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Densification of dense nano crystalline zinc oxide under electric field

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Mitglied der Helmholtz-Gemeinschaft

Deutsche Forschungsgemeinschaft DFG

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Priority Programme SPP 1959

Manipulation of matter controlled by electric and magnetic fields: Towards novel synthesis and processing routes of inorganic materials

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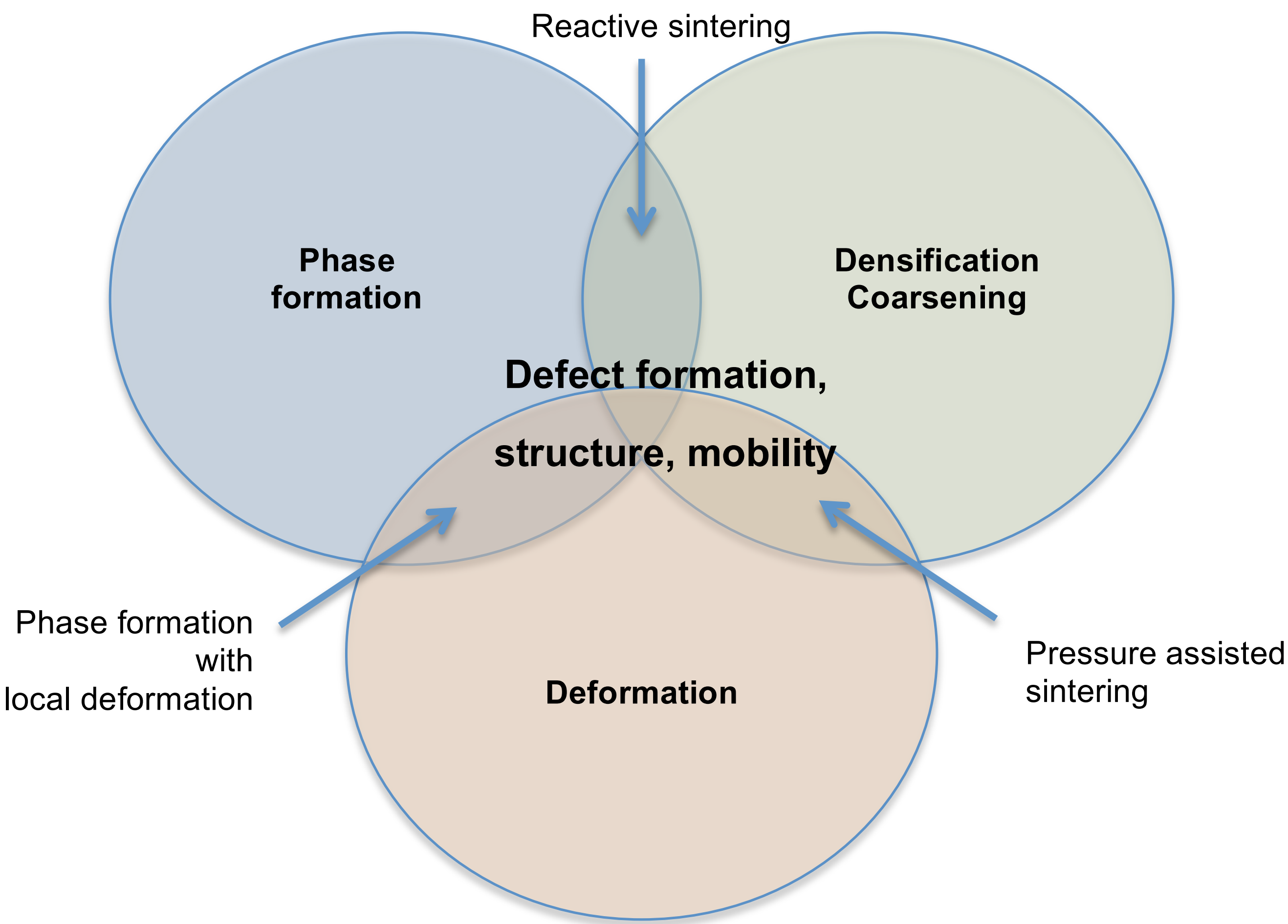
* coordinator

Duration: 2 x 3 years
Start: Summer 2016
Total funding: ca. 11.000.000 €

DFG Priority Programme



What are the interplays between electric / magnetic fields and defect formation, structure and mobility?

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Densification of nanocrystalline zinc oxide under electric field

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Institute of Energy and Climate Research
Materials Synthesis and Processing (IEK-1)

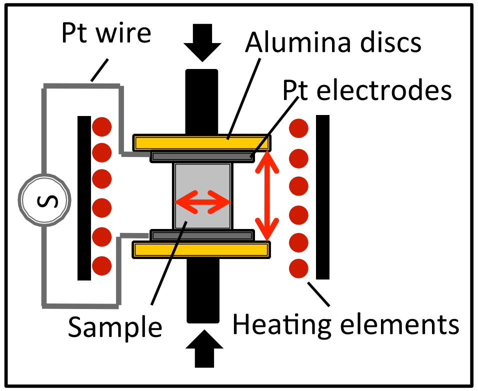
Motivation

To obtain dense ceramics with nano-grain size → improved properties

- Understanding of mechanisms involved in coarsening is critical to the retention of nanocrystallinity
- Powder quality, storage conditions, processing and sintering process all play a role

- Doping, modification of chemical composition and properties
- Promote the densification mechanisms instead of grain growth
  - High mechanical pressure (but reduced sample size)
  - Assistance by electric field/current

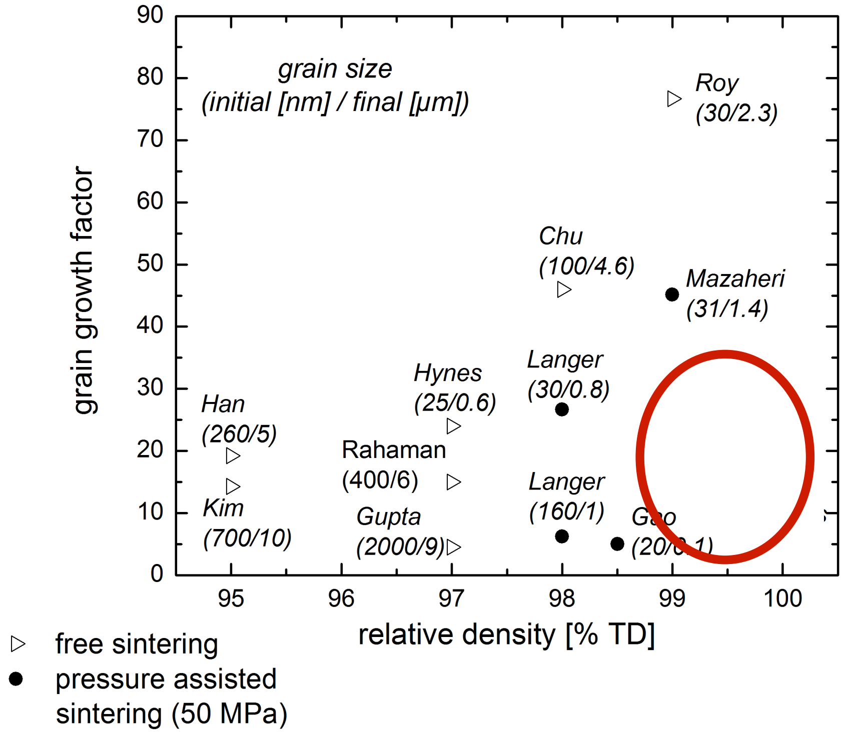
FAST/SPS



Sinter-forging (flash sintering)

