Microwave sintering and microstructural development of hydroxyapatite biomaterials

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Workshop COST Action MP1301

Sofia, Bulgaria, October 13-14th 2015

Contents

- Material & context
- Microwave heating
- Microwave sintering of HA small pellets
- Microwave sintering – Scaling up
- Microwave sintering of complex-shaped samples
- Conclusions

Material & context

➢ **Material:**

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$

☺ Composition close to the one of human bones

☺ Biocompatibility

⇨ Medical applications for bones subsitution

☺ Good absoprtion of microwave radiation

➢ **Context:** Try to improve the HA mechanical properties for structural applications : hardness, Young's modulus, fracture toughness, compression strength…

What are the consequences of the microwave process utilization on the microstructures and functional properties of the HA sintered samples ?

Material & context

- **Microwave sintering advantages:**

  - ✓ Short thermal treatment time
  - ✓ Low energy consumption
  - ✓ Fine microstructure
  - ✓ Higher mechanical properties
  - ✓ Ability to sinter complex-shaped pieces

- **Final goal:**

Develop the elaboration and sintering of customised bones substitute, in terms of shape, by coupling the stereolithography and the microwave sintering

Ability to obtain a piece in few hours

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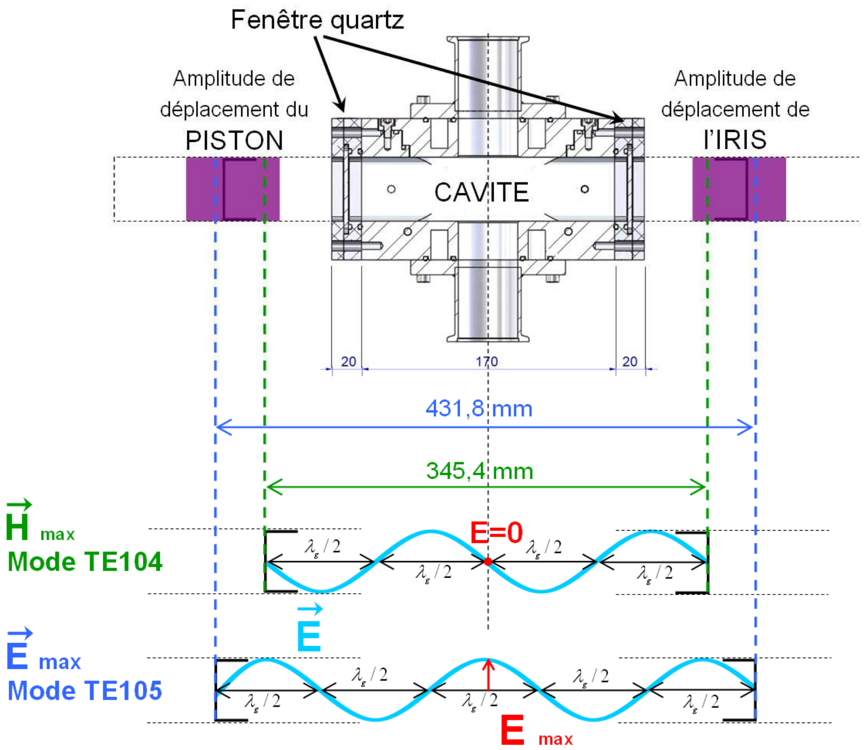
Microwave heating

- Electromagnetic radiation at 2.45 GHz or 915 MHz
- Heating induced by microwave / matter interaction

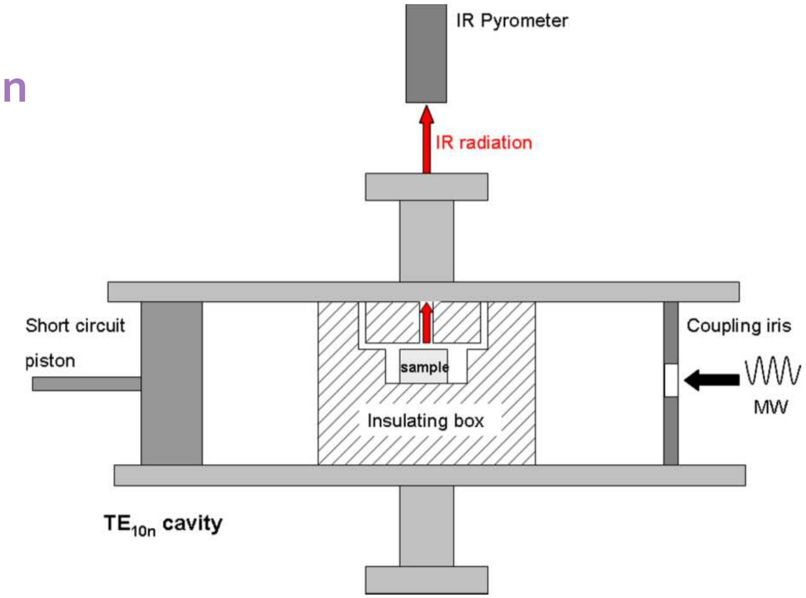
  Very high heating rates (>200°C.min^{-1})

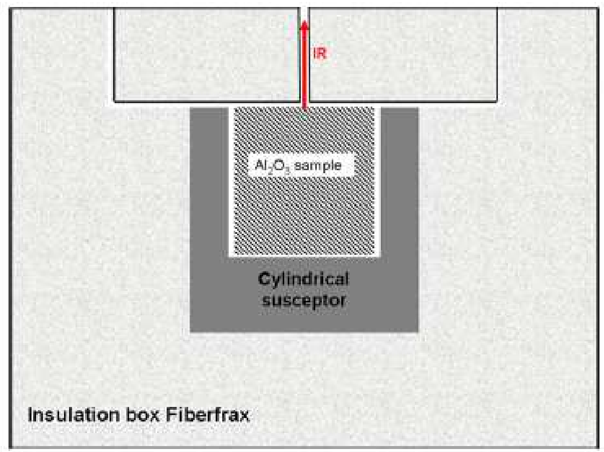
  Very short thermal treatments (few minutes)



R. Heuguet, Thesis, University of Caen Basse-Normandie, France

direct heating

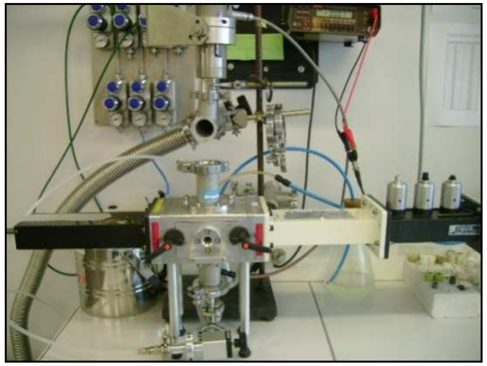




hybrid heating (using susceptor)

Microwave sintering

- **Depending on the samples dimensions, different microwave equipments are used :**



Single-mode cavity

2.45 GHz

Small size pellets (Ø < 20 mm)

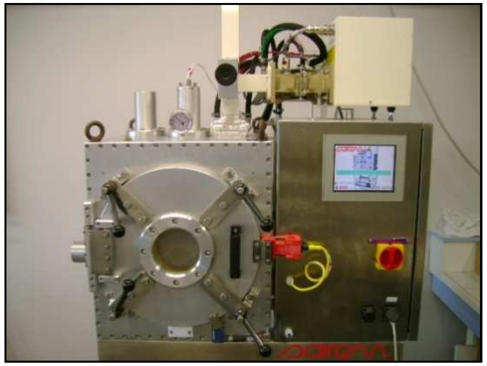
HA direct heating

Single-mode cavity

915 MHz

Big size pellets (20 < Ø < 80 mm)

HA hybrid heating



Multi-mode cavity

2.45 GHz

Big size pellets (20 < Ø < 150 mm)

