Óbuda University

Doctoral School of materials sciences and technologies

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Development and structural characterization of bioceramics

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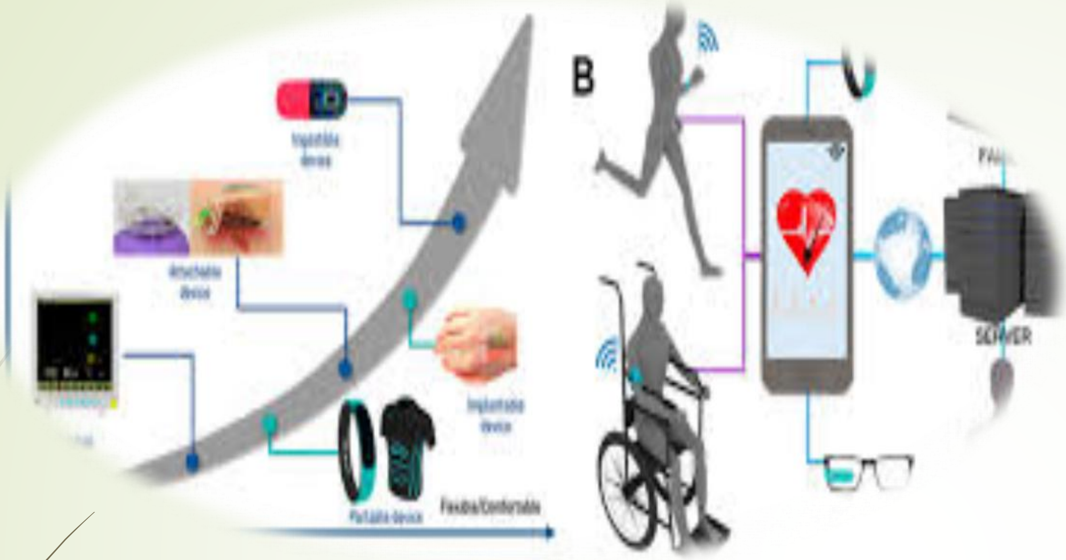
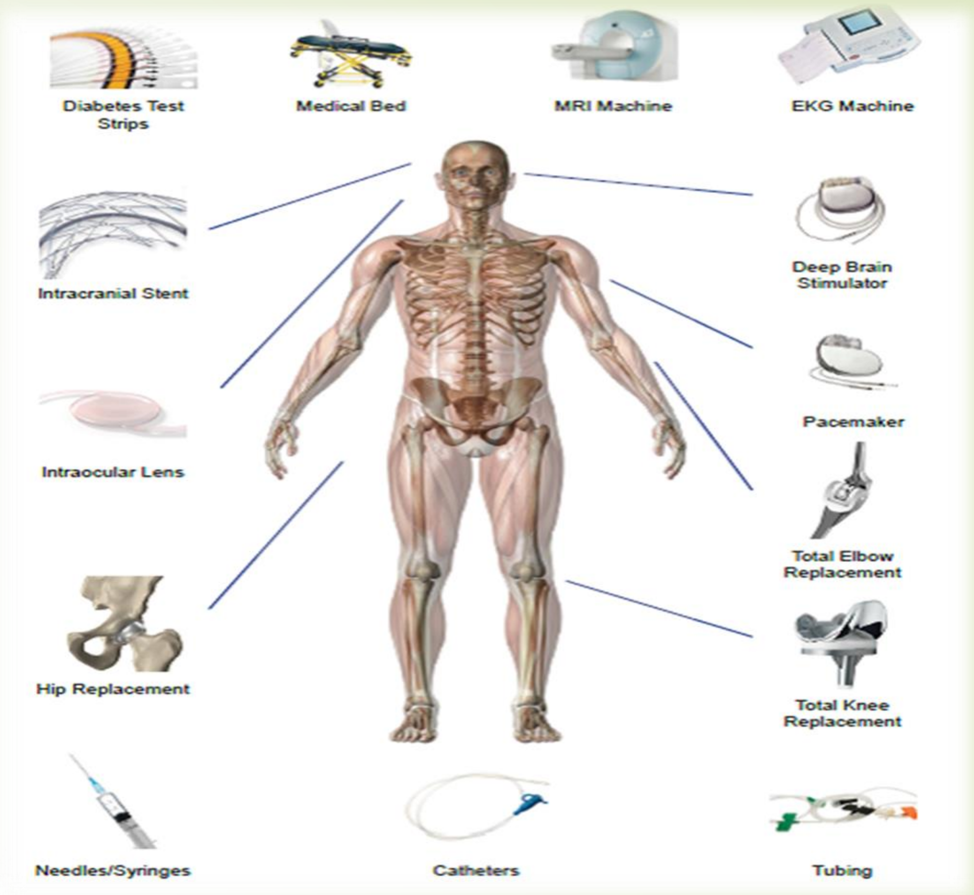




