MESA+
INSTITUTE FOR NANOTECHNOLOGY

UNIVERSITY OF TWENTE.

Use of Microwave Technology in Materials Science

Synthesis, Sintering and “MW-effect”

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Journal Club, IMS Group 20-12-2011

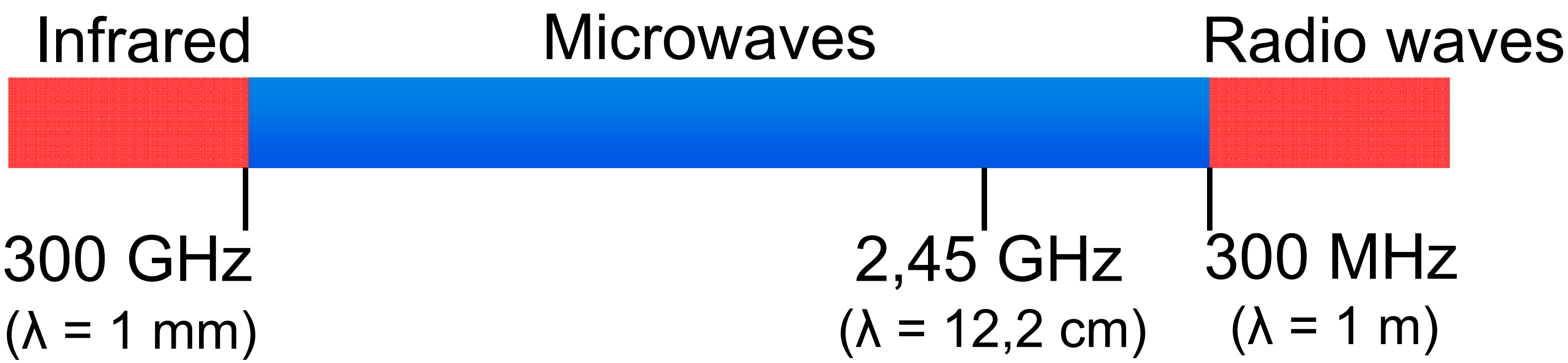
Outline

- Introduction
  - What are Microwaves? How does a MW-oven work?
  - General use
- Synthesis of Metal Oxides
- Sintering (and Rapid Thermal Annealing)
- Microwave Effect (?)
- Conclusions / Outlook
- Propositions

Introduction (I)

What are microwaves:

Electromagnetic waves which consist of an electric and magnetic field component, in the range:



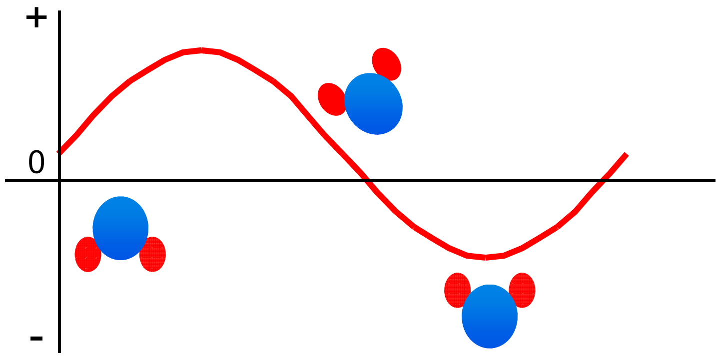
The electric field component: important interaction for organic synthesis

The magnetic field component: relevant with transition metal oxides

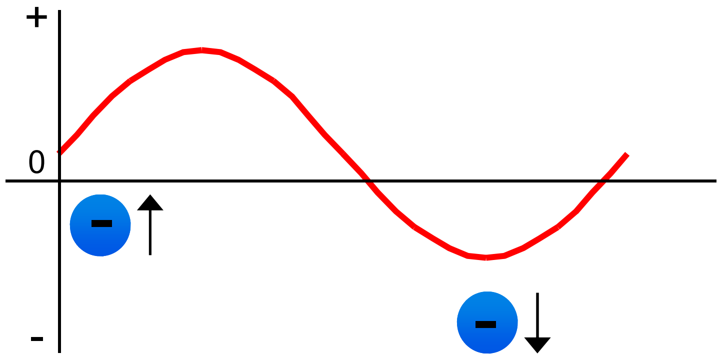
C.O. Kappe, D. Dallinger, S.S. Murphree, *Practical Microwave Synthesis for Organic Chemists*, WILEY-VCH Verlag GmbH, 2009

