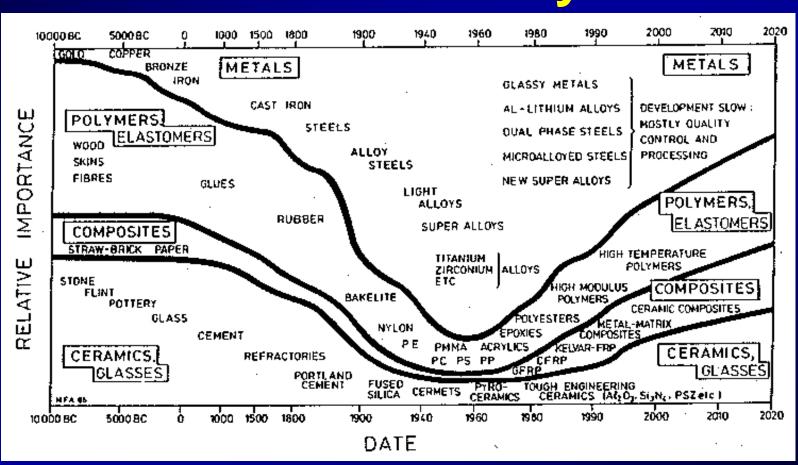


FIG. 12.—EGYPTIANS MAKING POTTERY, WITH FURNACE. BENI HASAN, 1900 B.C.

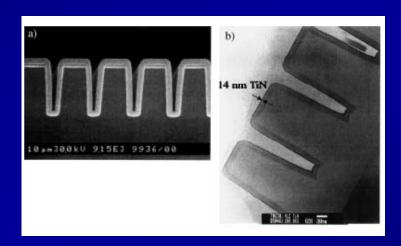
## Development of Materials in Human History

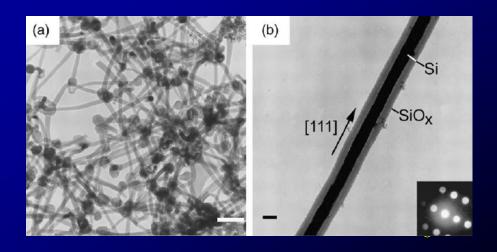


## Compounds vs. Materials

- \* Chemical compounds
  single use (pharmaceuticals, fertilizers, fuels)
- \* Materials

- repeated or continual use
- shaping





## **Shaping of Materials**

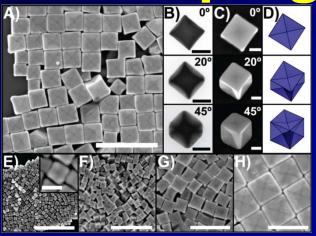




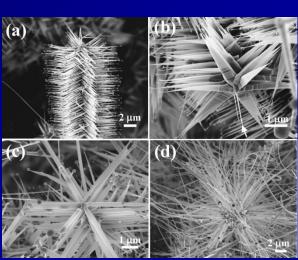




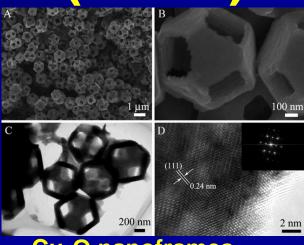
## **Shaping of (Nano) Materials**



Au concave cubes



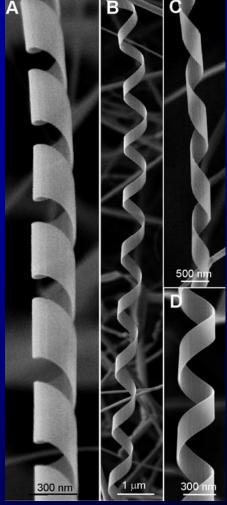
**ZnO** nanopropellers



Cu<sub>2</sub>O nanoframes



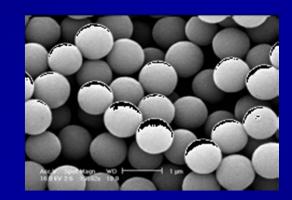
**ZnO** nanorings



**ZnO** nanobelts

#### **Materials**

**Ceramics (oxides, carbides, nitrides, borides)** 



Glasses (oxides, fluorides, chalcogenides, metallic)