Are they accepted by the living body ???

☺ All implantable items <u>must be prepared</u> from a special class of tolerable materials

→ **Biomaterials**

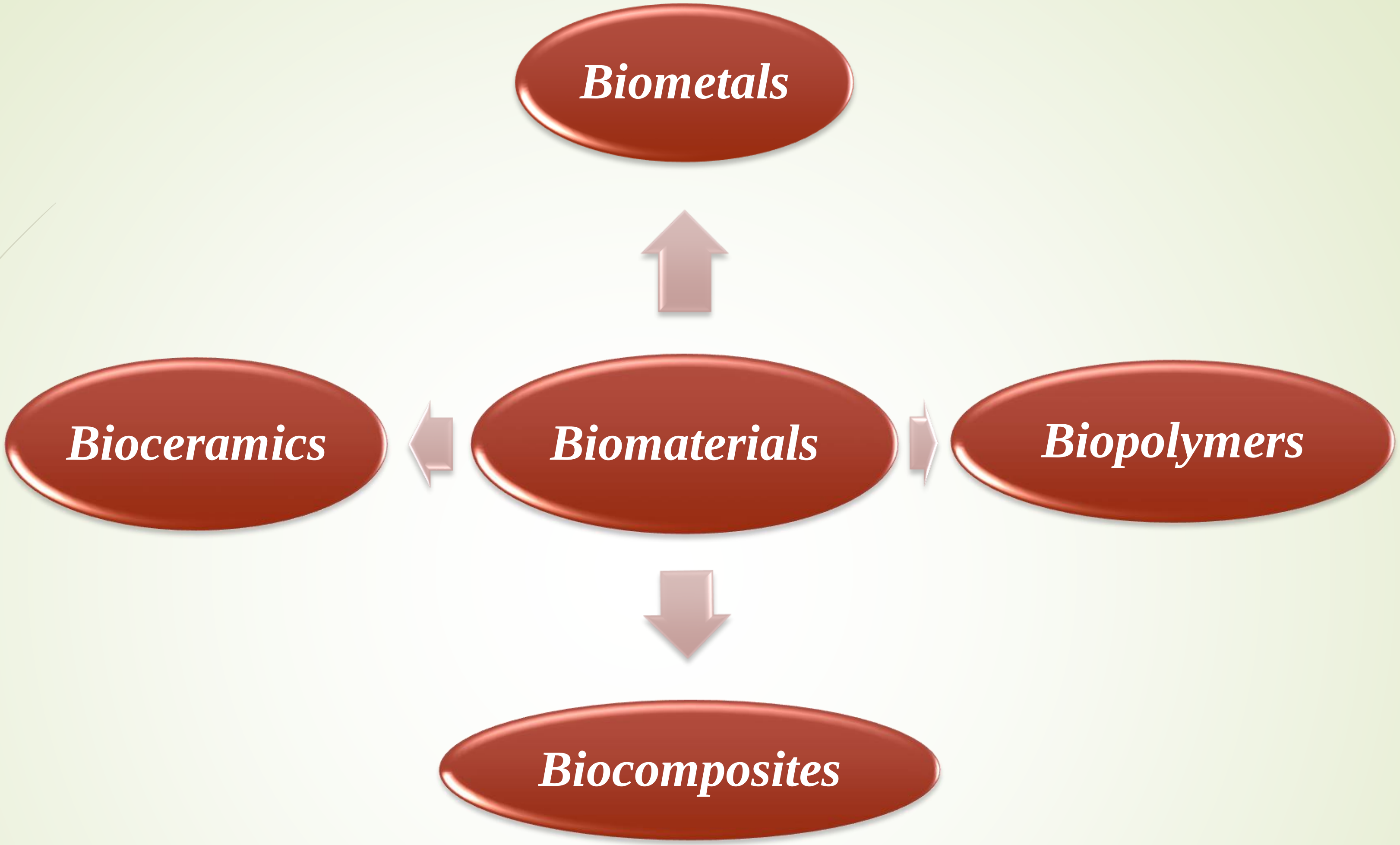


Fig.1 Classification of biomaterials

Bioceramics

- Polycrystalline materials
- Amorphous materials (glasses)
- Blends thereof (glass-ceramics)

😐 The chemical elements used to manufacture bioceramics form just a small set of the Periodic Table

Bioceramics
- Alumina
- Zirconia
- Magnesia
- Carbon
- Silica-contained compounds
- Calcium-contained compounds
- Limited number of other chemicals

→

- ✓ Both dense and porous forms in bulk
- ✓ Crystals
- ✓ Powders
- ✓ Particles
- ✓ Granules
- ✓ Scaffolds and/or Coatings

CaPO4-based formulations

☺ The chemical similarity to mammalian bones and teeth

☹ CaPO4 alone have some restrictions

↓

(Lack the compositional, mechanical and elastic properties of natural calcified tissues)

Thinking about solutions in order to improve their properties

=

$CaPO_4$ are functionalized by doping with other chemical elements and/or by adding compounds possessing the desired properties

~ $2.3 billion by 2017

↑

Only in USA!!!!!

2010, the sales of bone graft substitutes were valued at ~ $1.3 billion

In the ternary aqueous system $Ca(OH)_2$–H_3PO_4–H_2O (or CaO–P_2O_5–H_2O)