HA hybrid heating

Elaborate high density materials while limiting the grain growth

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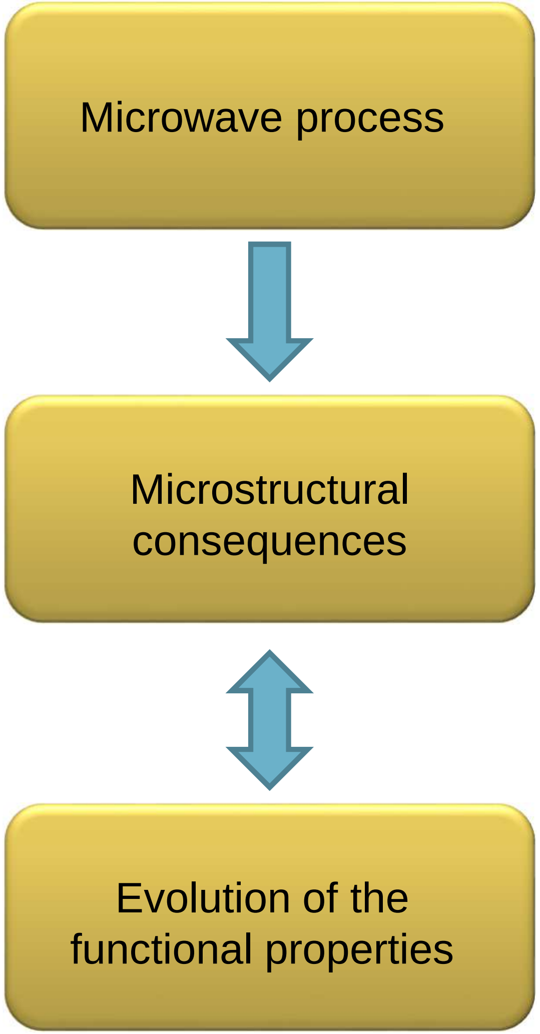
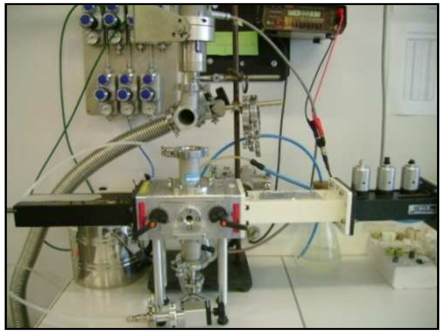
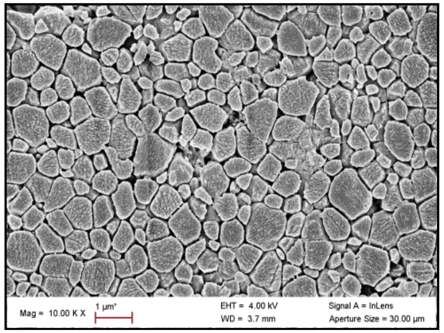
Microwave sintering of HA small pellets

➢ **Aim of the experiments:**

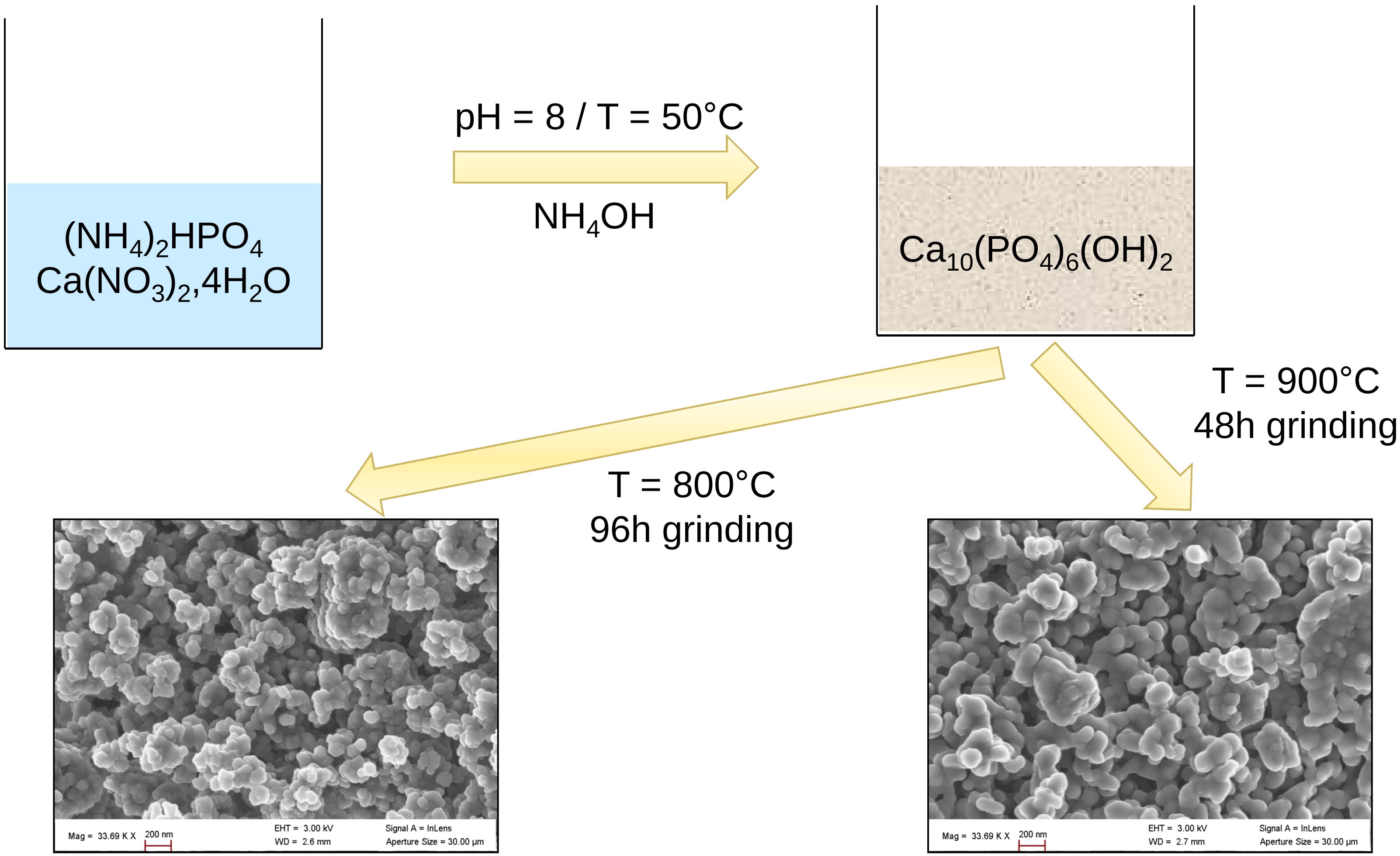






Microwave sintering of HA small pellets

➢ **HA powder synthesis:**



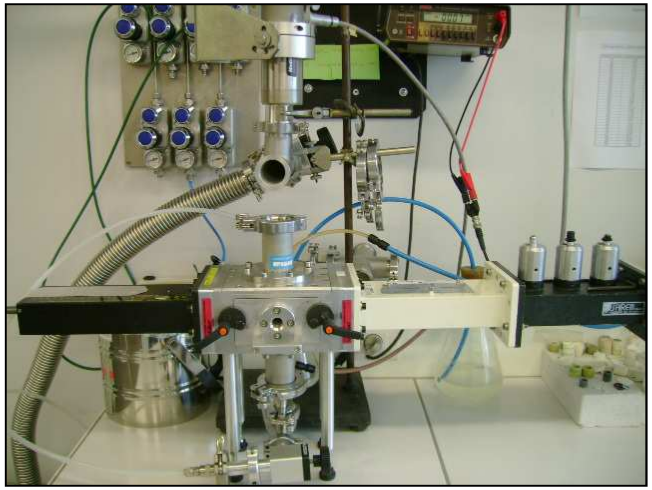
Specific surface : 25,3 m²/g
Average grain size : 75 nm

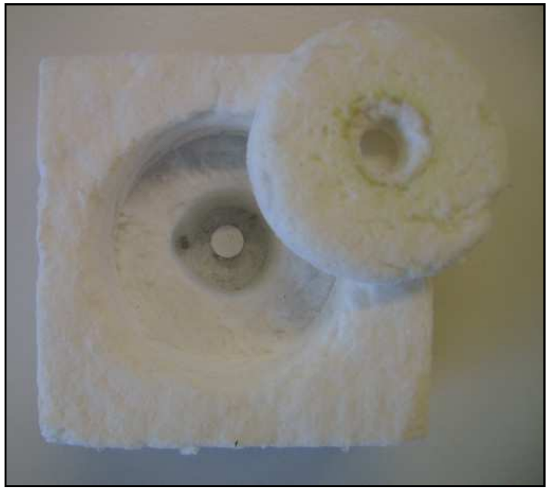
Specific surface : 10,7 m²/g
Average grain size : 177 nm

Microwave sintering of HA small pellets

➤ **Experimental device:**

- ✓ Single-mode microwave cavity at 2.45GHz
- ✓ TE105 mode (electric field)
- ✓ 7mm-diameter pellets elaborated by slip casting
- ✓ Direct heating (no susceptor)
- ✓ Thermal insulation box made of fibrous alumina / silica
- ✓ Temperature measured by using a pyrometer



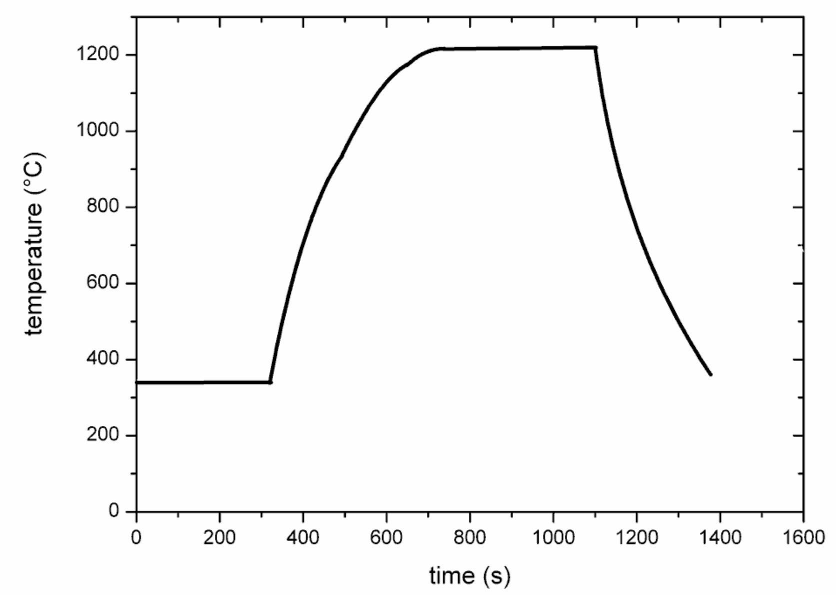


Microwave sintering of HA small pellets

➢ Microwave sintering parameters:

