# FROM WET SPONGES TO OPTOCERAMICS

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*T02: High Temperature Processes and Advanced Sintering*

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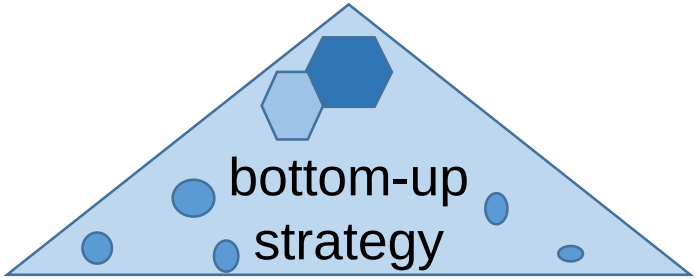
# Topics of discussion

- Context and objective
- Growing and modifying the “sponges”
- Consolidation – spark plasma sintering
- Characterization of ceramics
- Conclusions and perspectives

# Motivation

To control the grain size of ceramics on our way to self-healing nano-grained transparent ceramics

EUROfusion

MILITARY

Applications as optical windows in nuclear (fusion) power plants, transparent armors, nose cones for heat seeking missiles (YAG), space engineering, medicine …

# Growing alumina monoliths*

UPA

99% porosity of the monolith makes it easy to dope by gas or liquid

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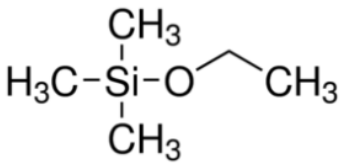
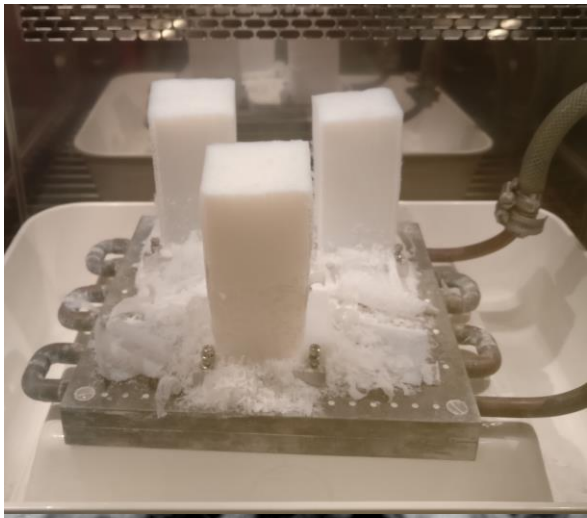


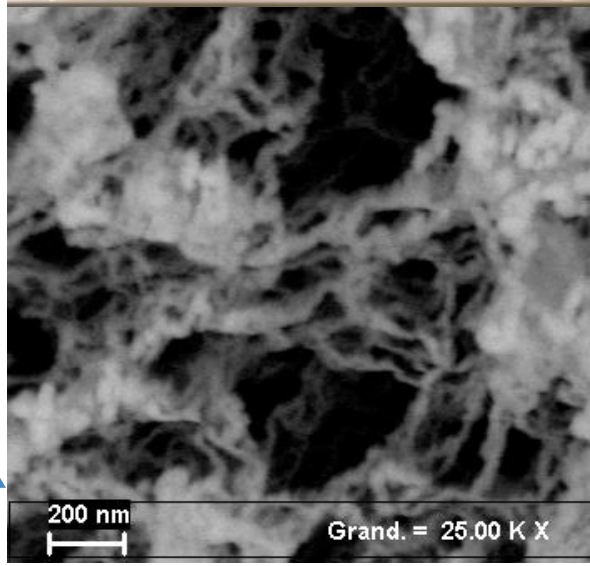

TMES

1 cm/h = 0,5 g (43 m% water)