Ca/P molar ratio	Compounds and their typical abbreviations	Chemical formula	Solubility at 25°C, $-\log(K_s)$	Solubility at 25°C, g/L	pH stability range in aqueous solutions at 25°C
0.5	Monocalcium phosphate monohydrate (MCPM)	$Ca(H_2PO_4)_2 \cdot H_2O$	1.14	~18	0.0-2.0
0.5	Monocalcium phosphate anhydrous (MCPA or MCP)	$Ca(H_2PO_4)_2$	1.14	~17	[c]
1	Dicalcium phosphate dehydrate (DCPD), mineral brushite	$CaHPO_4 \cdot 2H_2O$	6.59	~0.088	2.0-6.0
1	Dicalcium phosphate anhydrous (DCPA or DCP), mineral monetite	$CaHPO_4$	6.9	~0.048	[c]
1.33	Octacalcium phosphate (OCP)	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$	96.6	~0.0081	5.5-7.0
1.5	α-Tricalcium phosphate (α-TCP)	α-$Ca_3(PO_4)_2$	25.5	~0.0025	[a]
1.5	β-Tricalcium phosphate (β-TCP)	β-$Ca_3(PO_4)_2$	28.9	~0.0005	[a]
1.2-2.2	Amorphous calcium phosphates (ACP)	$Ca_xH_y(PO_4)_z \cdot nH_2O$, n=3-4.5; 15-20% H_2O	[b]	[b]	~ 5-12 [d]
1.5-1.67	Calcium-deficient hydroxyapatite (CDHA or Ca-def HA)[g]	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ $(0<x<1)$	~85	~0.0094	6.5-9.5
1.67	Hydroxyapatite (HA, HAp or OHAp)	$Ca_{10}(PO_4)_6(OH)_2$	116.8	~0.0003	9.5-12
1.67	Fluorapatite (FA or FAp)	$Ca_{10}(PO_4)_6F_2$	120	~0.0002	7-12
1.67	Oxyapatite (OA, OAp or OXA)[f], mineral voelckerite	$Ca_{10}(PO_4)_6O$	~69	~0.087	[a]
2	Tetracalcium phosphate (TTCP or TetCP), mineral hilgenstockite	$Ca_4(PO_4)_2O$	38-44	~0.0007	[a]