➢ 5 sintering temperatures: 1190°C, 1210°C, 1230°C, 1250°C, 1270°C

➢ 3 dwell times: 5, 15 et 30 minutes



✓ P = 250W to set up the heating, 5 minutes required to reach 350° C

✓ P = 300-320W to reach the sintering temperature in 5 minutes

✓ Cut-off of the microwave at the end of the dwell time, cooling in 5 minutes

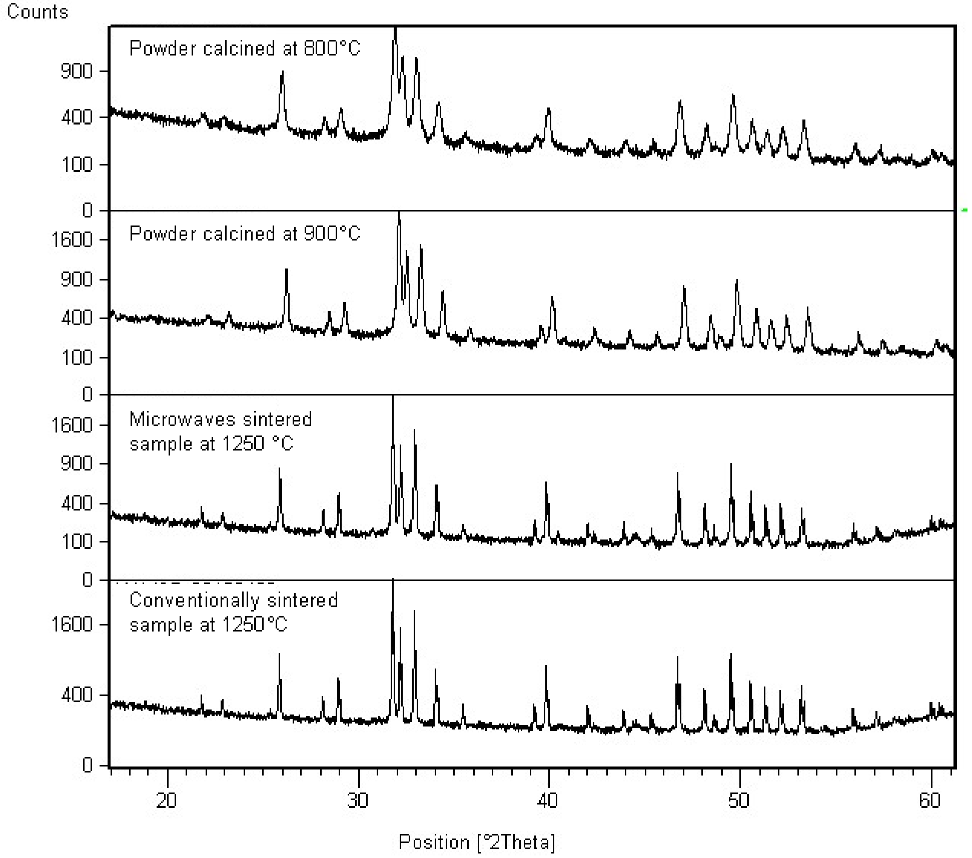
Very short heating cycles: about 20 minutes

A. Thuault, E. Savary, J-C. Hornez, M. Descamps, G. Moreau, S. Marinel, A. Leriche, "Improvement of the hydroxyapatite mechanical properties by direct microwaves sintering in single mode cavity", *Journal of European Ceramic Society,* Vol 34 (7) 1865-1871, July 2014

Microwave sintering of HA small pellets

- **Phase conservation:**

- X-ray diffraction



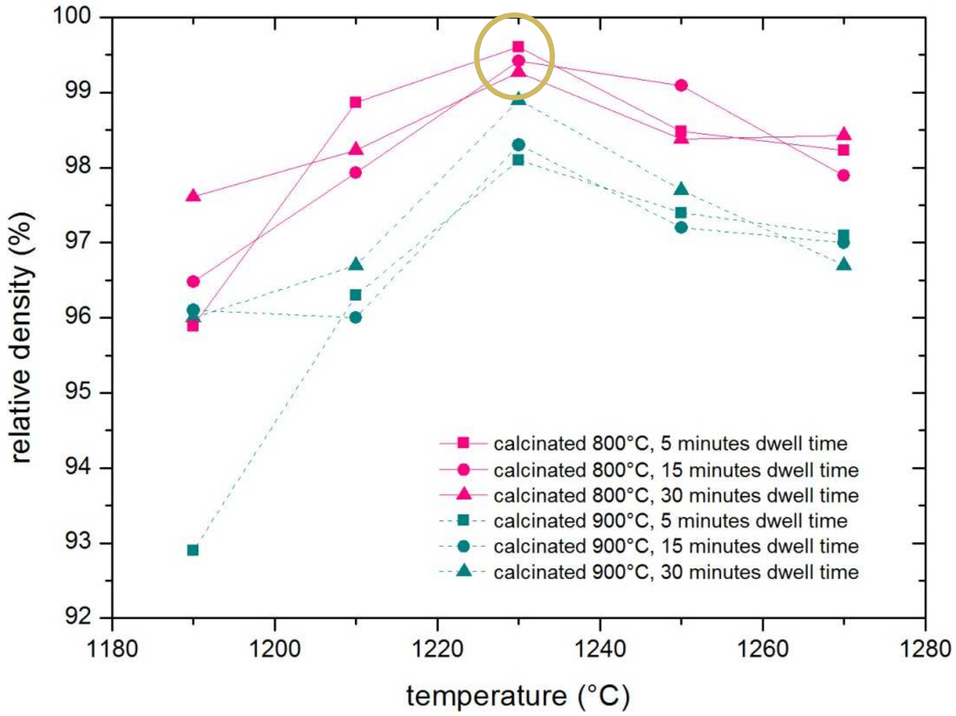
- ✓ No TCP trace
- ✓ Sligthly larger peak width for higher calcination temperature
- ✓ No influence of the microwave process on the sintered samples composition

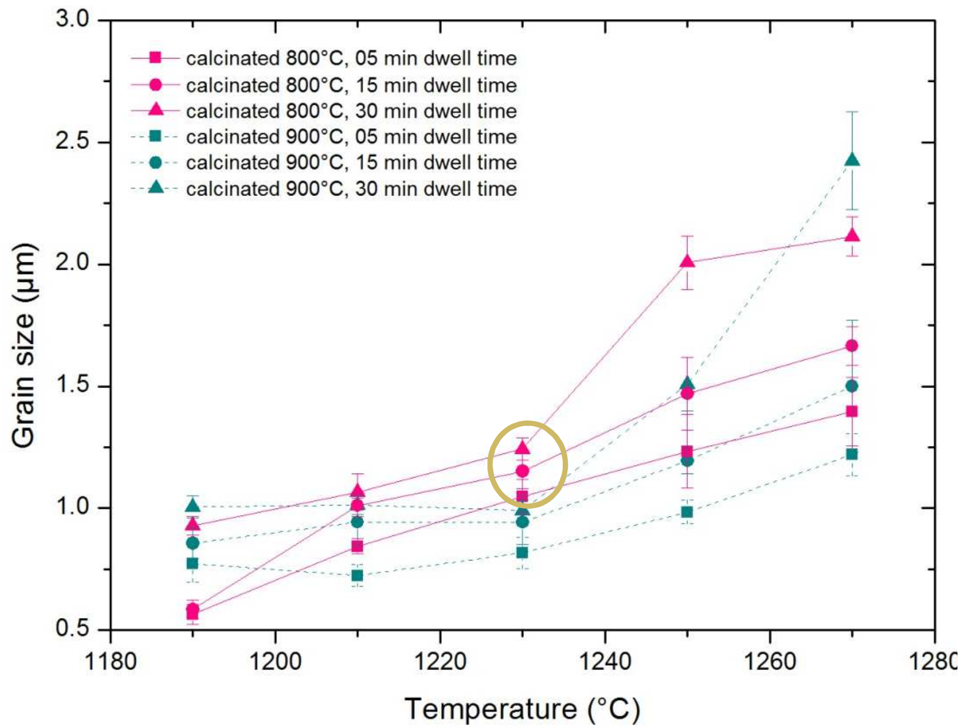
HA phase conserved after microwave sintering

Microwave sintering of HA small pellets

➢ **Density & grain size:**

➢ Density measurements by Archimedes' method and grain size calculation by a linear intercept method





Samples successfully sintered in very short times (d > 99% for T=1230° C)