Motivation

ZnO



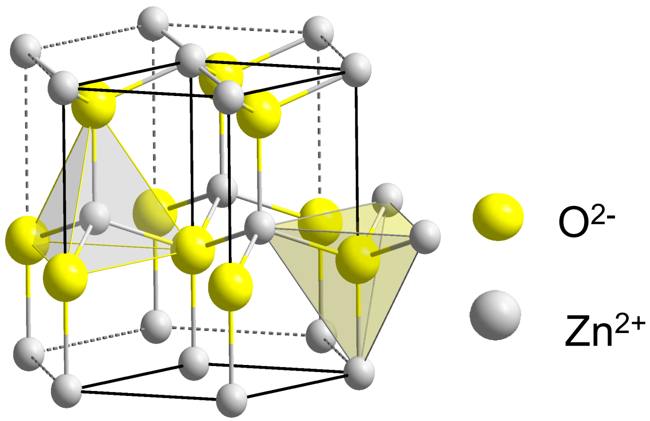
- Full densification with final nanosized grains is very challenging
- Mechanical pressure decreases grain size for a given sintering density
- Reduction of initial particle size does not necessarily result into smaller grain size

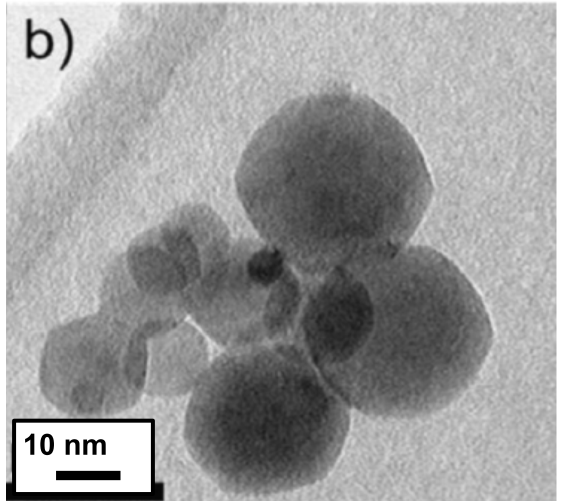
Objective:

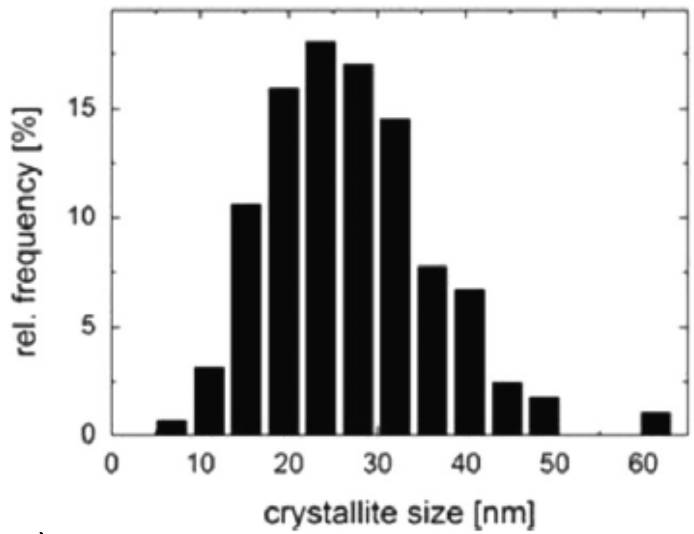
To find a new strategy to fully densify bulk ceramics with nano-grain size

Electric field and water will be used to promote sintering of ZnO ceramic

ZnO powder



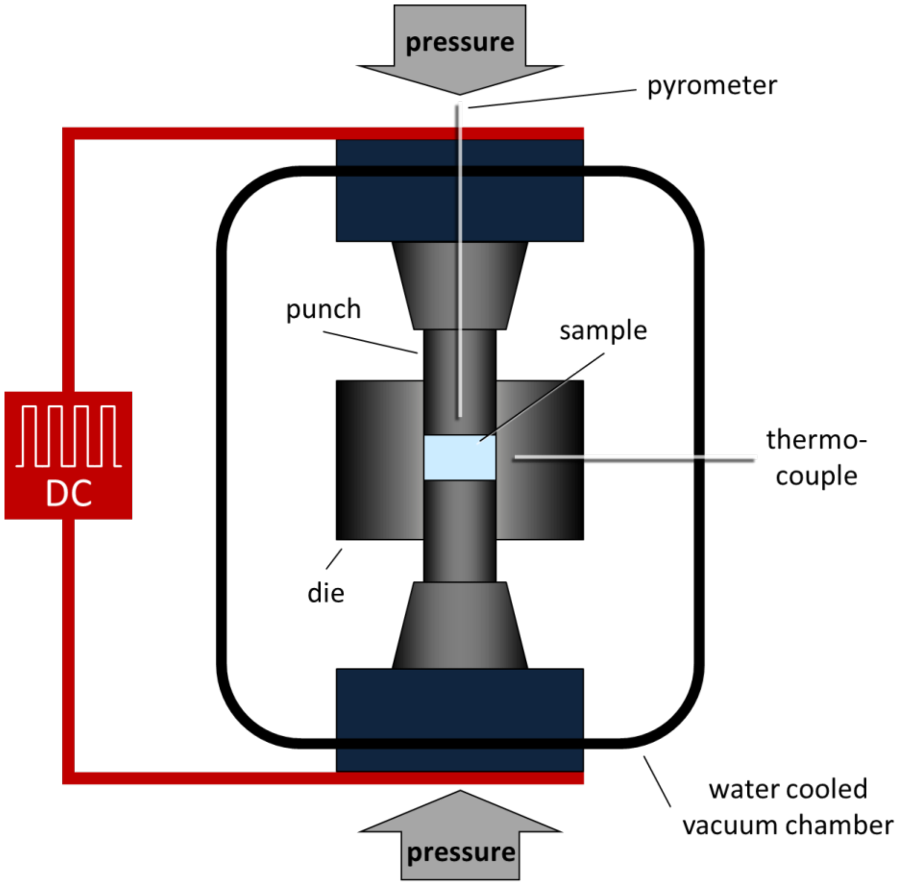




NG20; purity >99.99 wt.%

- Polyhedral, nearly spherical shape
- Same aspect ratio
- TEM and XRD in agreement
- Storage in environmental chamber (humid /dry conditions)

FAST/SPS of ZnO



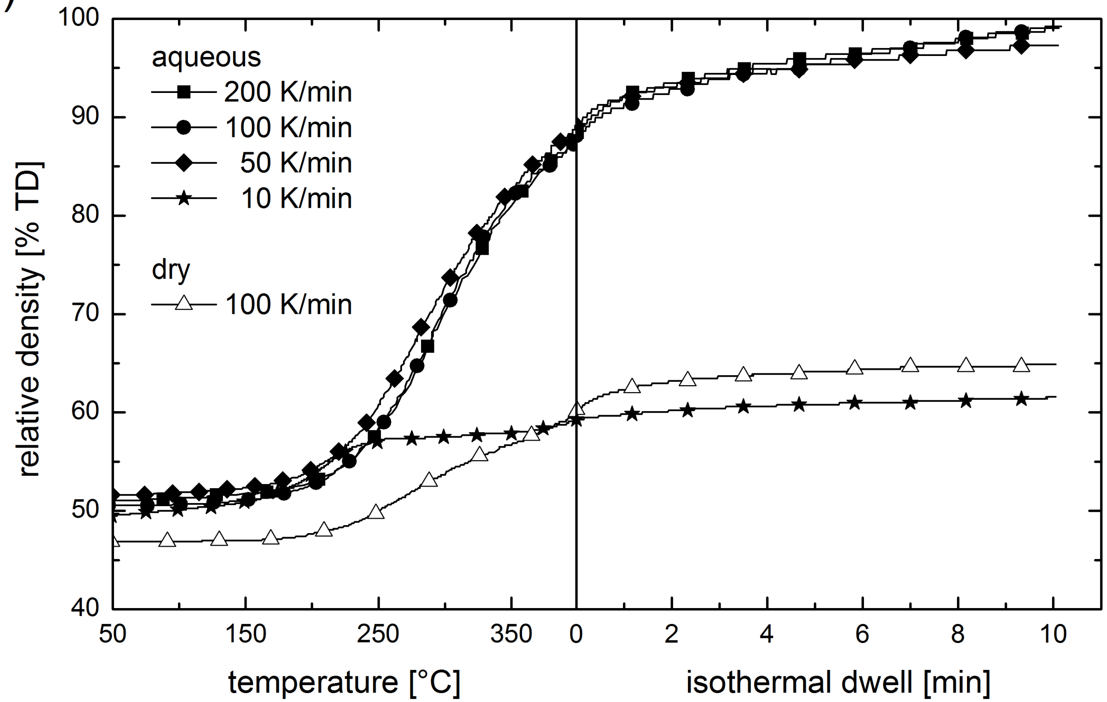
- DC pulsed current process
- External mechanical pressure
- Joule heating effect
- High heating rates and short dwell time
- Temperature control by pyrometer