**Metals, Alloys, Intermetallics** 

Polymers - inorganic, organic, hybrid

Semiconductors (Si, Ge, 13/15, 12/16 compounds)

**Composites, Inorganic-Organic Hybrid Materials** 

**Zeolites, Layer and Inclusion Materials** 

**Biomimetic Materials, hydroxyapatite** 

Carbon-based Materials: Fullerenes, Fullerene Tubes, Graphene

## **Properties of Materials**

A property = a material trait, the kind and magnitude of response to a specific stimulus

#### **Properties**

Mechanical
Electrical
Thermal
Magnetic
Optical
Deteriorative (corrosion)
Catalytic
Biocompatibility

Metals	Ceramics	Polymers
Strong	Strong	Usually not strong
Ductile	Brittle	Very ductile
Electrical Conductor	Electrical Insulator	Electrical Insulator
Heat Conductor	Thermal Insulator	Thermal Insulator
Not transparent	May be transparent	Not transparent
Shiny	Heat Resistant	Low Densities

#### **Materials Science:**

Studies relationships between the structure and properties of materials

#### **Materials Engineering:**

Designing and engineering the structure of a material to produce a predetermined set of properties

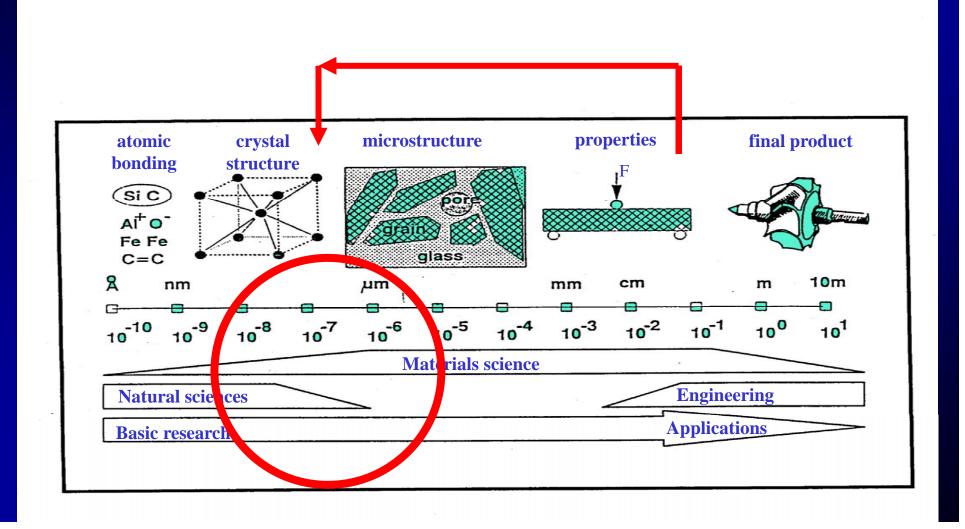
Chemistry Chemistry Processing Structure Properties Function

Chemistry Waterials Science Materials Science atomic Chemistic atomistic electronic electronic

**Length Scale** 

14

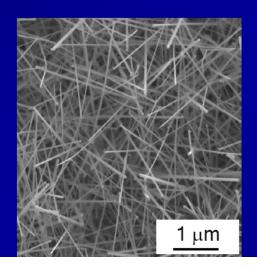
## Materials Chemistry among Natural and Technical Sciences