Mean grain size ~ 1 µm for a sintering temperature of 1230°C

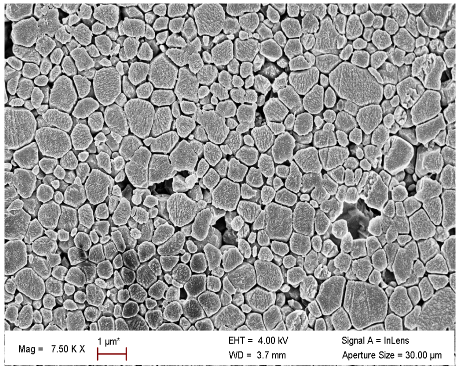
Microwave sintering of HA small pellets

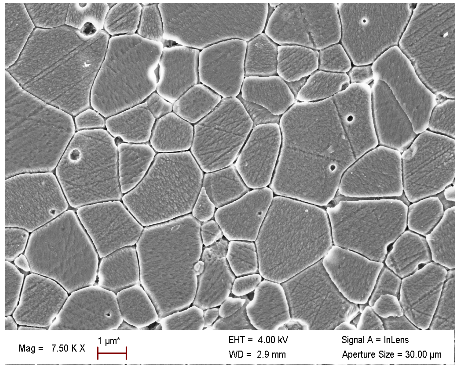
- **Microstructure:**

- SEM micrographs

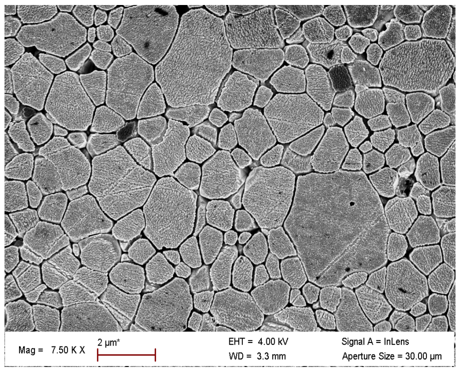
1190°C → 1270°C

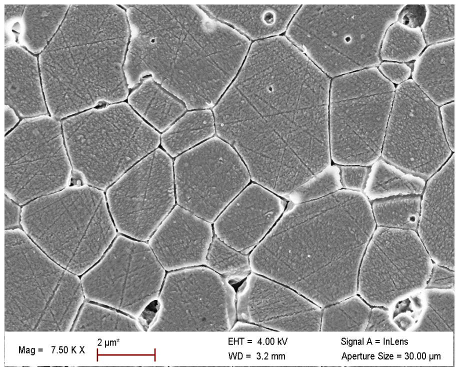
5 min





30 min





Grain size increases with :

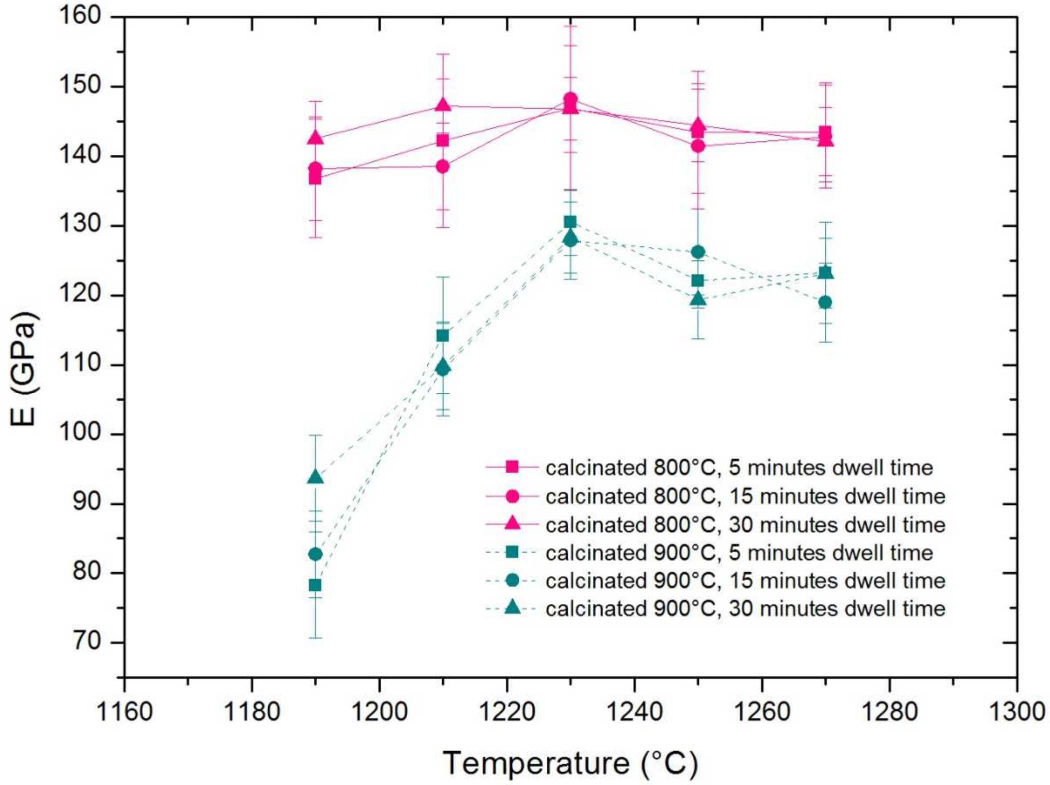
- ✓ Powder grain size
- ✓ Sintering temperature
- ✓ Dwell time

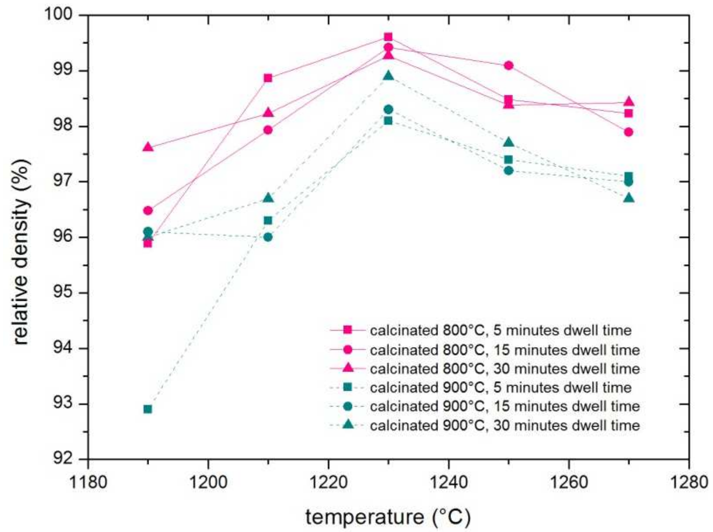
To increase the mechanical properties : need to reach high density for small grain size

Microwave sintering of HA small pellets

➢ **Young's modulus:**

➢ Young's Modulus measurements by indentation:





✓ E strongly correlated to the relative density

✓ No influence of the dwell time on E values

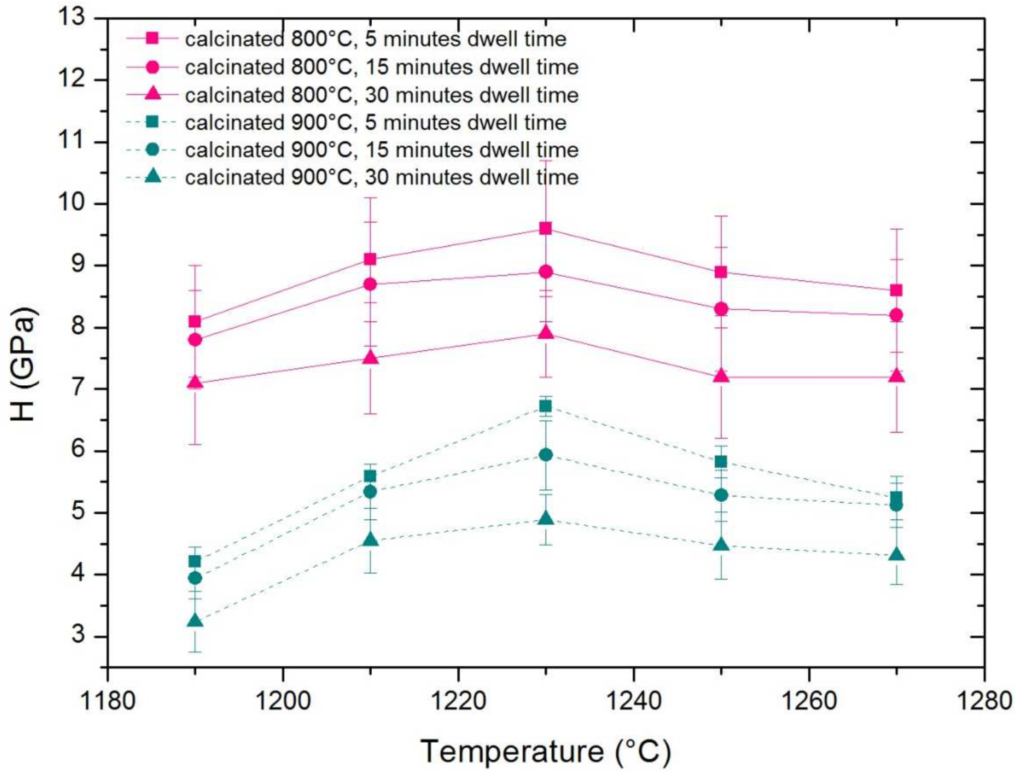
E values slightly higher than those reported in the literature