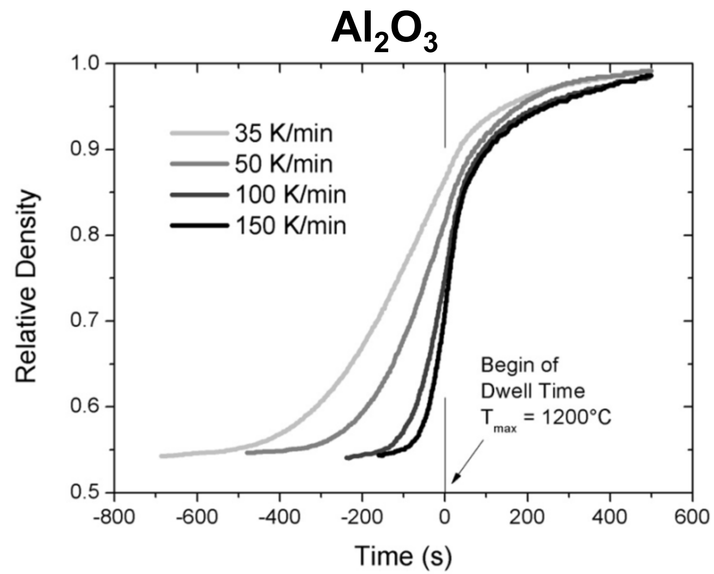
sintering conditions

- 50 MPa uniaxial pressure
- Maximal temperature of 400 °C or 800 °C
- Heating rates of 10, 50, 100 or 200 K/min
- 10 min isothermal sintering time

FAST/SPS: Effect of heating rate

a)

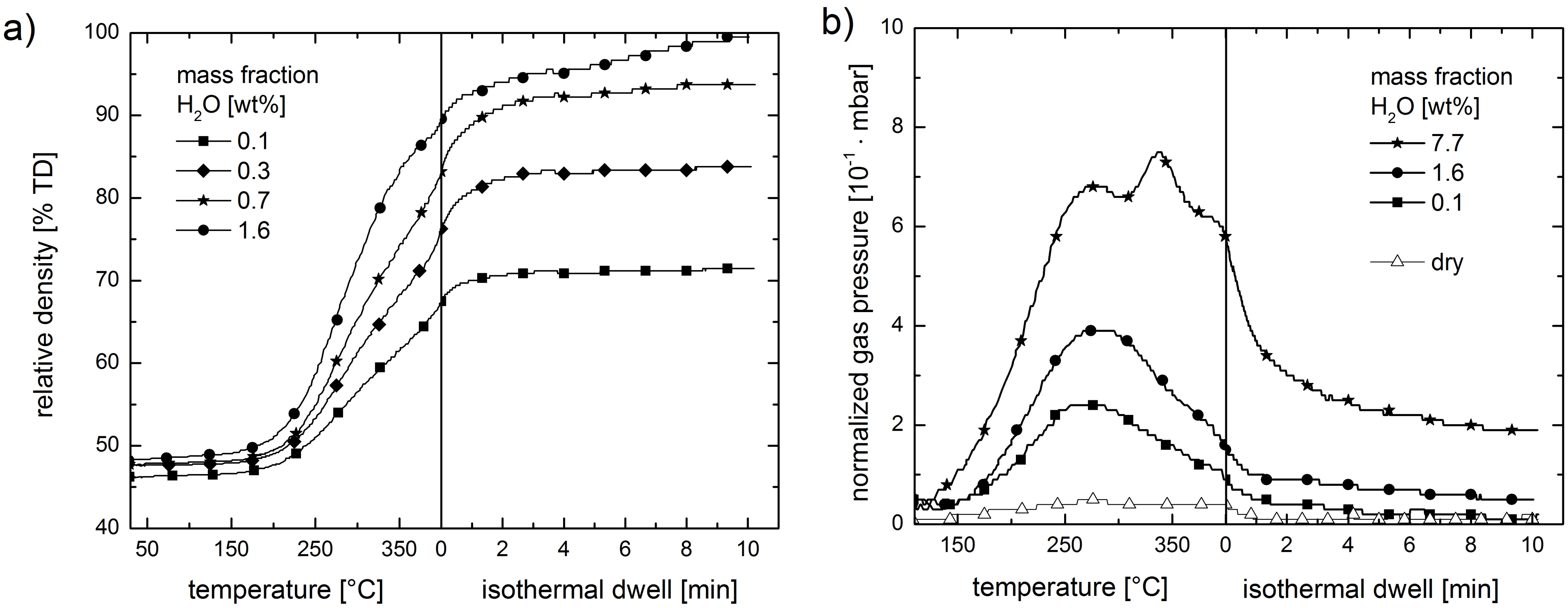




Guillon and Langer, *J. Mat. Sci.*, 45 (2010)

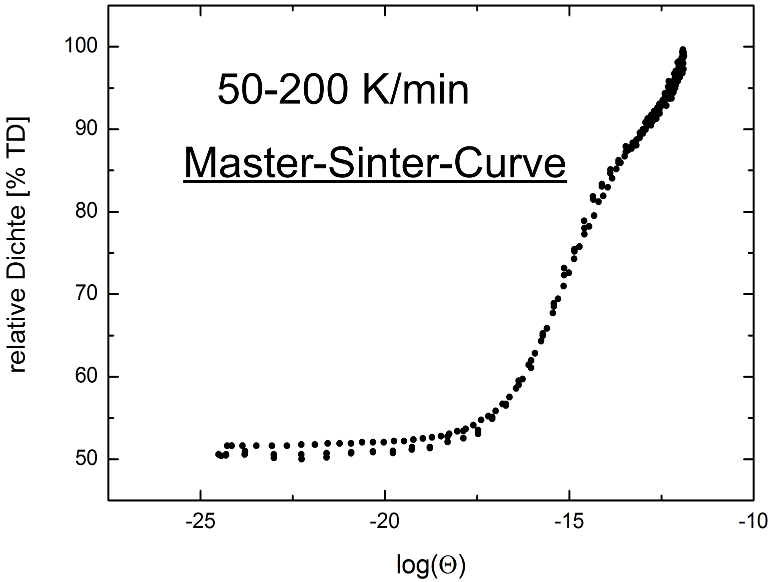
- Full densification takes place only for high heating rates in presence of bound water
- Therefore, kinetics of water desorption may play a significant role and limit the temperature-time window in which crystal interfaces are modified.