Introduction (II)

Dipolar polarization



Ionic conduction



Energy (in the form of heat) is lost due to:

- Molecular friction
- Dielectric loss

C.O. Kappe, D. Dallinger, S.S. Murphree, *Practical Microwave Synthesis for Organic Chemists*, WILEY-VCH Verlag GmbH, 2009

Introduction (III)

Heating characteristics:

Loss tangent $\tan \delta = \varepsilon'' / \varepsilon'$

where ε'' = dielectric loss (efficiency to convert radiation into heat)

ε' = dielectric constant

➡ A higher $\tan \delta$ leads to more effective absorption and thus rapid heating

Solvent	**tan δ**	**Solvent**	**tan δ**
Ethylene glycol	1.350	Water	0.123
Ethanol	0.941	Chloroform	0.091
2-Propanol	0.799	Ethyl acetate	0.059
Methanol	0.659	Acetone	0.054
Acetic acid	0.174	Toluene	0.040

B.L. Hayes, *Microwave Synthesis: Chemistry at the Speed of Light*, CEM Publishing, Matthews, NC, 2002

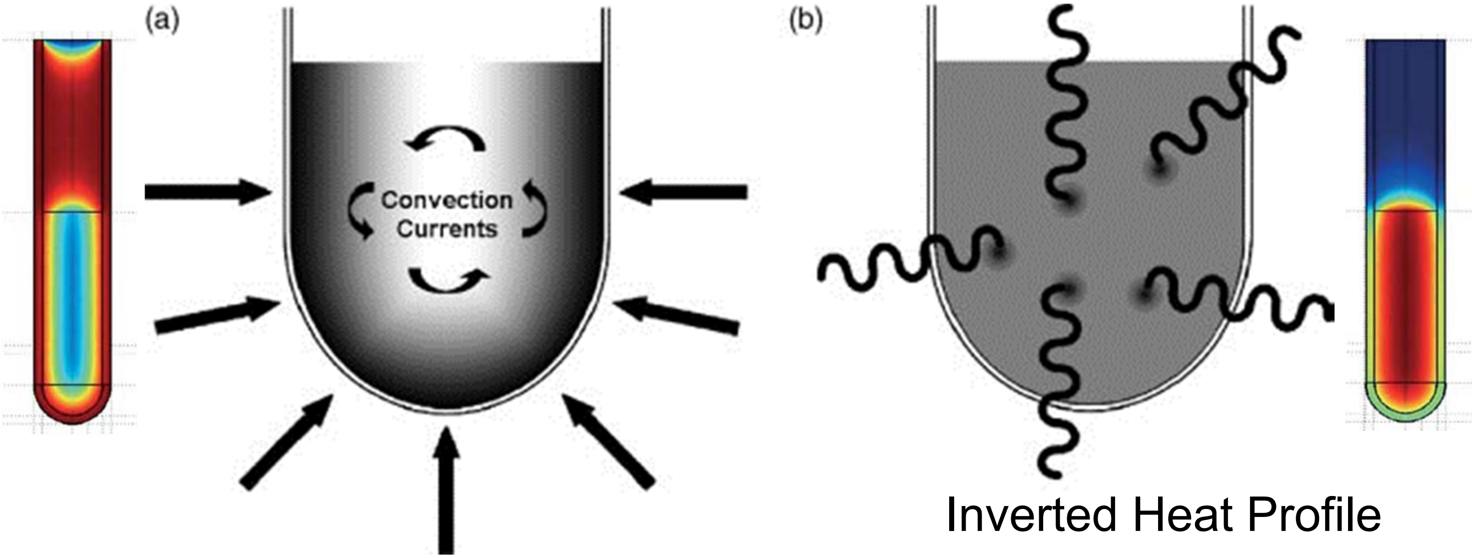
Introduction (IV)

How does it work?