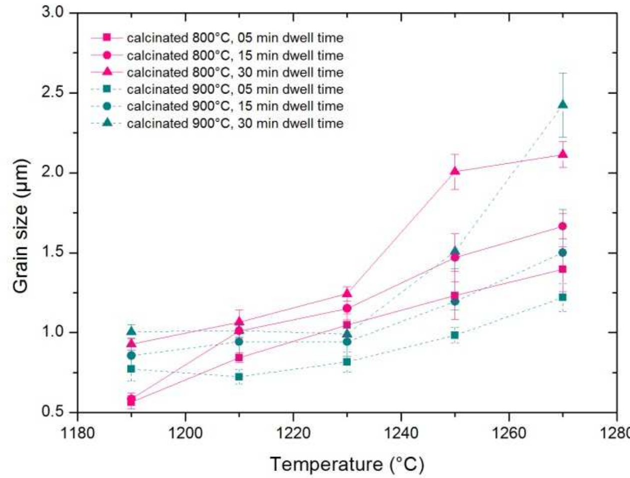
✓ Compression strength: 531.3 ± 42.2 MPa

Microwave sintering of HA small pellets

➢ **Hardness:**

➢ Hardness measurements by indentation:





✓ Influence of the dwell time on H values

✓ H strongly correlated to the grain size and density

H values improved compared to the literature

✓ Fracture toughness (K_1C): 1.12 ± 0.07 $MPa.m^{1/2}$

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Microwave sintering – Scaling up

- **2,45GHz single mode microwave cavity:**

☺ Elaboration of HA samples with high mechanical properties: E=148,5 GPa and H=9,6GPa

☹ Results obtained on small pellets: 7 mm diameter

Development of a microwave process for the sintering of larger samples

(50 mm diameter and 13 mm thickness pellets)

- **915 MHz single mode microwave cavity:**

E. Savary, A. Thuault, J-C. Hornez, A. Leriche, S. Marinel "Sacling-up of the single mode microwave sintering process: Example of the 915MHz sintering of hydroxyapatite", submitted, june 2015

Microwave sintering – Scaling up

➢ **Why using a 915 MHz microwave furnace to sinter large-sized pellets ?**

✓ Microwave penetration depth D_p :

$$D_p \cong \frac{c\varepsilon'}{f\pi\varepsilon''\sqrt{\varepsilon_r}}$$

When the frequency decreases, the penetration depth increases

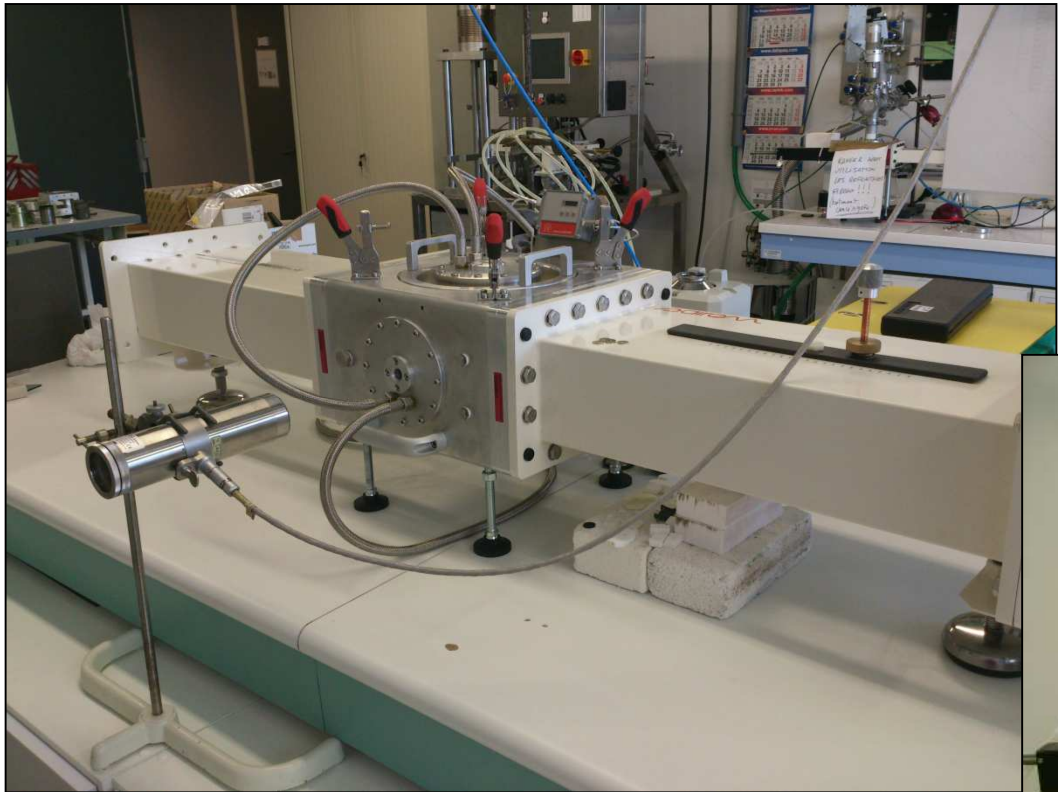
✓ Dimensions of the resonant cavity:

$$\frac{c}{f_r} = \frac{2}{\sqrt{\left(\frac{m}{a}\right)^2 + \left(\frac{n}{b}\right)^2 + \left(\frac{p}{L}\right)^2}}$$

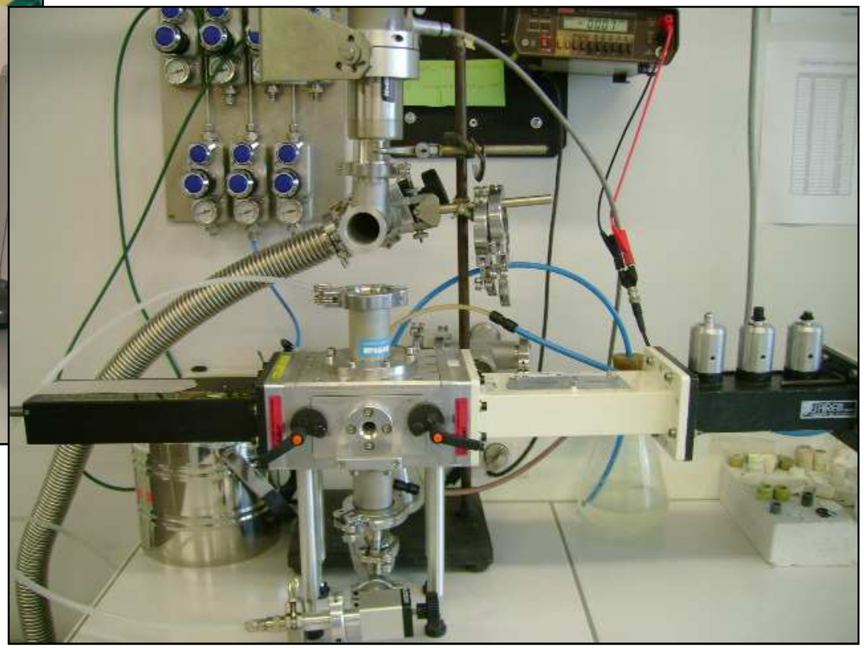
When the frequency decreases, the dimensions of the resonant cavity (a, b, L) increase

Microwave sintering – Scaling up

➢ **Experimental device:**



915 MHz :
Cavity section dimensions:
123.8 mm x 247.6 mm
Volume : ~10 L



2.45 GHz :
Cavity section dimensions:
86.36 mm x 43.18 mm
Volume : ~0.3 L

Microwave sintering – Scaling up

Experimental device:

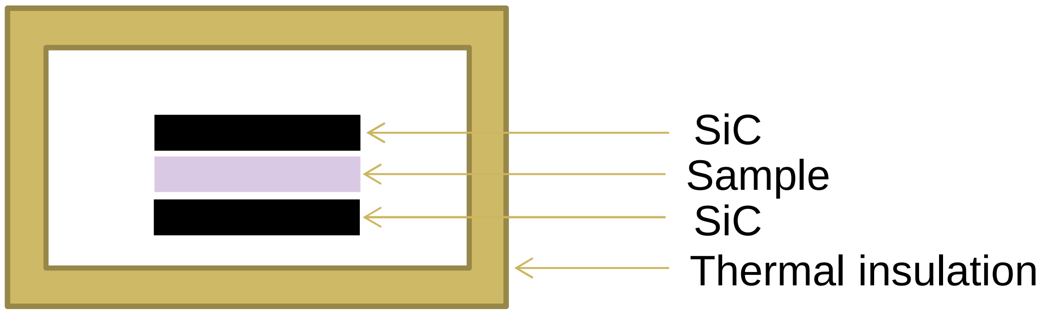
However…

$$P_d = 2\pi f \varepsilon' \tan(\delta) E^2$$

When the frequency decreases, the power dissipated within the sample decreases

➡ Higher power levels and SiC susceptors are required to reach the sintering temperature