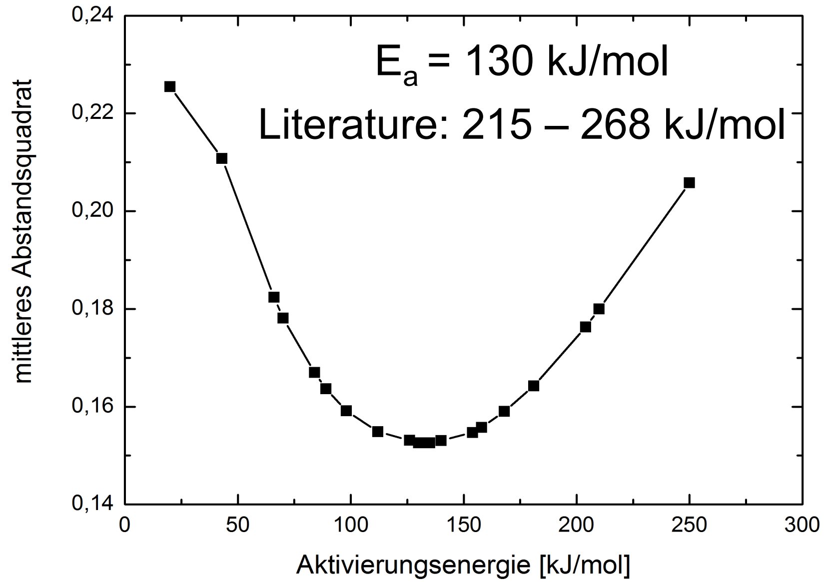
FAST/SPS: Effect of water content



- Increasing amount of water enhances densification
- Loss of water can be tracked by measuring partial pressure in FAST/SPS chamber

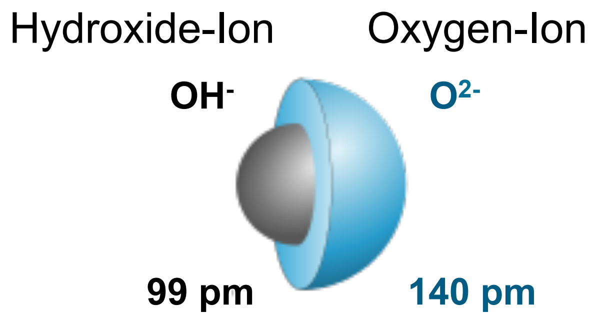
FAST/SPS: Densification mechanism





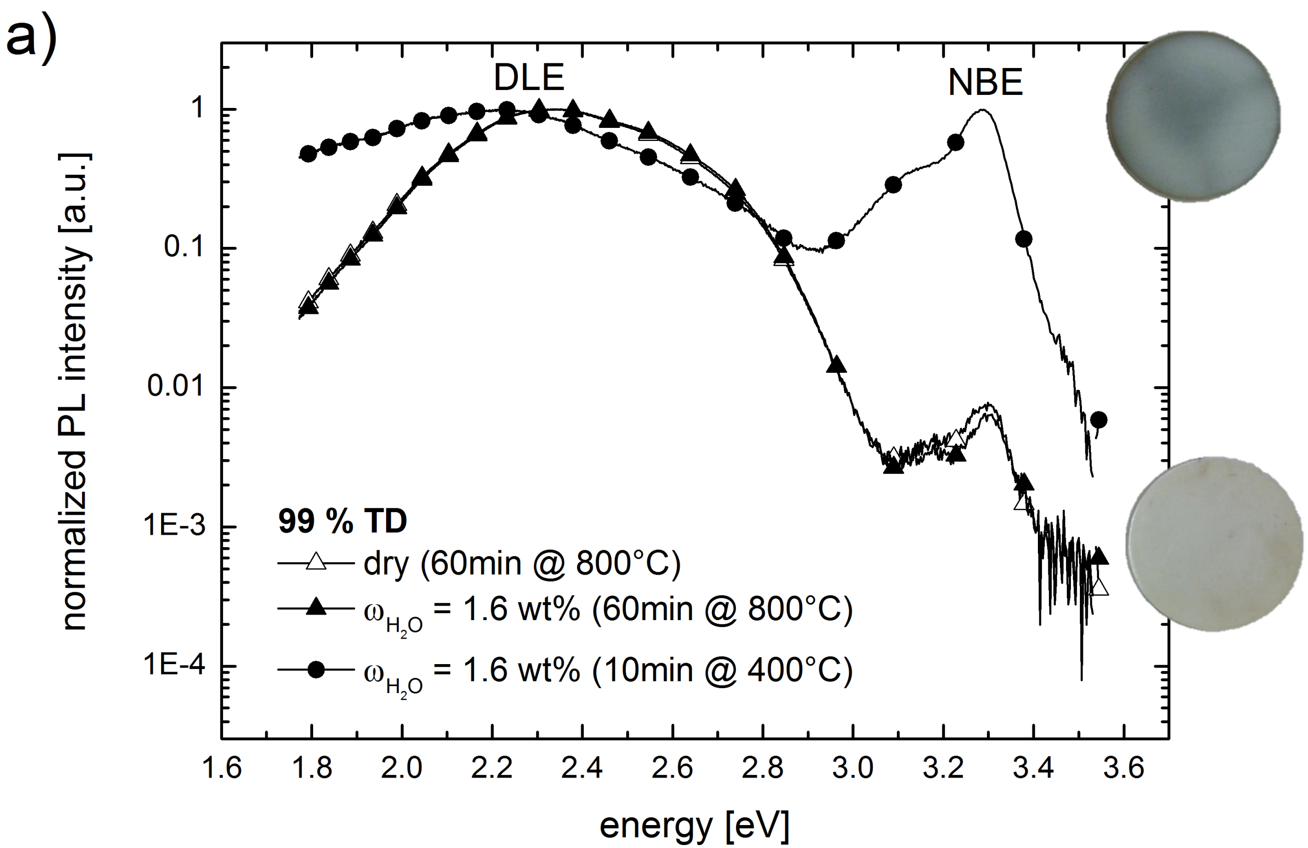
Assumption: Limitation of mass transport by diffusion of O^{2-} along grain boundaries

Hypothesis: Decrease of E_a because of easier OH^- diffusion (lower valence and ionic radius)



Defect analysis

Photoluminescence at low temperature (5 K)



Hydrogen-related defects are indicated in the Near Band Edge domain

Chemical analysis

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GD-OES

	H [at%]	Zn [at%]	O [at%]
humid (T_{max} = 400 °C/ *w* = 1,6 %)	0,5 ± 0,3	51,2 ± 0,1	48,3 ± 0,1
dry	---*	50,8 ± 0,1	49,2 ± 0,1

* Detection limit ~ 50 ppm

⇨ **Incorporation of hydrogen in humid samples**

XPS

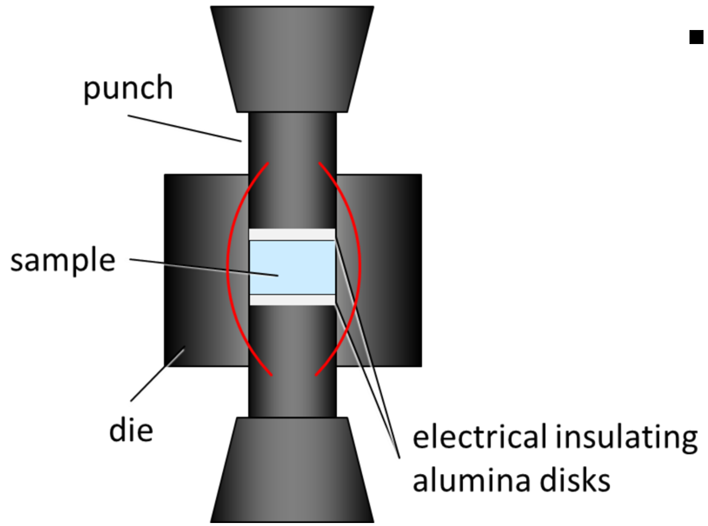
	Zn [at%]	O [at%]	C [at%]
humid *(T_{max} = 400 °C/ w = 1,6 %)*	59,9	40,1	---
dry	53,8	41,0	4,3