80% humidity, 25°C, cooling plate 23°C

Al plate + Ag-Hg amalgam -> Al(OH)3 monolith

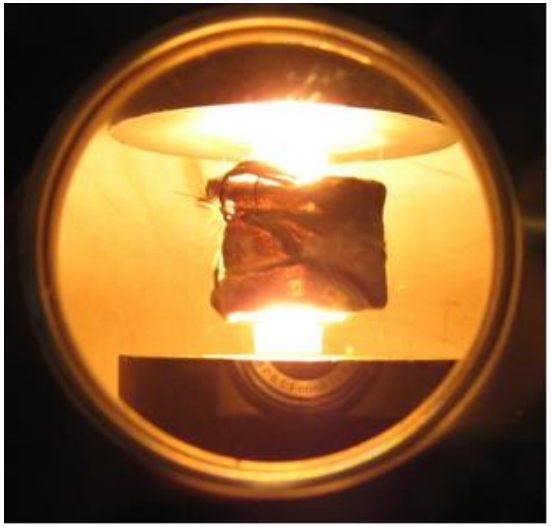





*Vignes, J. L. *et al. J. Mater. Sci.* **43** (2008)

**Khatim, O. *et al. Acta Materialia* **71** (2014)

# Spark plasma sintering



*Dr. Sinter LAB Series SPS-515S*

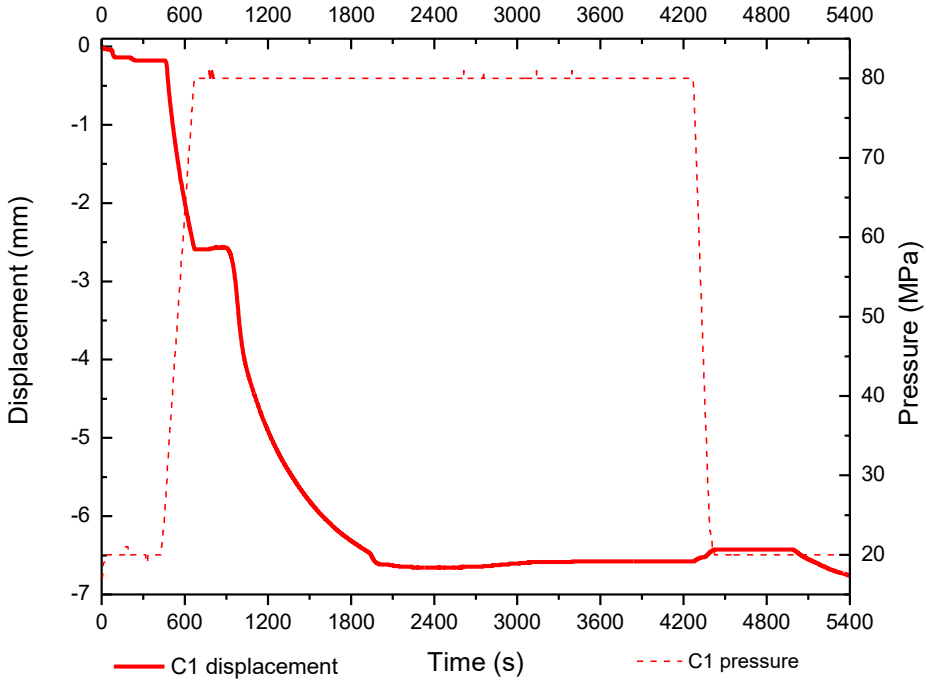
- Vacuum or argon
- Conductive or not
- 3.5 – 50 kN
- 20 – 2000°C
- Sample displacement