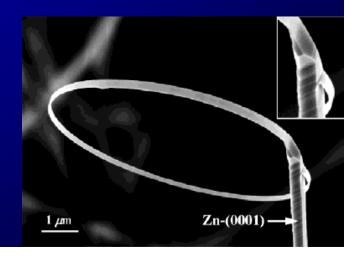


## **Materials Chemistry**

#### **Role of Materials Chemistry**

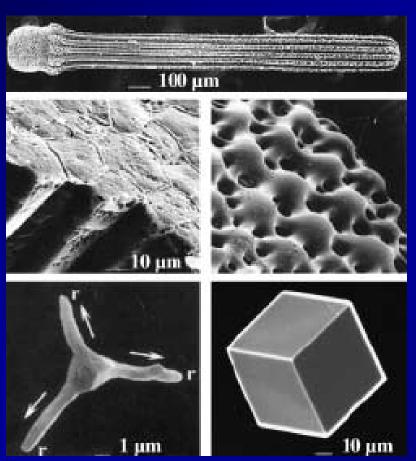
- Synthesis of new materials new atom architecture
- Preparation of high purity materials
- Fabrication techniques for tailored morphologies (shapes and sizes)
- Fabrication of functional materials



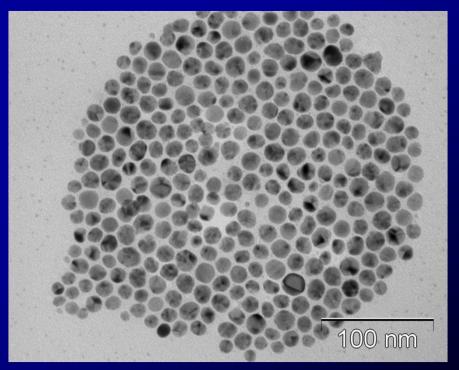


## **Shapes of Natural and Synthetic Single Crystals**

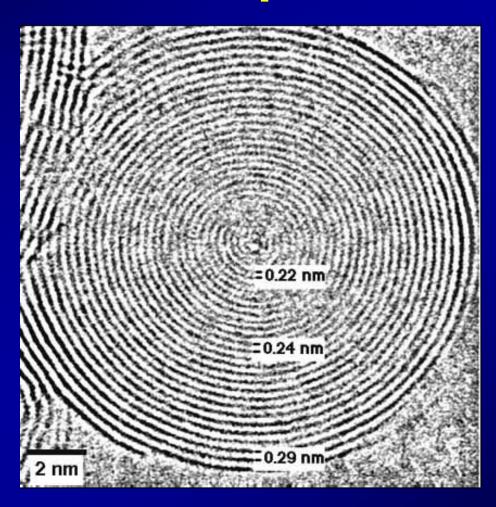
Calcite CaCO<sub>3</sub>



Cu-Ag nanoalloy



## **Onion-Like Graphitic Particles**

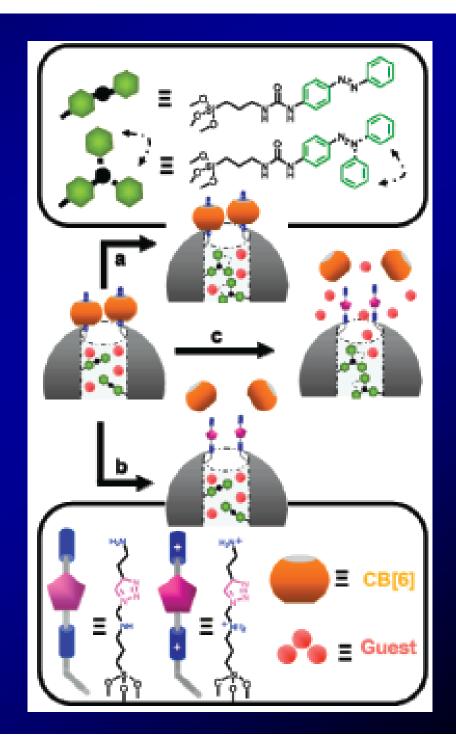


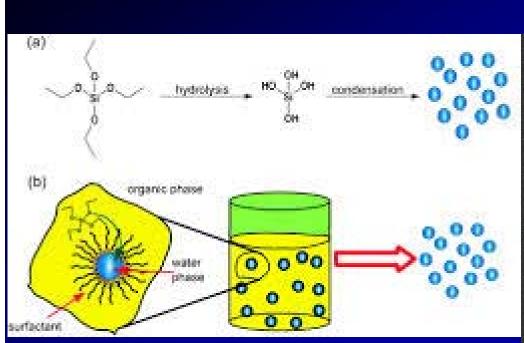
#### **Functional Materials**

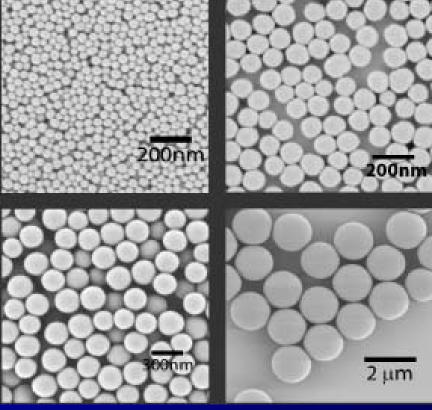
**Dual-controlled nanoparticles exhibit AND logic function** 

- (a) Excitation with 448 nm light induces the dynamic wagging motion of the nanoimpellers, but the nanovalves remain shut and the contents are contained.
- (b) Addition of NaOH opens the nanovalves, but the static nanoimpellers are able to keep the contents contained.
- (c) Simultaneous excitation with 448 nm light AND addition of NaOH causes the contents to be released.

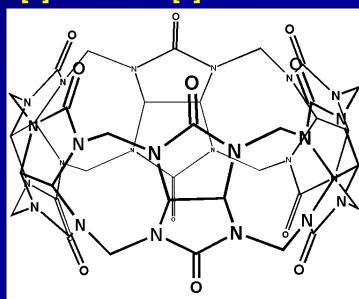
CB[6] = cucurbit[6]uril