Measurement of a fresh fracture surface in high vacuum

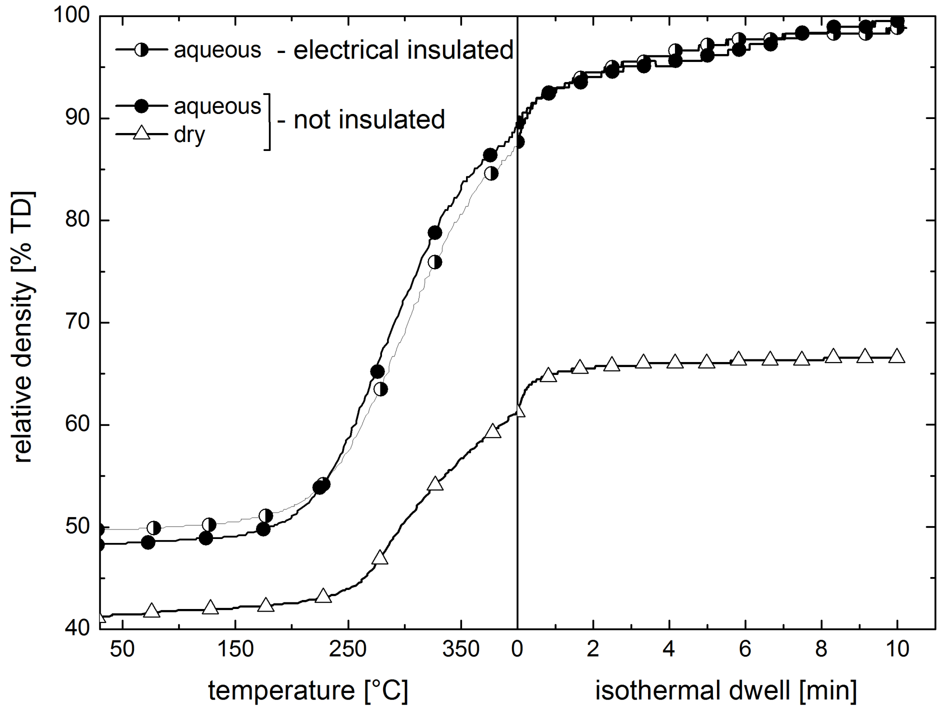
⇨ **No presence of carbonates in humid samples which normally hinder densification**

FAST/SPS sintering: Field effect?

Does the electrical current play a role?

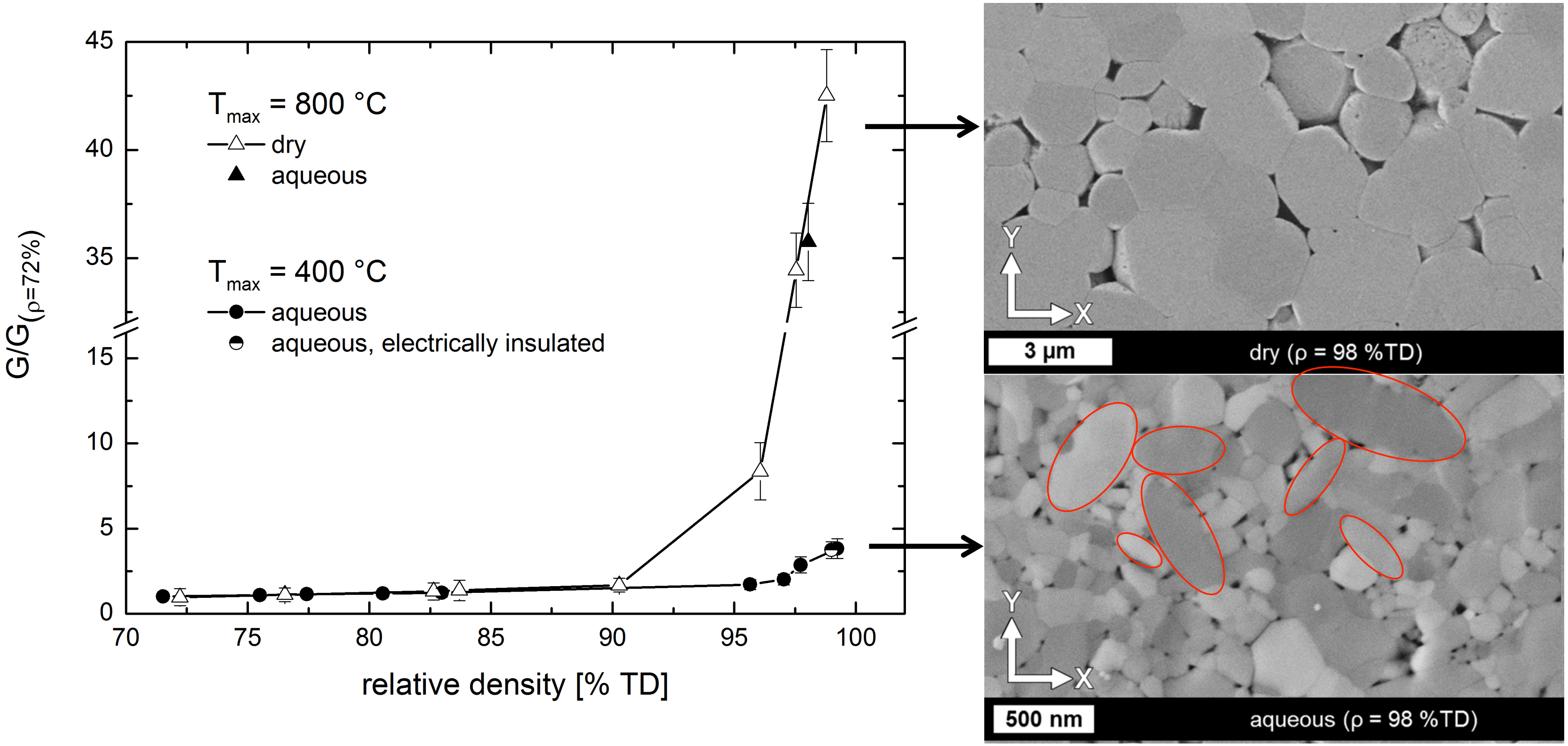


- Alumina disks between punch and powder prevent the flow of electrical current through ZnO sample