- Joule effect

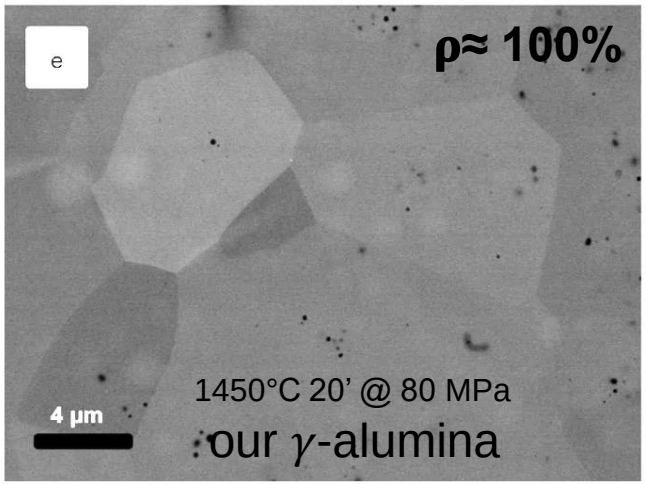
=> fast process, grain size control

- High temp + pressure

=> dense materials

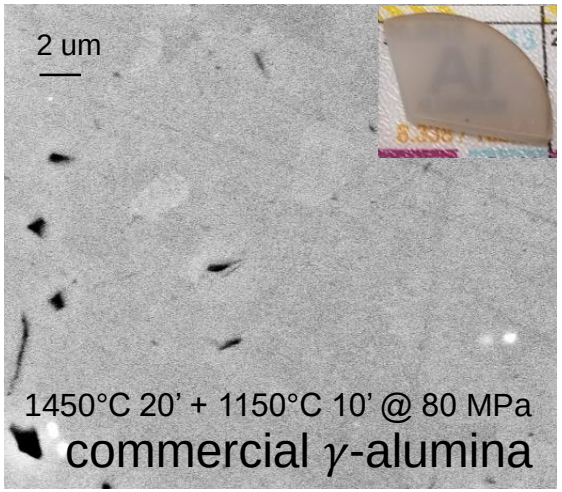


# Alumina ceramics




From previous work in LSPM*

Powder crystallite size: 10 nm



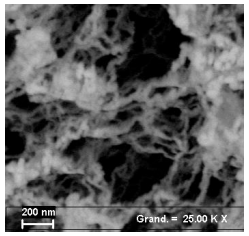

**ρ=97,8%**

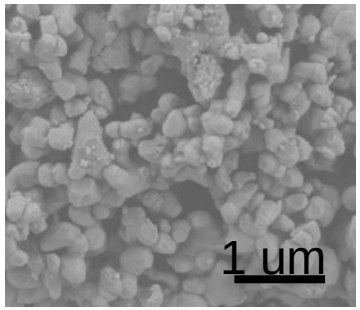
Powder crystallite size: 50 nm

Although our $\gamma$-alumina powder crystallite size is smaller than the commercial powder’s, the sintered ceramic has bigger grain size

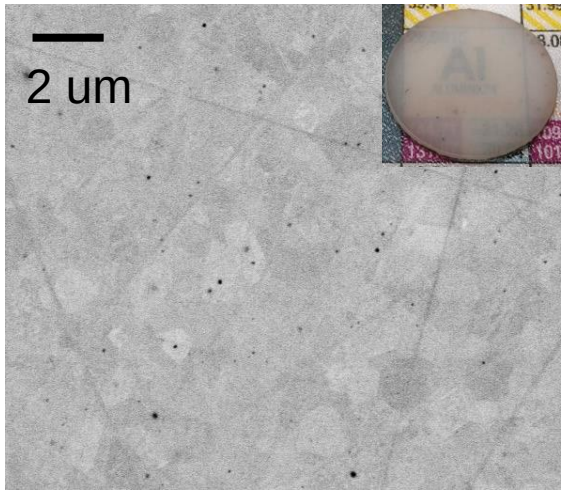
*Tõldsepp, E. *et al. Ceram. Int.* **42** (2016)