#### CB[6] = cucurbit[6]uril



#### **Materials Chemistry**

Single crystals, defects, dopants, non-stoichiometry **Monoliths Coatings** Thin or thick films - singlecrystalline, polycrystalline, amorphous, epitaxial Fibers, Wires, Tubes Powders – primary particles, aggregates, agglomerates polycrystalline, amorphous, nanocrystalline (1-100 nm) **Porous materials** micropores (< 20 Å), mesopores (20-500 Å), macropores (> 500 Å) **Micropatterns** Nanostructures – spheres, hollow spheres, rods, wires, tubes, photonic crystals **Self-assembly – supramolecular chemistry: rotaxenes,** catenanes, cavitands, carcerands

#### **Materials Chemistry Tool Box**

**Direct reactions of solids – "heat-and-beat"** 

**Precursor methods** 

Chimie douce, soft-chemistry methods, synthesis of novel metastable materials, such as open framework phases

**lon-exchange methods, solution, melt** 

Intercalation: chemical, electrochemical, pressure, exfoliation-reassembly

Crystallization techniques, solutions, melts, glasses, gels, hydrothermal, molten salt, high P/T

Vapor phase transport, synthesis, purification, crystal growth, doping

#### **Materials Chemistry Tool Box**

Electrochemical synthesis, redox preparations, anodic oxidation, oxidative polymerization

Preparation of thin films and superlattices, chemical, electrochemical, physical, self-assembling mono- and multilayers

Growth of single crystals, vapor, liquid, solid phase chemical, electrochemical

High pressure methods, hydrothermal, diamond anvils

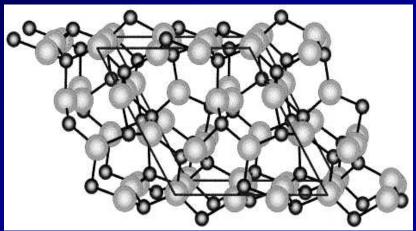
Combinatorial materials chemistry, creation and rapid evaluation of gigantic libraries of related materials