The most important parameters of CaPO4

The ionic Ca/P ratio, basicity/acidity and solubility $\propto pH$

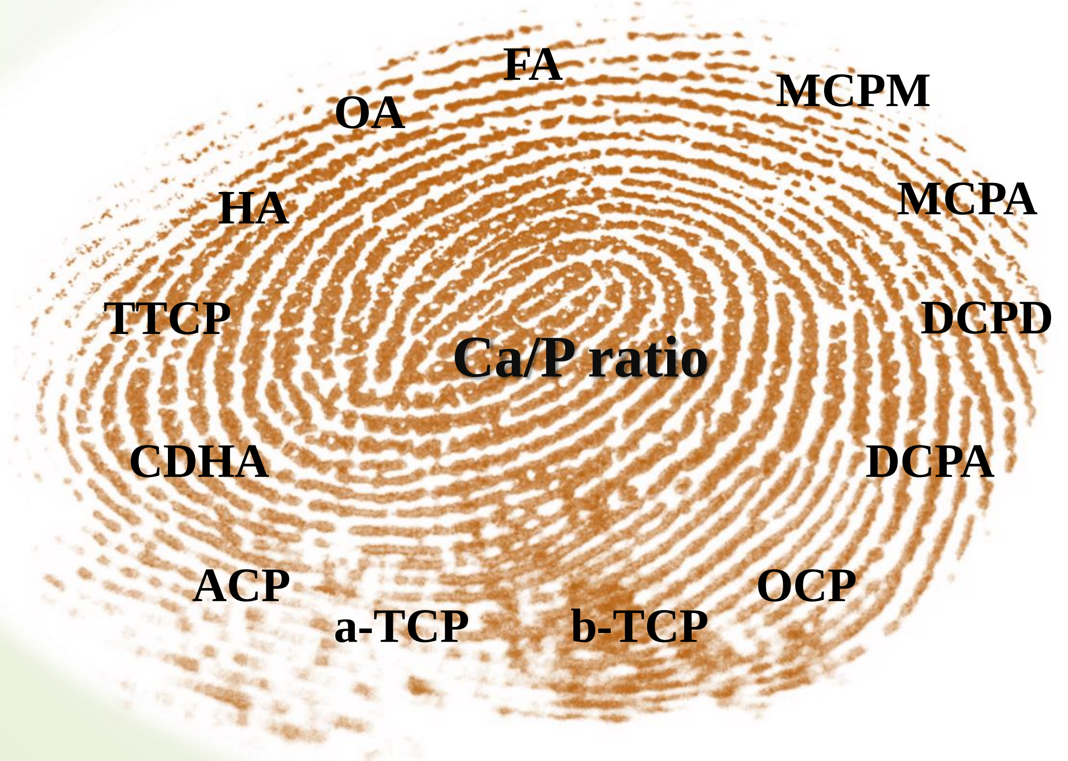
Low — High: The Ca/P molar ratio

more acidic and water-soluble

High — Low: Solubility

Acidic compounds

Basic compounds



Biphasic, triphasic and multiphasic CaPO4 formulations

CaPO4

- Biphasic
- Triphasic
- Multiphasic (Polyphasic)