# Effect of green body preparation



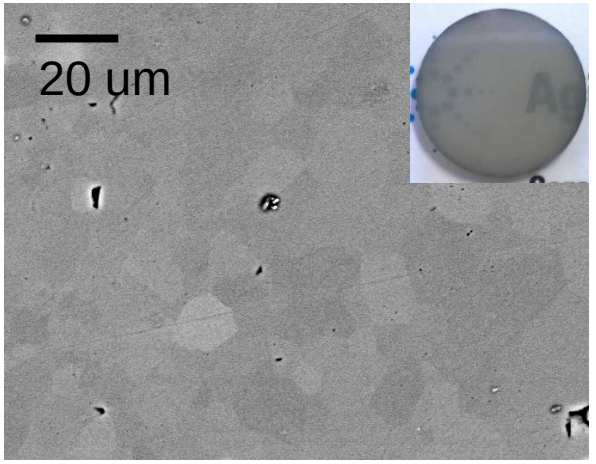




SPS cycle: 3’ at 1450°C, **300 MPa**




our alumina, no pre-pressing

**ρ=96,6%**




our alumina, pre-pressing with 4t

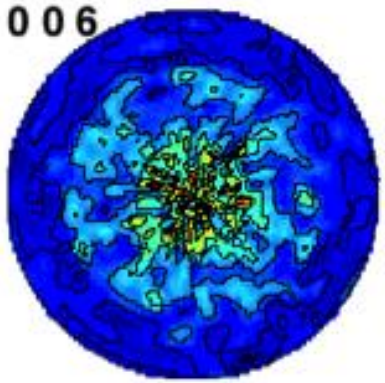
**ρ=98,6%**

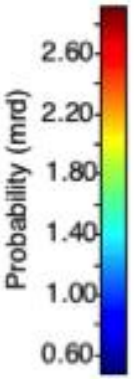
Pre-pressing with 4t for better densification leads to a tenfold increase in grain size

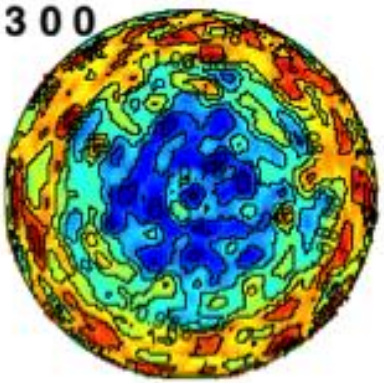
# XRD texture study

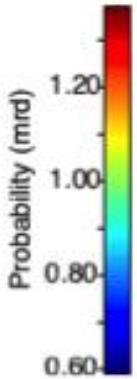
5° ×5° grid with **0°≤ χ ≤55°** and **0°≤ ϕ ≤ 355°**