### Si<sub>3</sub>N<sub>4</sub> Hexagonal

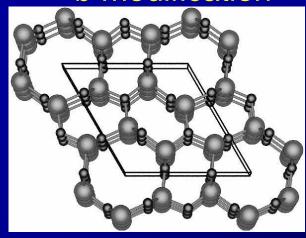
Si



a modification



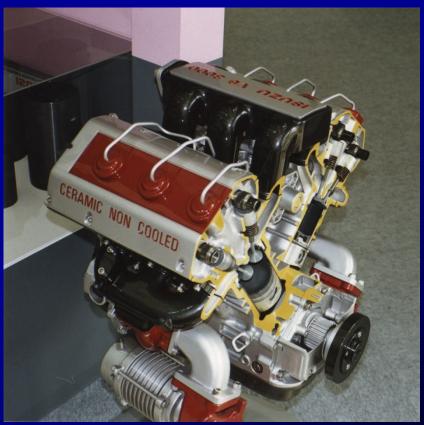
#### b modification



- Strong covalent bond (4.9 eV)
- Hardness (a-monocrystal, Vickers 21 GPa)
- Tensile Strength 1.5 GPa (b-whisker)
- Young modulus 350 GPa
- Decomposition temp. 1840 °C/1 atm N<sub>2</sub>
- Density 3.2 g cm<sup>-3</sup>

## Si<sub>3</sub>N<sub>4</sub> Ceramics





#### **Microstructure of Materials**



### Microstructure vs. Properties

**Sliding of grains** 

**Sliding of grains slowed down** improved mechanical properties

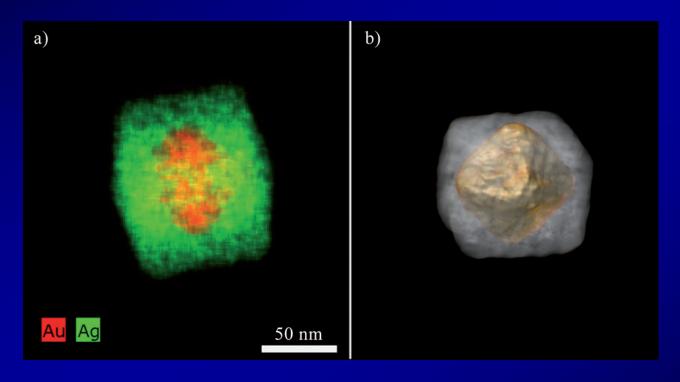
150 nm

Si<sub>3</sub>N<sub>4</sub> tensile stress tensile stress Si<sub>3</sub>N<sub>4</sub> **SiC inclusion** 

tens.str

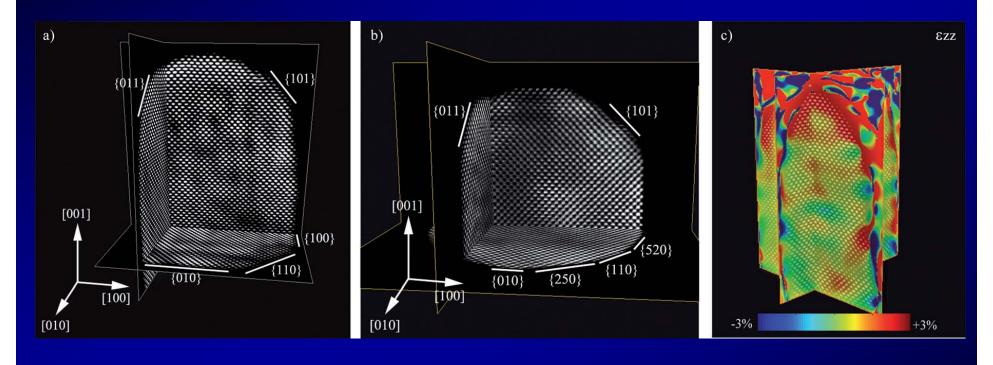
**SiC** inclusion

### **Imaging at Nanoscale**



a) 2D EDX map of a Au@Ag nanocube. Based on a tilt series of such 2D EDX maps the 3D reconstruction presented in (b) was obtained. The contrast in the 3D reconstruction is based on differences in chemical composition and it is clear that the core of the particle has an octahedral form.

### **Atomic Scale Imaging**



Atomic scale reconstruction of Au nanorods. a,b) Orthogonal slices through the atomic scale reconstruction of Au nanorods prepared using different surfactants. The side facets of these rods can be clearly recognized. c) Strain measurement along the major axis of the nanorod.