BCP

- CaPO4 having either the same (e.g., a-TCP and b-TCP) molar Ca/P ratios
- Different (e.g., b-TCP and HA) molar Ca/P ratios

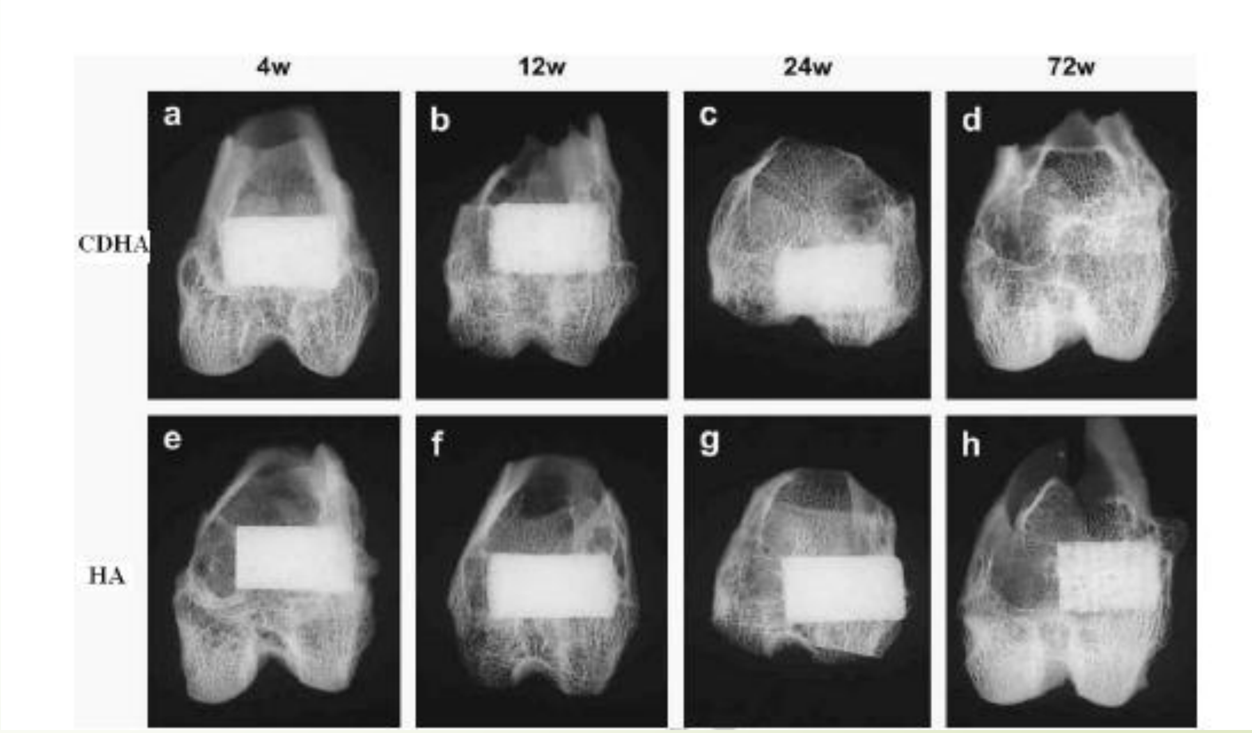


Fig.2, Soft X-ray photographs of the operated portion of the rabbit femur. Four weeks (a), 12 weeks (b), 24 weeks (c) and 72 weeks (d) after implantation of CDHA; 4 weeks (e), 12 weeks (f), 24 weeks (g) and 72 weeks (h) after implantation of sintered HA.