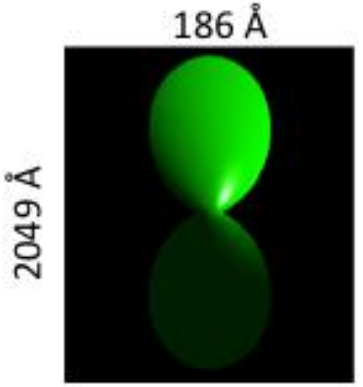
As received from SPS



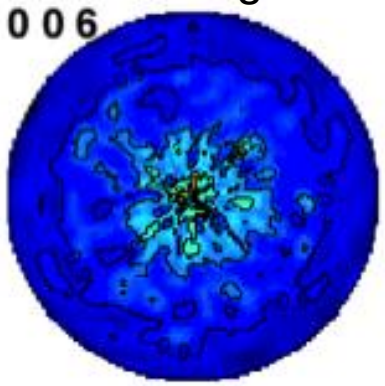



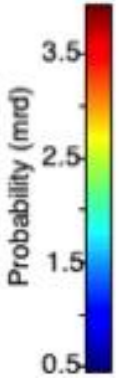



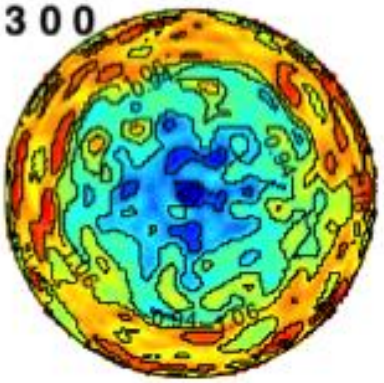



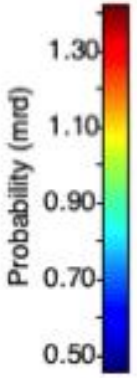



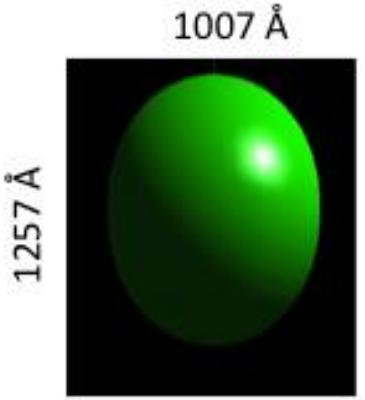

Post-annealing at 1000°C



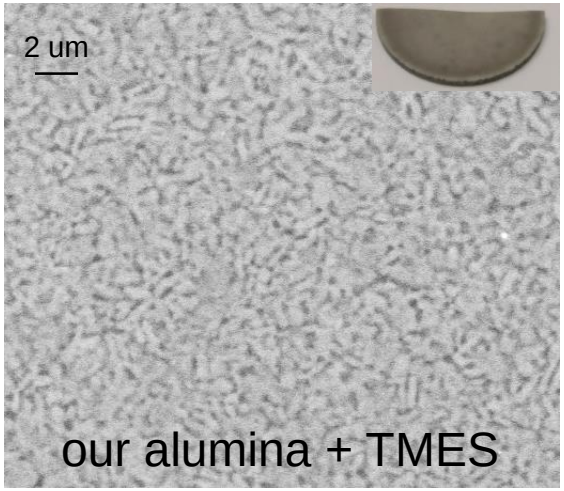



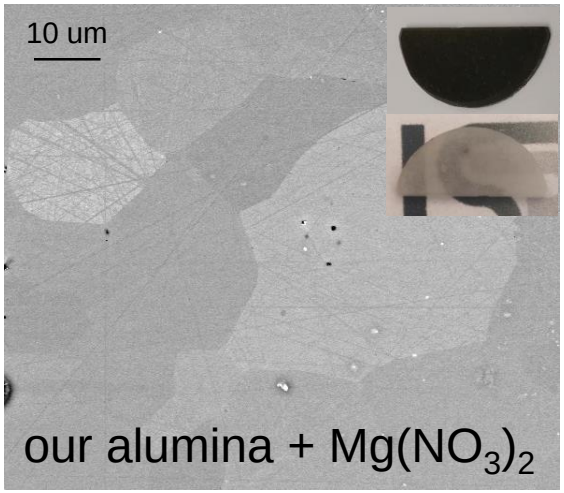

- Mild fibrous texture aligned with SPS pressure-axis
- Crystallite shape “spherifizes” during annealing

# Mullite, spinel – reactive sintering

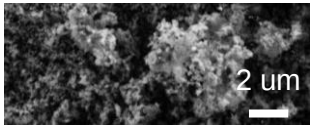
SPS cycle: 20’ at 1450°C + 10’ at 1150°C, 100 MPa
Our alumina doped with TMES in gas phase OR in liquid phase with $Mg(NO_3)_2 \cdot 6H_2O$