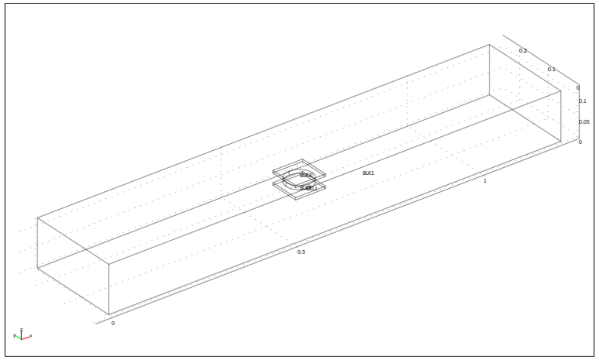
➡ Hybrid heating

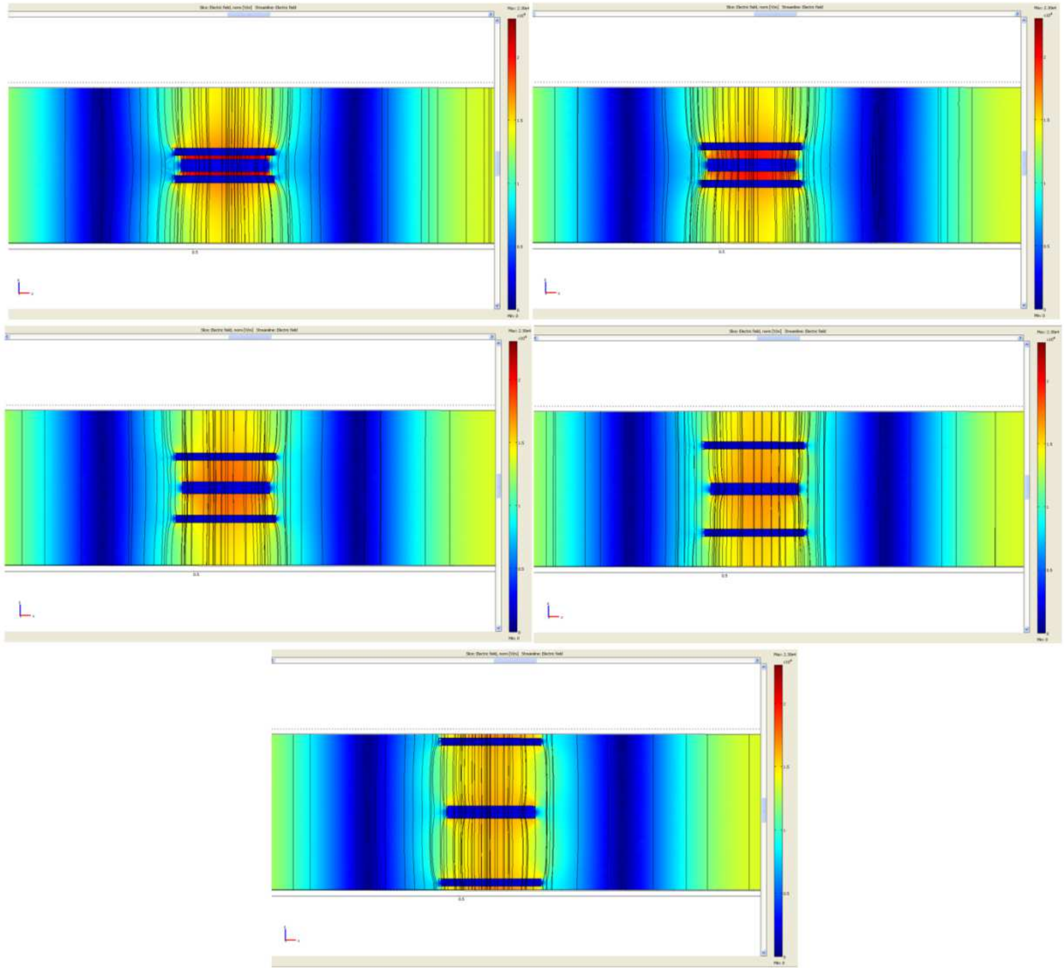


Microwave sintering – Scaling up

- **Experimental device:**

- Numerical simulation





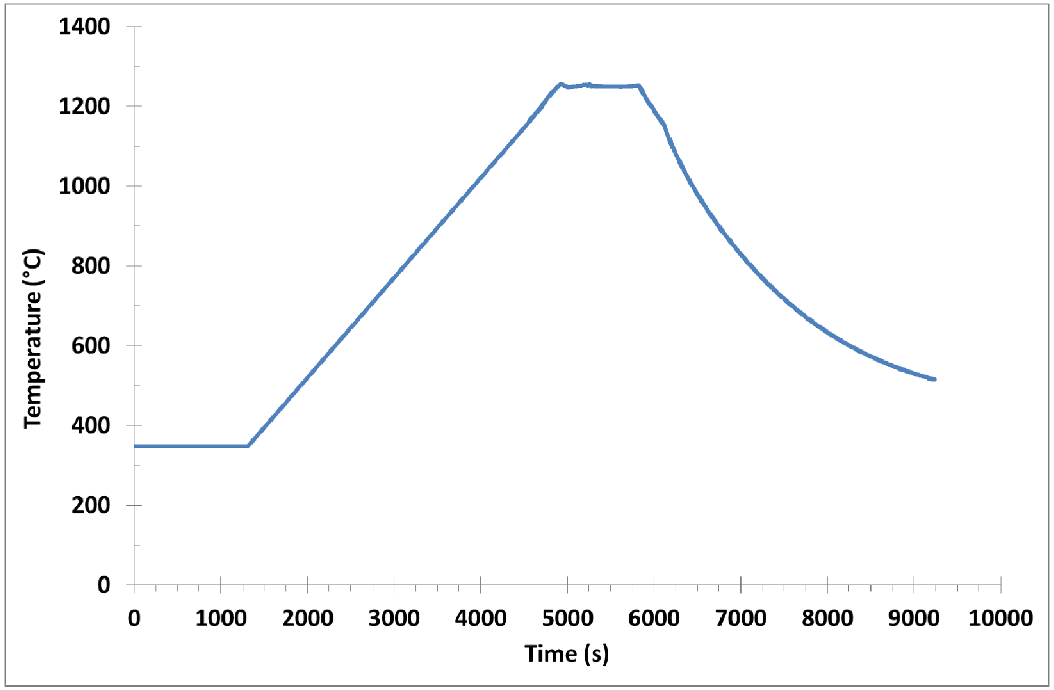
- No significant influence electrical conductiviy

- Weak influence of the dielectric properties

The weaker the distance between the susceptors and the sample is, the higher the electric field norm is

Microwave sintering – Scaling up

- **Samples shaping & sintering:**
  - ✓ HA nanometric powder (75nm)
  - ✓ 50mm diameter pellets shaped by uniaxial pressing (50 kN)
  - ✓ Green density: ~ 51%
  - ✓ TE105 mode (sample in a maximum of E field)
  - ✓ Sintering conditions : T = 1230°C dwell time = 15 min



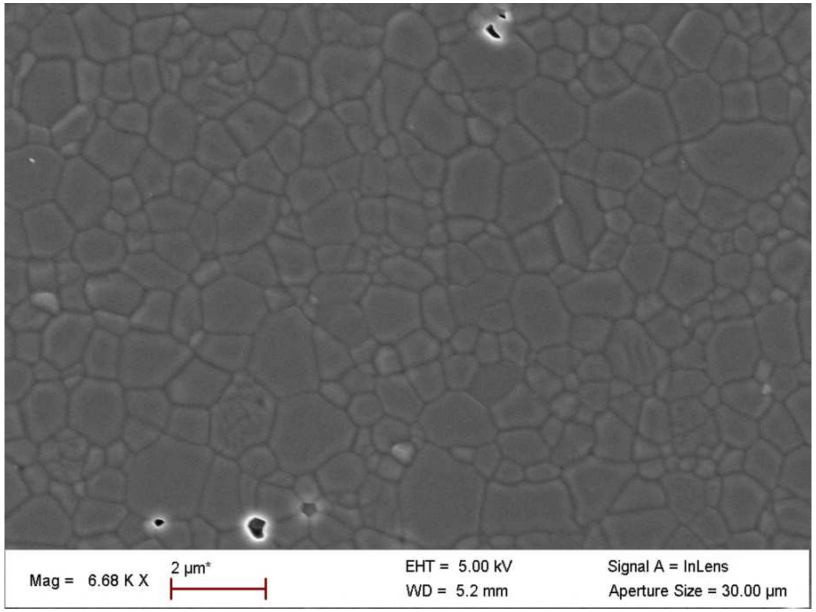
- ✓ P = 400 W to set up the heating, debinding, to reach 350° C
- ✓ P = 800 W to reach the sintering temperature in 30 minutes
- ✓ Cut-off of the microwave at the end of the dwell time