Biomedical applications

1/ Self-setting (self-hardening) formulations

Self-setting (or Self-hardening) formulations consisting of CaPO4 → Applied as injectable and/or mouldable bone substitutes

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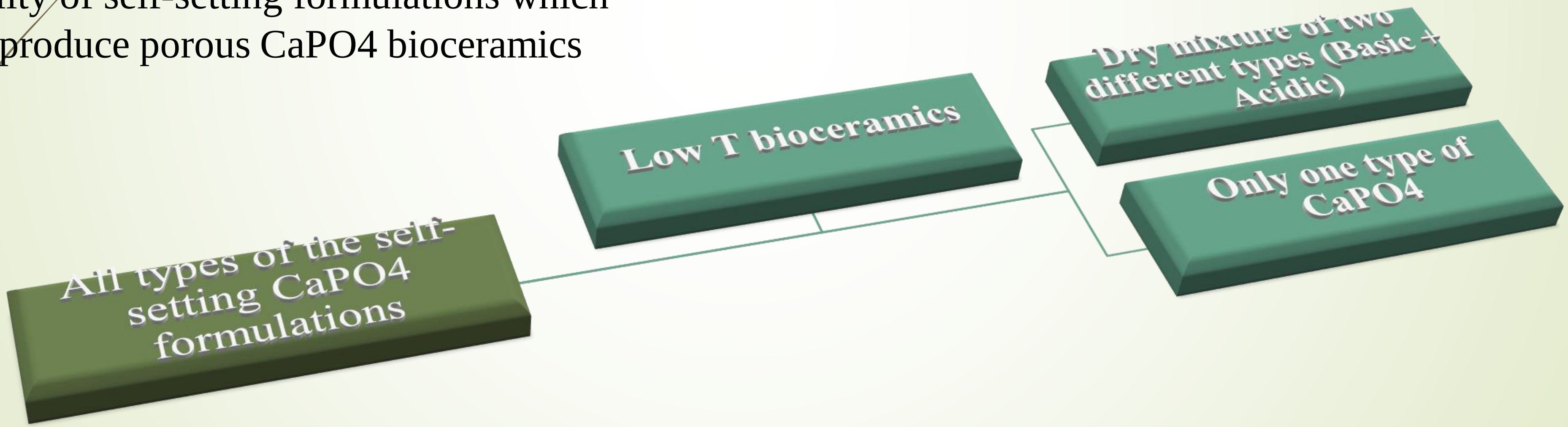
The availability of self-setting formulations which are able to produce porous CaPO4 bioceramics



High temperature CaPO4 bioceramics → Sintering the self-setting formulations

2/ Coatings, films and layers

Due to the inferior mechanical properties of bioceramics based on CaPO4 → 😐 Their clinical application has been largely restricted to non-load bearing parts of the skeleton

Several ways have been tried

😐 Metals do not undergo bone bonding

👍 The solution was in coating metals with CaPO4

- Thickness (50 – 100 µm)
- Crystallinity
- Phase and chemical purity
- Porosity
- Adhesion.

3/ Functionally graded bioceramics

Surface

Functionally gradient materials (FGMs)

↓

Gradient change

Composition

Structure

The interior of the materials

- ❖ Two different properties
  - ✓ Mechanical strength
  - ✓ Biocompatibility

Non-biomedical applications of CaPO4

Strong adsorption ability

Surface acidity or basicity ability

Ion exchange ability

Some types of CaPO4 possess a catalytic activity

CaPO4 are able to catalyze

- Oxidation and Reduction reactions
  - Oxidation of alcohol and Dehydrogenation of Hydrocarbons
  - Hydrogenolysis and Hydrogenation
- Formation of C–C bonds

Research Plan

Exams for 1. semester (successful)
1) Powder technology
2) Biomaterials for medical applications

Exams for 2. semester :
1) Selected chapters of material testing methods I: FITR, HPLC/MS
2) Transmission electron microscopy for structural investigations of different materials

- Literature overview of calcium oxide and silica bioceramics
- Knowledge of preparation techniques
  (attrition milling, ball milling, electrospinning, sol-gel methods)
- Knowledge of different tools for structural characterization of bioceramis
  (XRD, SEM, EDS, TEM, DM)
- Firs steps of bioceramics preparation

Thank you for your attention!