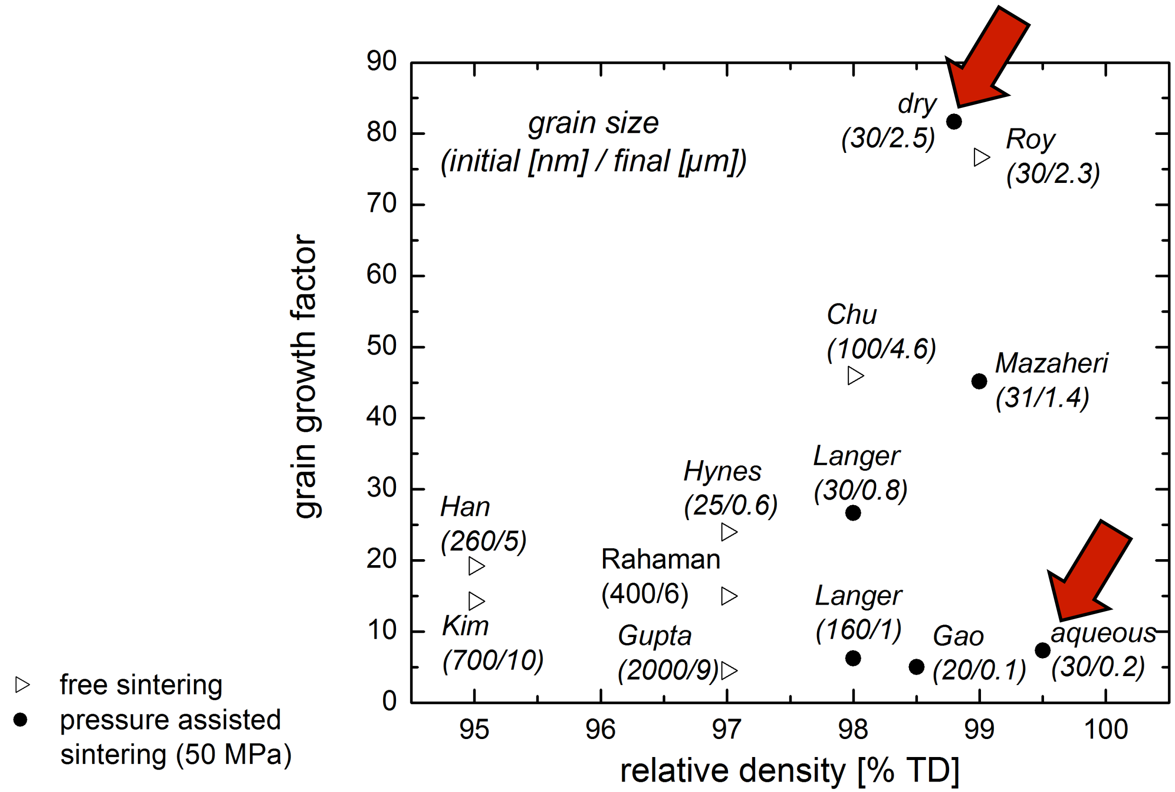
- Same sintering behavior for aqueous and dry conditions
- No effect of current

Microstructure analysis



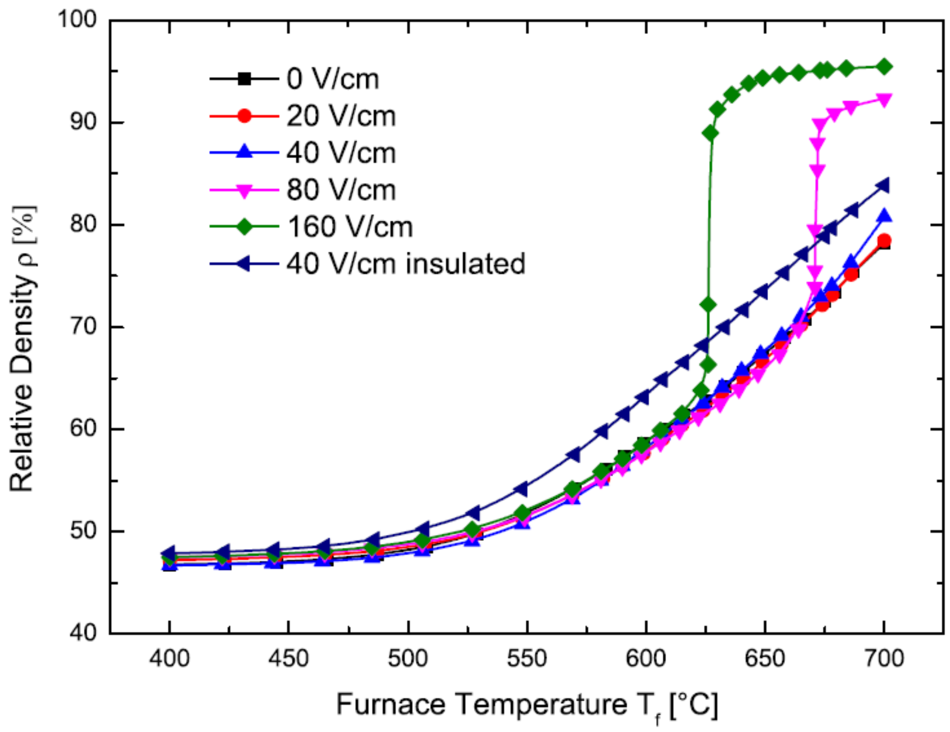
- Sintered dry powder shows more than one order of magnitude larger grain size than humid powder, as high temperature is required for densification
- Anisotropic grain morphology is observed for sintered humid ZnO.

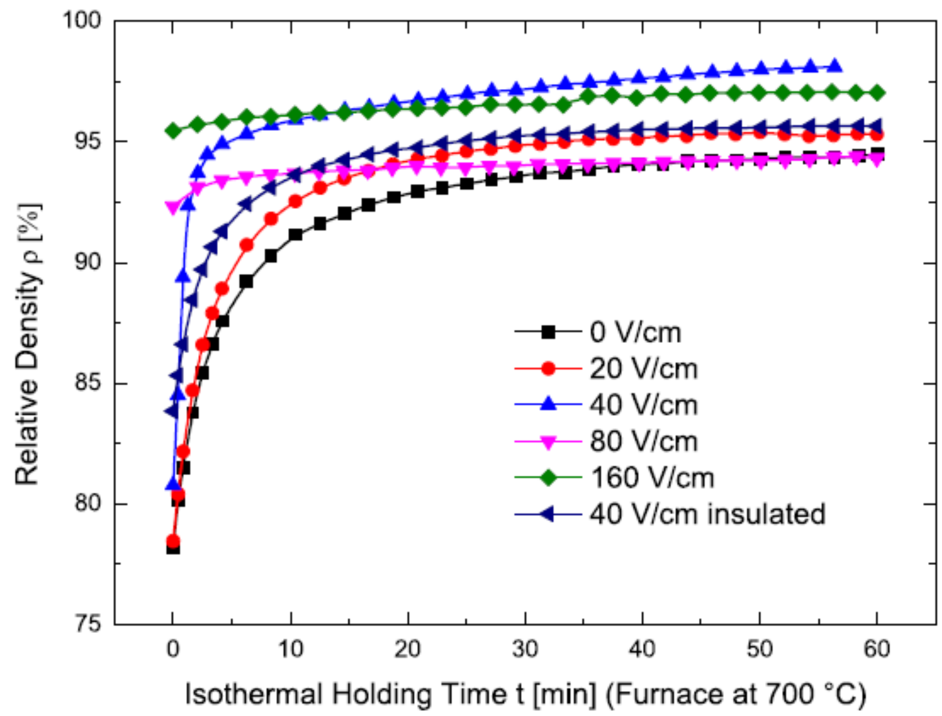
Microstructure analysis



- Full densification of ZnO with nanosized grains is possible through the addition of water and high heating rates
- The process is rapid and requires only low temperature

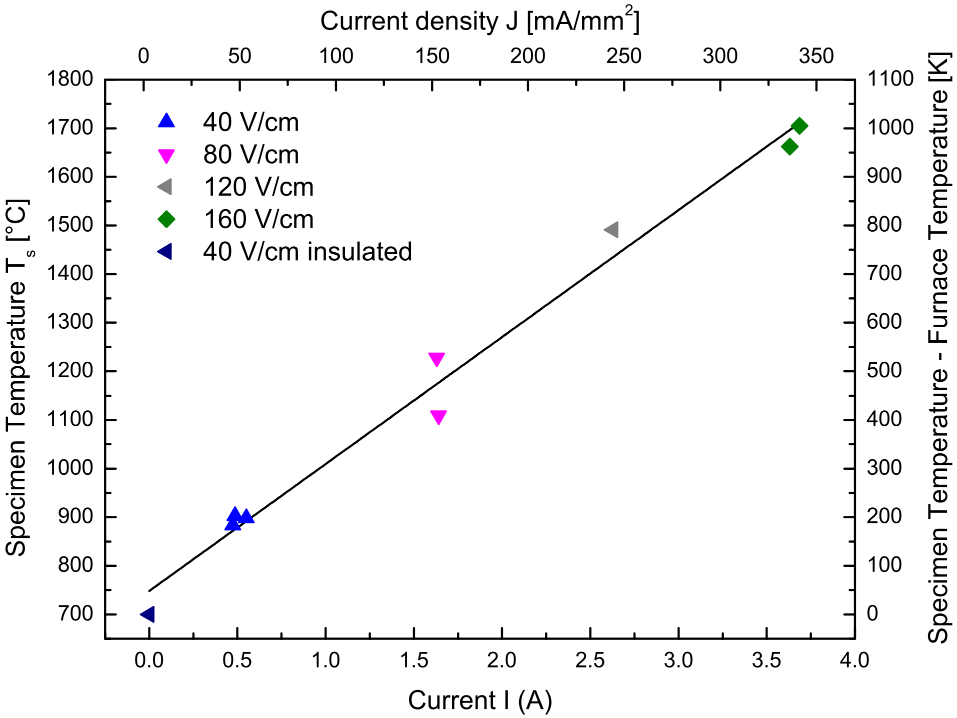
Electric field assisted sintering of ZnO