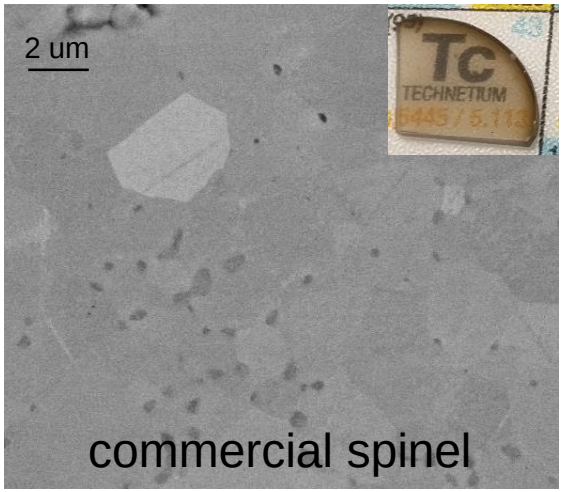



**ρ=3,54 g/cm³**

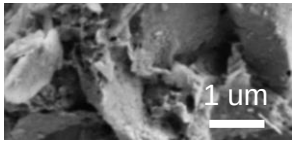



**ρ=97,3%**



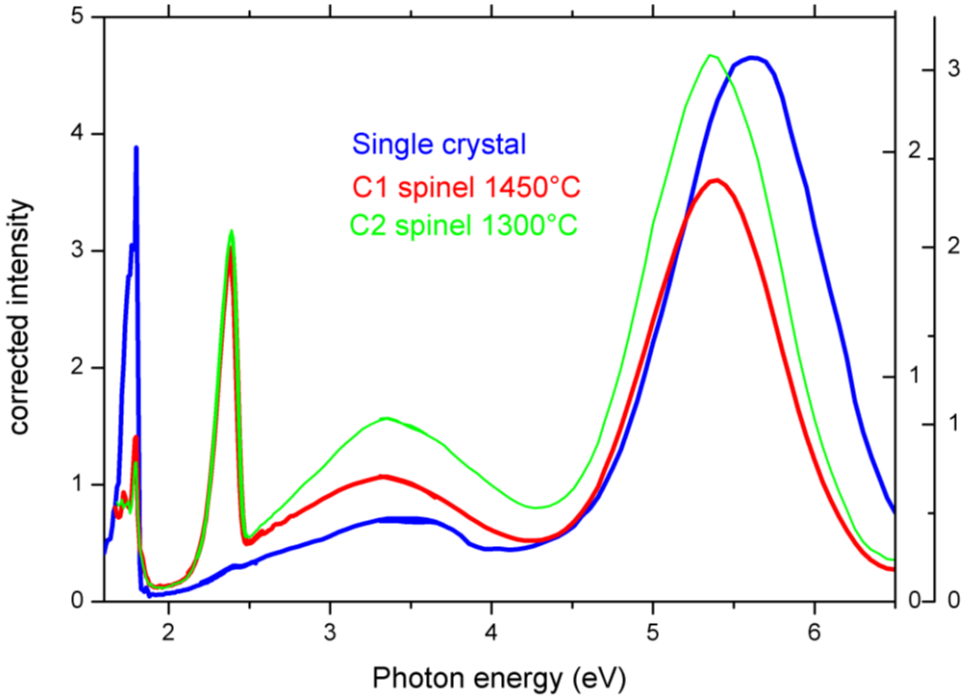

**ρ=96,5%**




- Stoichiometric $Al_2O_3$:MgO ratio gives monophasic spinel ceramic
- Average grain size of spinel produced by reactive sintering is about 5 times larger than that of spinel produced from commercial powder via the same cycle.

# Cathodoluminescence study

$MgAl_2O_4$ ceramics compared to a single crystal*




- **1.8 eV** -> the R-lines of **$Cr^{3+}$** impurity**
- **2.4 eV** -> tetrahedral **$Mn^{2+}$** impurity**
- **2.4 – 4 eV** -> **F**, **$F^+$** centres + complex intrinsic defects***
- **4.5-6.5 eV** -> **"anti-site" defects****

*Lushchik *et al J. Lum.* **102-103** (2003)
**Gritsyna *et al. Nucl. Instr. and Meth. in Phys. Res. B* **250** (2006)
***Sawai, Uchino *J. Appl. Phys.* **103523** (2012)

# Conclusions

- Dense ceramics with various grain sizes and transparencies, starting from UPA
- Starting from a phase with smaller crystallite size does not insure a smaller-grained ceramic
- Pre-pressing leads to a tenfold increase in grain size
- The spinel samples need annealing in air to get rid of coloration
- Slight fiber-like texture aligned with the pressure axis of SPS, crystallites more spherical after annealing
- High inversion level for spinels and common impurities

# Thank you for your attention!

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