➡ Thermal cycles are still short ~ 2h

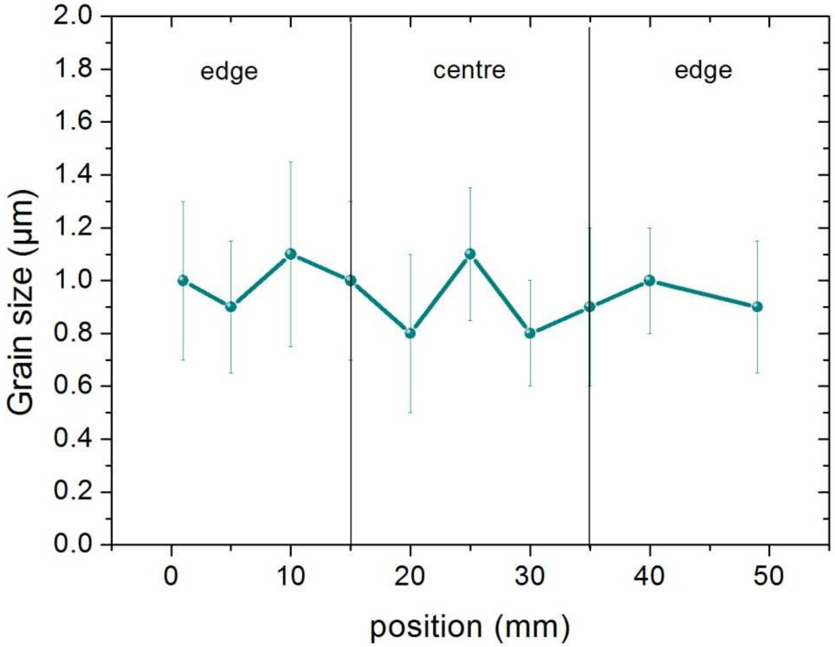
Microwave sintering – Scaling up

- **Microstructural characterizations:**

  - ✓ Relative density (Archimedes' method): 95.6 ± 0.6 %
  - ✓ Grain size (intercepts method on SEM micrographs): 0,9 ± 0.1 µm



Microstructure of a sample sintered at 1230°C during 15 minutes



Dense samples with controlled grain growth

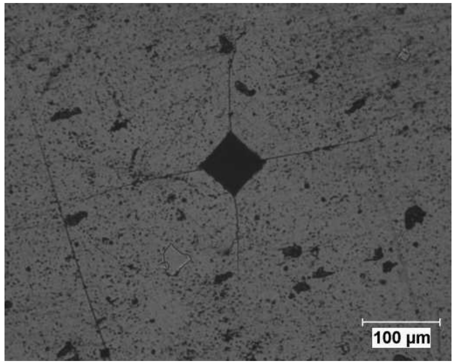
Microwave sintering – Scaling up

➢ **Mechanical characterizations:**

✓ Young's modulus (nanoindentation): 132.3 ± 1.5 GPa

✓ Hardness (Vickers microindentation): 6.0 ± 0.2 GPa

✓ Fracture toughness (K_1C): 1.00 ± 0.02 $MPa.m^{1/2}$



☺ Functional properties equivalent to those reported in the literature

☺ Good hardness values because of the small grain size

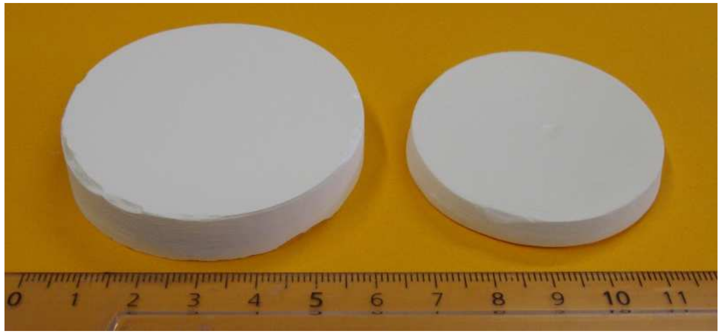
😐 A slightly higher density could improve the mechanical properties

Optimisation of the shaping could permit to improve the mechanical properties

Microwave sintering – Scaling up

➢ **Shaping optimization:**

- ✓ Slip casting shaping
- ✓ Green density: ~ 60 %
- ✓ Same thermal cycle as previously



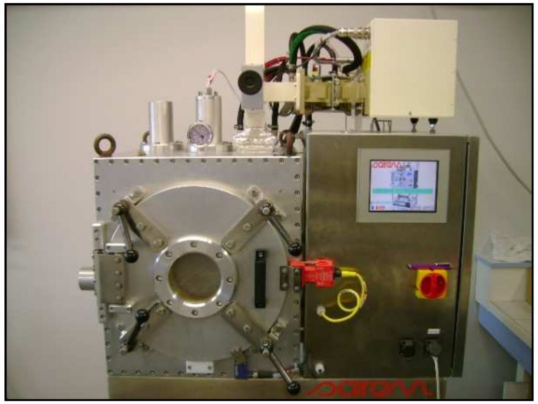
➢ **Samples characterizations:**

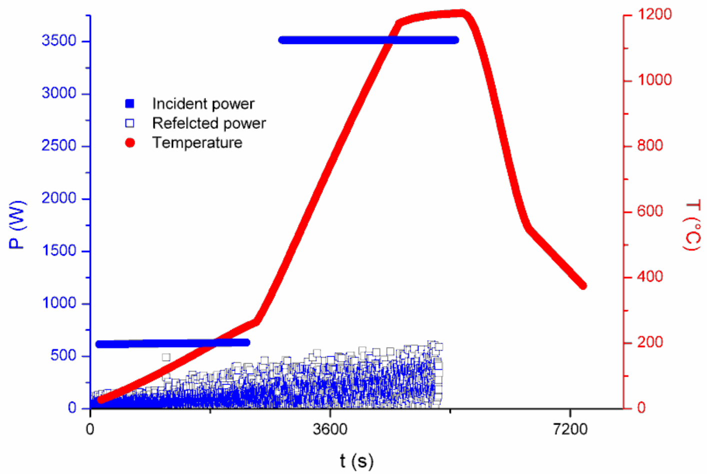
	Slip casting	Uniaxial pressing
Grain size	0.9 ± 0.1 µm	0.9 ± 0.1 µm
Density	99.1 ± 0.5 %	95.6 ± 0.6 %
Young's modulus	139.8 ± 2.4 GPa	132.3 ± 1.5 GPa
Hardness	7.0 ± 0.3 GPa	6.0 ± 0.2 GPa
Fracture toughness (K_1C)	1.04 ± 0.03 MPa.$m^{1/2}$	1.00 ± 0.02 MPa.$m^{1/2}$

Higher mechanical properties due to the shaping process optimization

Microwave sintering – Scaling up

- **A step forward:**
  - To densified larger sized samples: microwave multimode cavity at 2.45 GHz





✓Hybrid heating (SiC susceptors)

✓Cavity volume : ~ 96 L

✓90 mm diameter samples

✓3 sintering temperatures tested: 1210, 1230, 1250°C

✓2 dwell times tested : 15 and 60 minutes

✓P=600W to remove the organic parts (T<300°C)

✓P=3500W to reach the sintering temperature (~ 30 minutes)

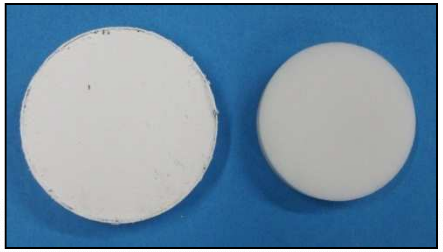
✓Stop of the microwave irradiation after the dwell time, cooling in ~ 30 minutes

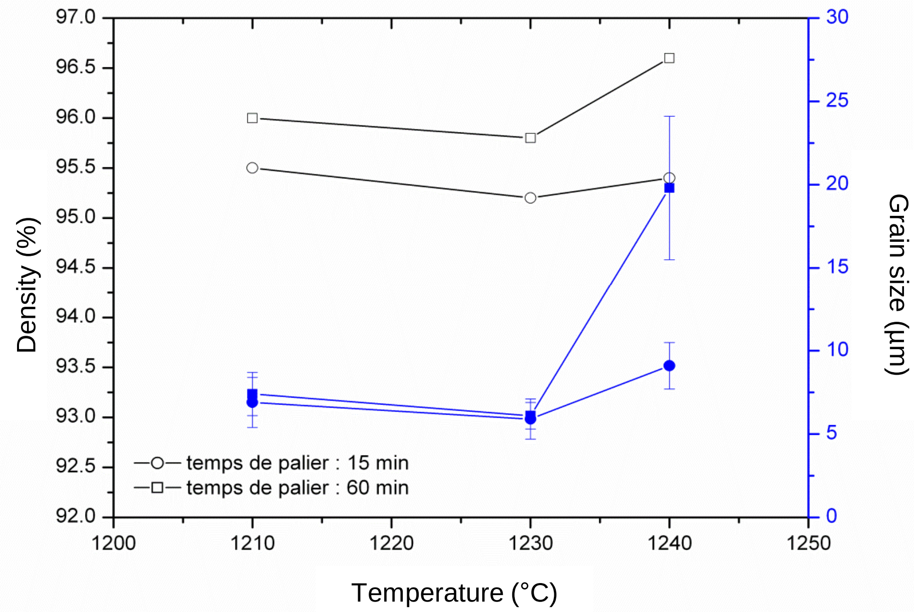
A. Leriche, E. Savary, A. Thuault, J-C. Hornez, M. Descamps, S. Marinel, « Comparison of conventional and microwaves sintering of bioceramics », in *Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials: A Collection of Papers Presented at the 38th International Conference on Advanced Ceramics and Composites January 27-31, 2014 Daytona Beach, Florida*, Published 02/10/2015, Editor John Wiley & Sons, Inc. pages 23-32, ISBN 9781119040354