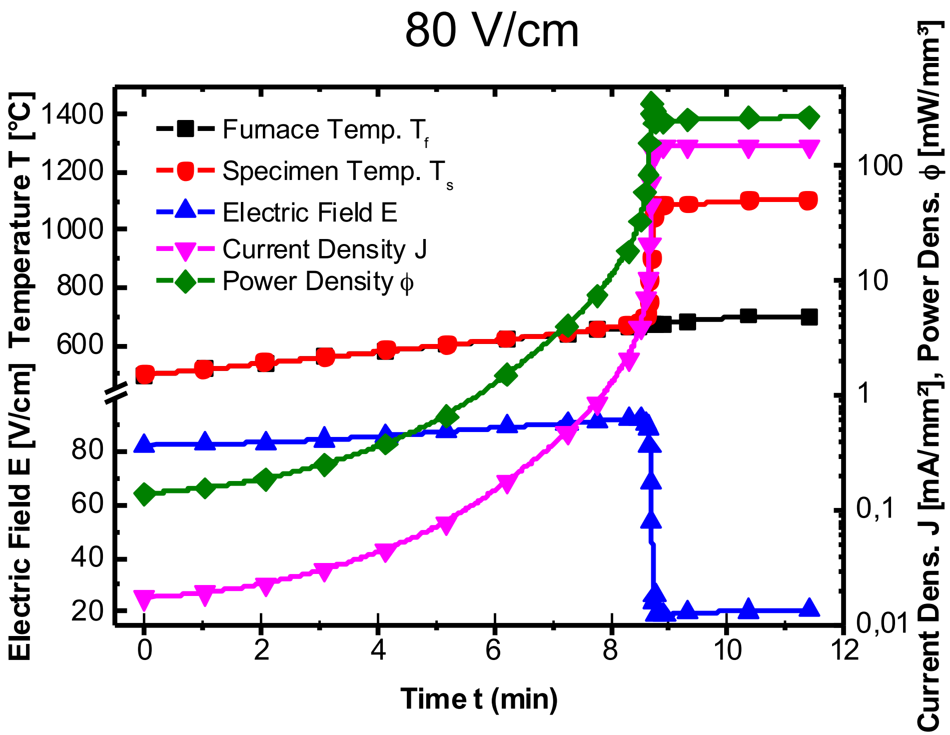




- Sintering behaviour is strongly affected by the electric field
- Maximal density obtained for 40 V/cm

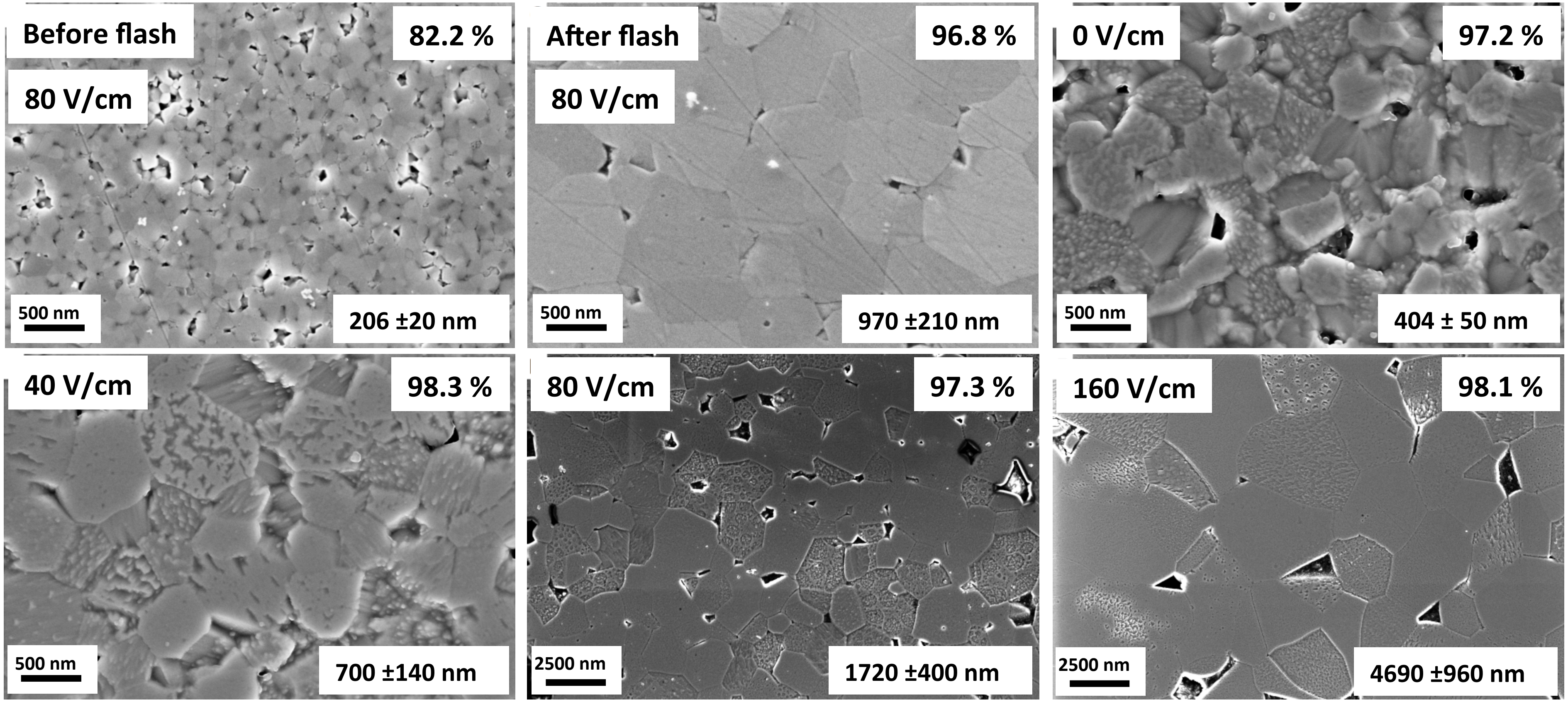
Electric field assisted sintering of ZnO





- Current flows through the specimen and causes drop of electric field and temperature increase
- Massive Joule heating due to electric current flow

Electric field assisted sintering of ZnO



- Electric field/current determines the evolution of the microstructure
- Fine grains (< 1 µm) for low fields and large grains (> 1 µm) for high fields
- Thermally activated diffusional process (massive matter transport) + ?

Photoluminescence of ZnO: Defects

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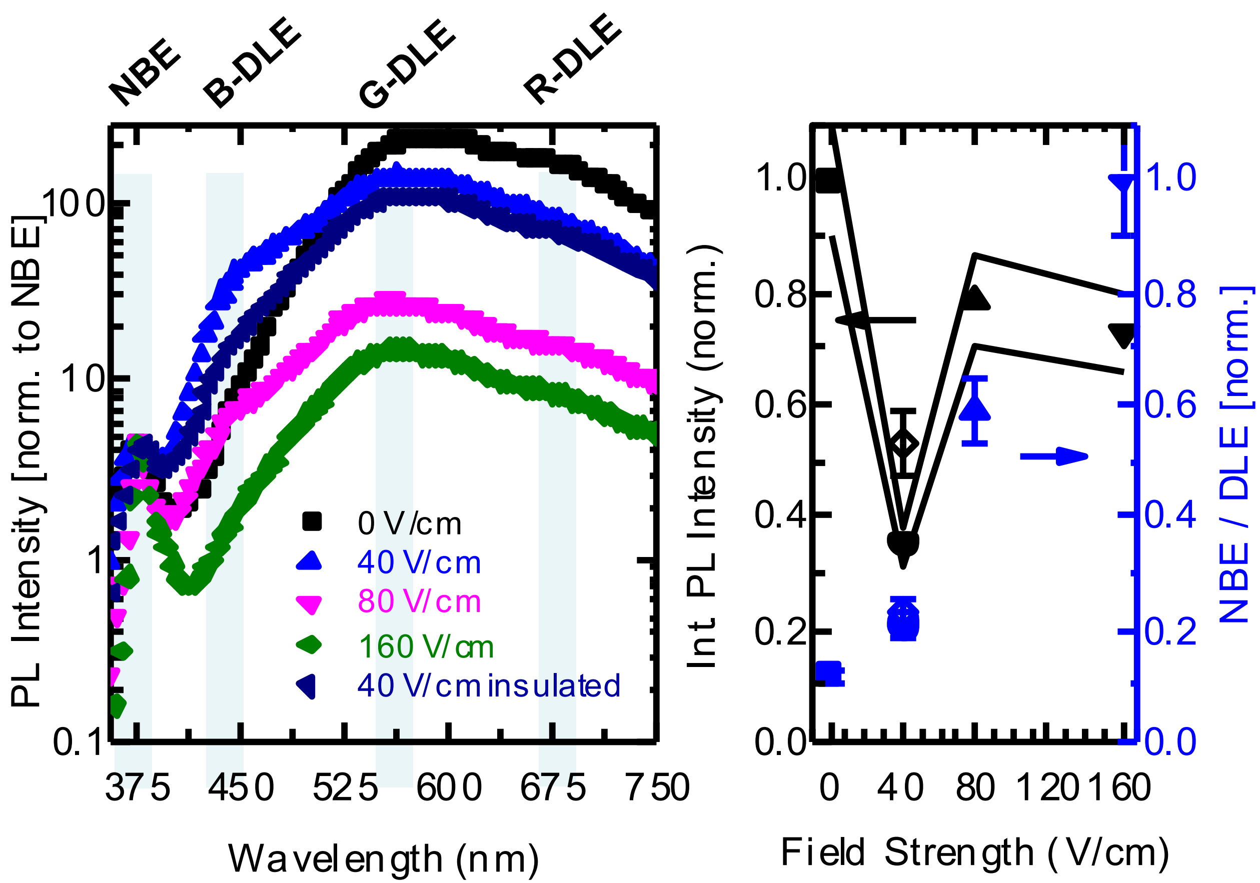


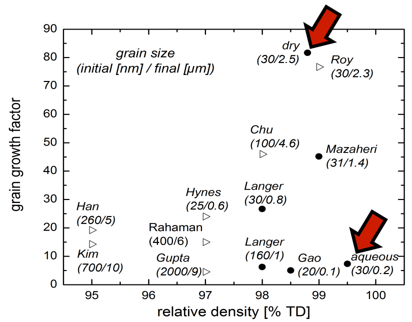
NBE Near Band Edge
DLE Deep level emission

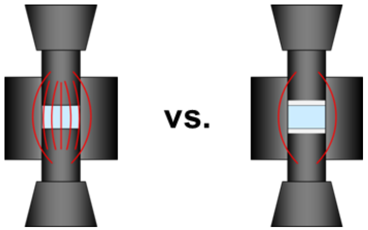
B-DLE
Donor-acceptor pair transition
G-DLE
Zinc on oxygen site
R-DLE
Oxygen interstitial

- Increase of NBE/DLE → higher crystal quality (less defects)
- 0 and 40 V/cm insulated have same grain size (400 nm) but different defects distributions
- Mobility of point defects under electric field?

Conclusions

- Full densification of ZnO with nano-grain sizes can be attained at only 400 °C using FAST sintering under high heating rate and the presence of water
- As evidenced by chemical analysis and photoluminescence, hydrogen is incorporated and modifies densification behavior, color and electrical properties of ZnO
- Sintering path and densification are not affected by electrical current in standard FAST/SPS
- In contrast, higher electric fields can significantly modify the sintering behavior of ZnO, especially if current flows through the sample, leading to different defect configurations and exaggerated grain growth.





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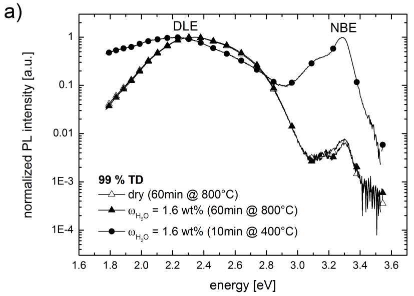

Publications

FAST/SPS sintering of nanocrystalline zinc oxide - Part 1: Enhanced densification and formation of hydrogen-related defects in presence of adsorbed water
B. Dargatz, J. Gonzalez-Julian, M. Bram, P. Jakes, L. Schade, R. Röder, C. Ronning, O. Guillon
Journal of the European Ceramic Society, 36, pp. 1207-1220, 2016

FAST/SPS sintering of nanocrystalline zinc oxide - Part 2: Abnormal grain growth, texture and mechanical properties
B. Dargatz, J. Gonzalez-Julian, M. Bram, Y. Shinoda, F. Wakai, O. Guillon
Journal of the European Ceramic Society, 36, pp. 1221-1232, 2016

Flash Sintering of Zinc Oxide and its Influence on Microstructure and Defect Formation
C. Schmerbauch, J. Gonzalez-Julian, R. Röder, C. Ronning, O. Guillon
Journal of the American Ceramic Society, vol. 97[6], pp. 1728-1735, 2014

Anomalous coarsening of nanocrystalline zinc oxide particles in humid air
B. Dargatz, J. Gonzalez-Julian, O. Guillon
Journal of Crystal Growth, 419, pp. 69-78, 2015

Improved compaction of ZnO nano-powder triggered by the presence of acetate and its effect on sintering
B. Dargatz, J. Gonzalez-Julian, O. Guillon
Science and Technology of Advanced Materials, 16, 025008 (10 p.), 2015

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Expertenkreis
Field Assisted Sintering Technique / Spark Plasma Sintering (FAST/SPS)

ADVANCED ENGINEERING MATERIALS

REVIEW

DOI: 10.1002/adem.201300409

Field-Assisted Sintering Technology/ Spark Plasma Sintering: Mechanisms, Materials, and Technology Developments**

By *Olivier Guillon,* Jesus Gonzalez-Julian, Benjamin Dargatz, Tobias Kessel, Gabi Schierning, Jan Räthel* and *Mathias Herrmann*

Field-assisted sintering technology/Spark plasma sintering is a low voltage, direct current (DC) pulsed current activated, pressure-assisted sintering, and synthesis technique, which has been widely applied for materials processing in the recent years. After a description of its working principles and historical background, mechanical, thermal, electrical effects in FAST/SPS are presented along with the role of atmosphere. A selection of successful materials development including refractory materials, nanocrystalline functional ceramics, graded, and non-equilibrium materials is then discussed. Finally, technological aspects (advanced tool concepts, temperature measurement, finite element simulations) are covered.

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