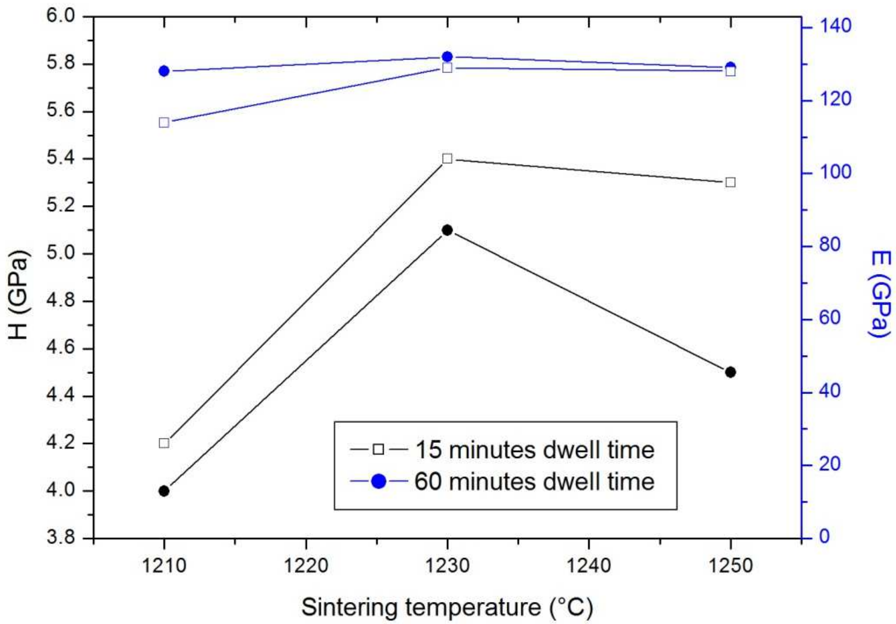
Microwave sintering – Scaling up

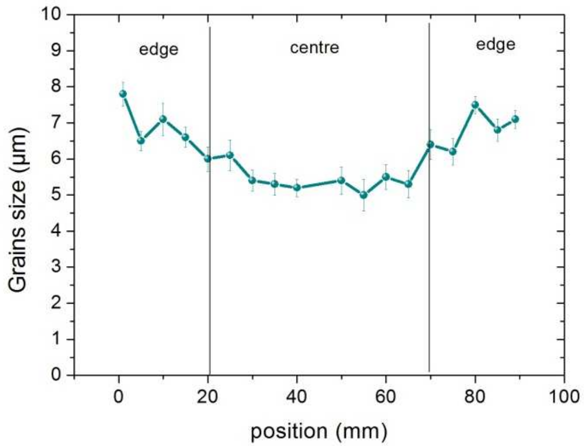
➢ **A step forward:**

➢ Samples characterizations:









Mainly indirect heating due to less intense electromagnetic fields

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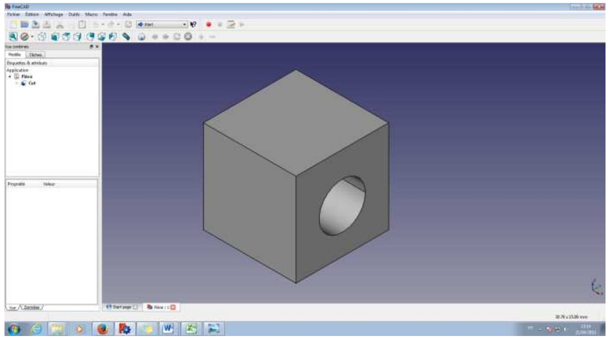
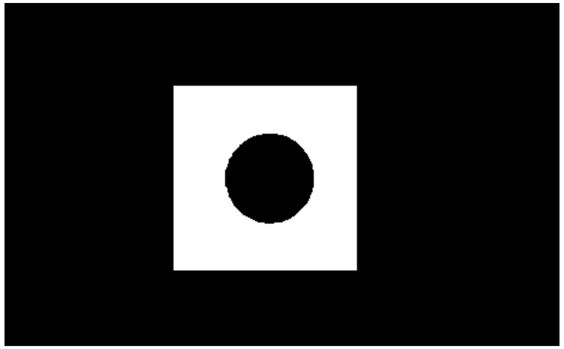
Microwave sintering of complex-shaped samples

- **Stereolithography:**

CAD raw piece design → Slicing → Mask projection





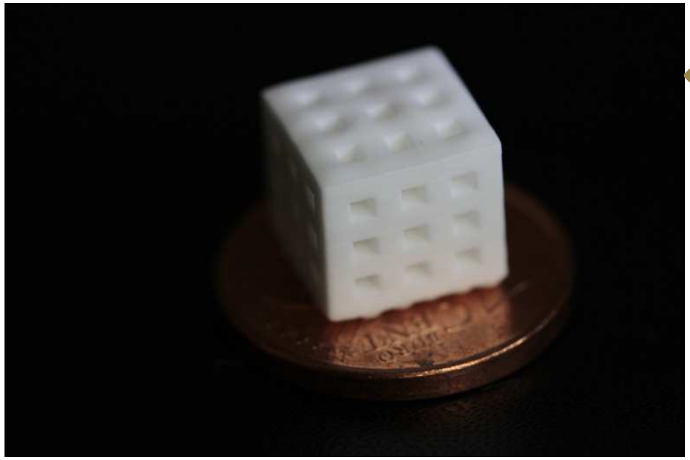
Suspension:
60% mass HA powder
40% mass resin

→ Resin polymerization → Green ceramic piece

8 mm

Microwave sintering of complex-shaped samples

- **Microwave sintering:**
  - ✓ Single-mode microwave cavity at 2.45 GHz
  - ✓ Direct heating



Conventional Sintering

Microwave sintering

Density : 98.3 %

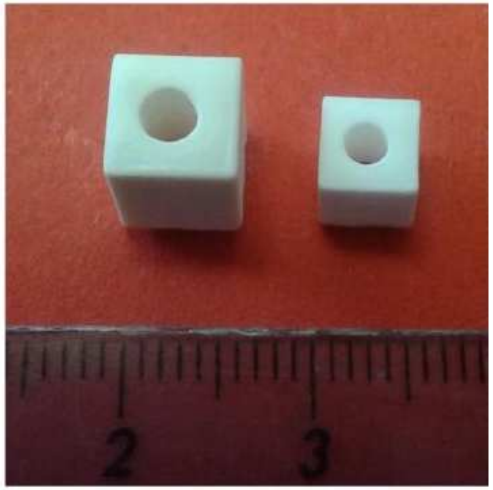
Cracks due to the debinding and delamination

Strong interaction between microwave and resin: thermal runaway

Optimization of the device and thermal cycle

Microwave sintering of complex-shaped samples

- **Microwave sintering:**
  - ✓ Single-mode microwave cavity at 2.45 GHz
  - ✓ Direct heating



2 steps

Debinding in conventional furnace: 5 hours at 400°C (1°C/min)

Sintering single MW: 15 min at 1250°C

Uncracked an dense parts

Density : 97 %

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Conclusions

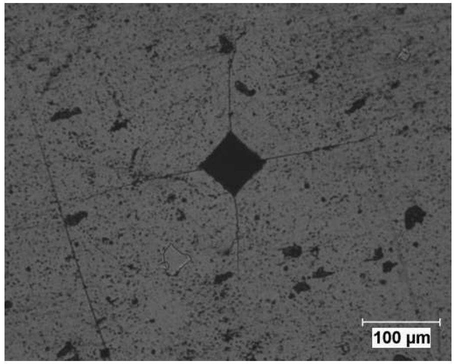
- ✓ Microwave process allows to get dense HA small samples in a few minutes
- ✓ Obtaining pellets with fine microstructures ⇒ Increase of Young's Modulus and hardness (structural applications)
- ✓ Scaling up: possibility to sinter bigger samples, whose dimensions are close to the ones of bones' substitutes (50 mm diameter and 13 mm thickness) with a 915MHz single mode cavity
- ✓ Microwave could permit the sintering of complex-shaped piece for short thermal treatment times

Optimization of the shaping parameters and thermal cycle

Microstructural, mechanical and biological characterizations of the complex-shape sintered samples


Thank you for your attention

K1C



$$K_{IC} = \alpha \left(\frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}}$$

With α=0.016, P the applied load and c the cracks length