- Conventional (a) – slow / inefficient heat transfer, convection

  ➡ temperature difference reaction vessel and reaction mixture

- Microwave (b) – fast, bulk heating, direct coupling of MW with molecules

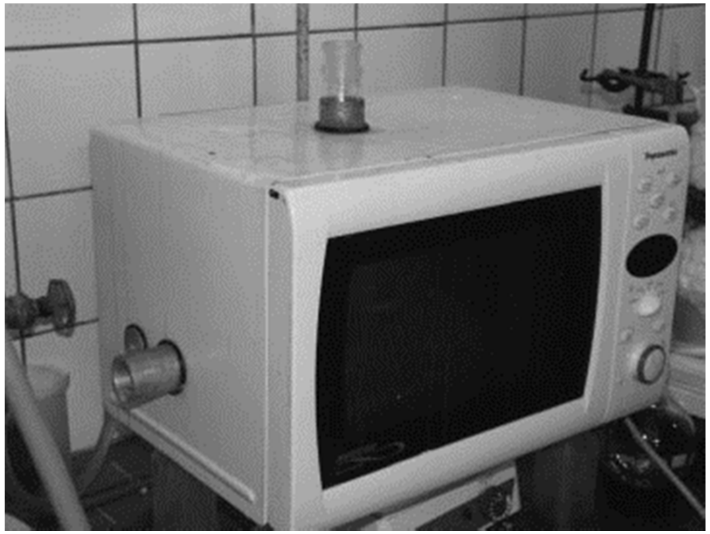


Inverted Heat Profile

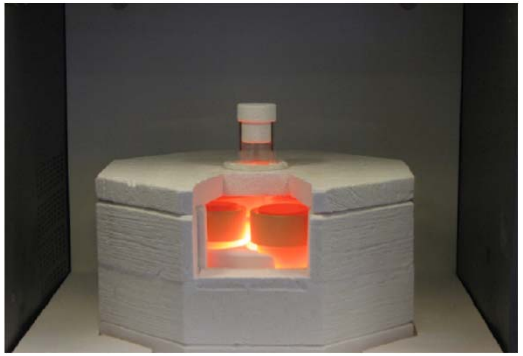
C.O. Kappe, D. Dallinger, S.S. Murphree, *Practical Microwave Synthesis for Organic Chemists*, WILEY-VCH Verlag GmbH, 2009

Introduction (V)

General use:



Domestic household MW oven



Commercially available MW oven

Introduction (V)

General use:

- Organic syntheses – Grignard , Diels-Alder, N-alkylation, etc etc…

  ➡ Fast, reproducible, high yield / purity

  ➡ Not all organic media (solvents) suitable – passive heating elements necessary, e.g. SiC)

- Synthesis of inorganic materials

  ➡ solid state / in organic media

- Microwave-assisted rapid thermal annealing (RTA) and sintering

Synthesis of Metal Oxides

Binary Oxides Synthesized in Nonaqueous Reaction Media			
α,γ-Al_2O_3	Spherical	MnO, Mn_2O_3, Mn_3O_4	Spherical
CeO_2	Spherical, rods	ReO_3	Spherical
Co_3O_4	Spherical	SnO_2	Spherical
CoO	Cubelike	Ta_2O_5	Spherical
Cr_2O_3	Spherical	TiO_2	Spherical, rods
Cu_2O, CuO	Spherical	V_2O_3	-
Fe_2O_3, Fe_3O_4	Spherical	$WO_3 \cdot H_2O$	Platelets
Ga_2O_3	Spherical	$W_{18}O_{49}$	Rods, wires
HfO_2	Spherical, ellipsoidal	ZnO	Spherical, rods, wires
In_2O_3	Spherical, cubelike	ZrO_2	Spherical
NiO	Spherical		

Main solvents: benzyl alcohol, 1,4-butanediol, benzylamine

N. Pinna, M, Niederberger, *Angew. Chem. Int. Ed.*, **2008**, 47, 5292-5304

Synthesis of Metal Oxides

Ternary / Multi-Metal Oxides Synthesized in Nonaqueous Reaction Media			
$BaSnO_3$	Spherical	$LiNbO_3$	-
$BaTiO_3$	Spherical	$MnNb_2O_6$	-
$BaZrO_3$	Slightly elongated	$NaNbO_3$	Spherical
$(Ba,Sr)TiO_3$	Spherical	$NaTaO_3$	-
$CaNb_2O_3$	-	$PbTiO_3$	Spherical
$CoFe_2O_4$	Spherical	$Pb(Zr,Ti)O_3$	Spherical
$CrNbO_4$	-	$PbZrO_3$	Spherical
$FeNbO_3$	-	RE_3NbO_7*	-
$InNbO_4$	Spherical	$SrTiO_3$	-
ITO	Spherical	$YNbO_4$	Spherical
$La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba)	-	$Zr_6Nb_2O_{17}$	Spherical

Main solvents: benzyl alcohol, 1,4-butanediol, benzylamine *RE = rare earth metal

N. Pinna, M, Niederberger, *Angew. Chem. Int. Ed.*, **2008**, 47, 5292-5304

ZnO – Synthesis

Reactants:

- Zinc(II) acetate
- Benzyl alcohol (anhydrous; bp ~205ºC)

Procedure:

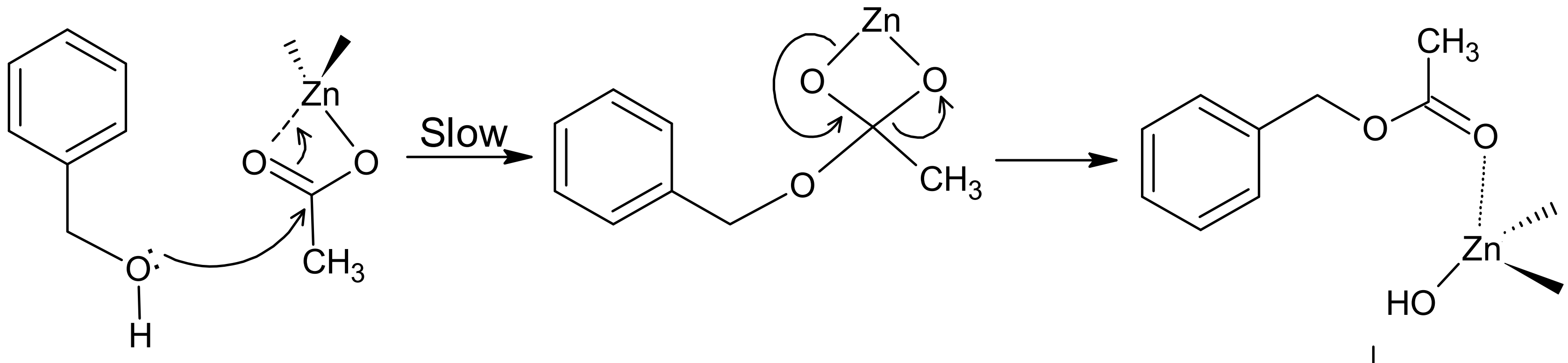
- Zinc(II) acetate is dissolved in benzyl alcohol under Ar-atmosphere
- Reaction vessel is sealed and placed in microwave oven

Reaction Conditions:

- Temperature Range : 120 – 180 ºC (iso-thermal)
- Reaction Time : 30 s – 35 min

I. Bilecka *et al*., *ACS Nano*, **2009**, 3 (2), 467-477

ZnO – Reaction Scheme



Reaction followed with:

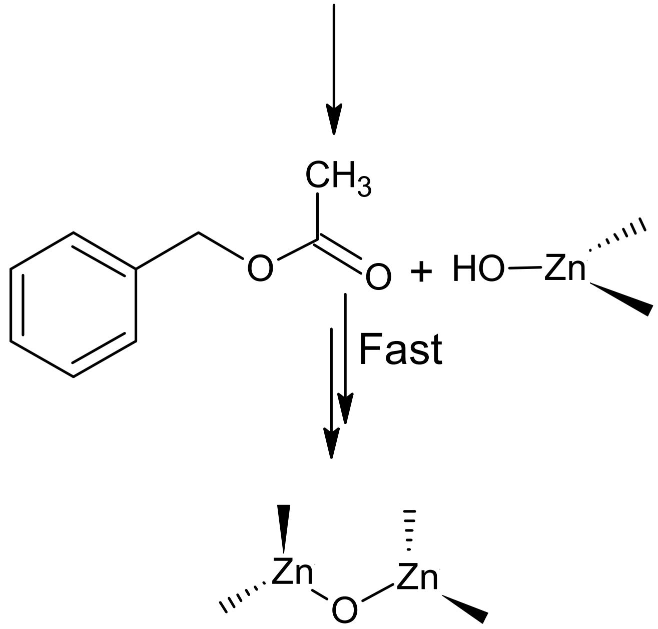
- FTIR
- XRD
- GC/MS

Reaction Kinetics

$$\frac{d[\mathrm{Zn(II)Ac}]}{dt} = -k_{esterification}[\mathrm{Zn(II)Ac}]$$

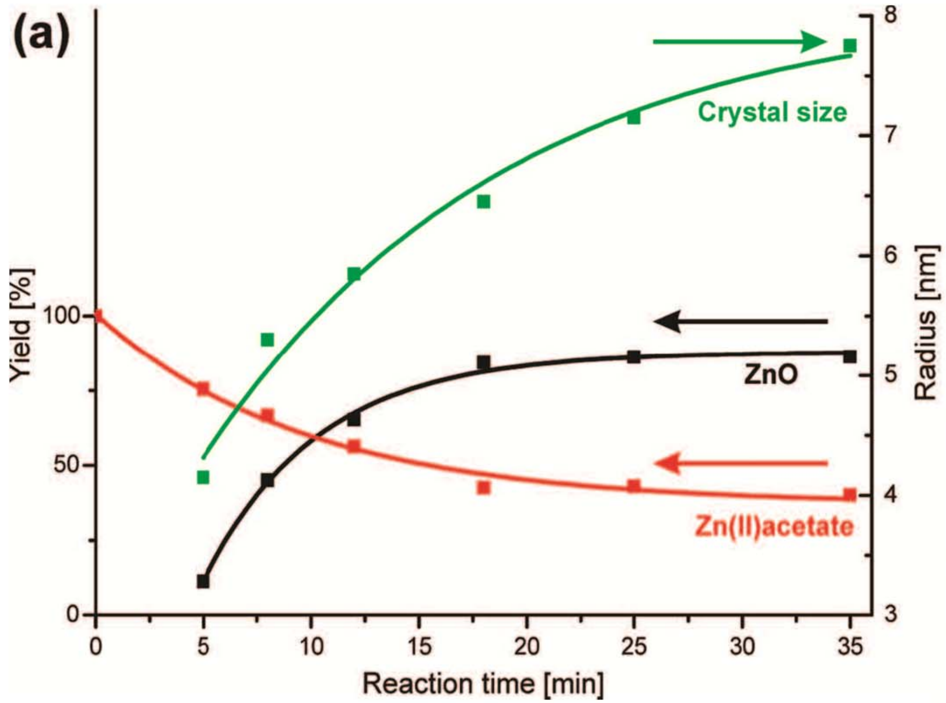
Crystallite Growth

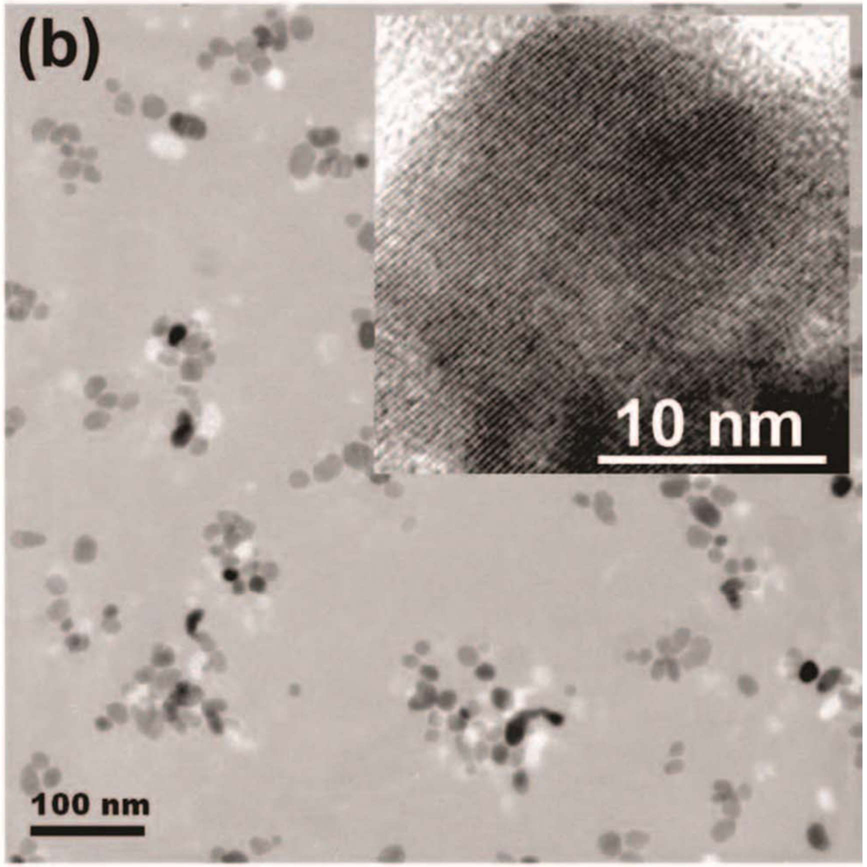
$$r^3 - r_0^3 = k_{growth} \cdot t$$



I. Bilecka *et al.*, *ACS Nano*, **2009**, 3 (2), 467-477

ZnO – Results (I)

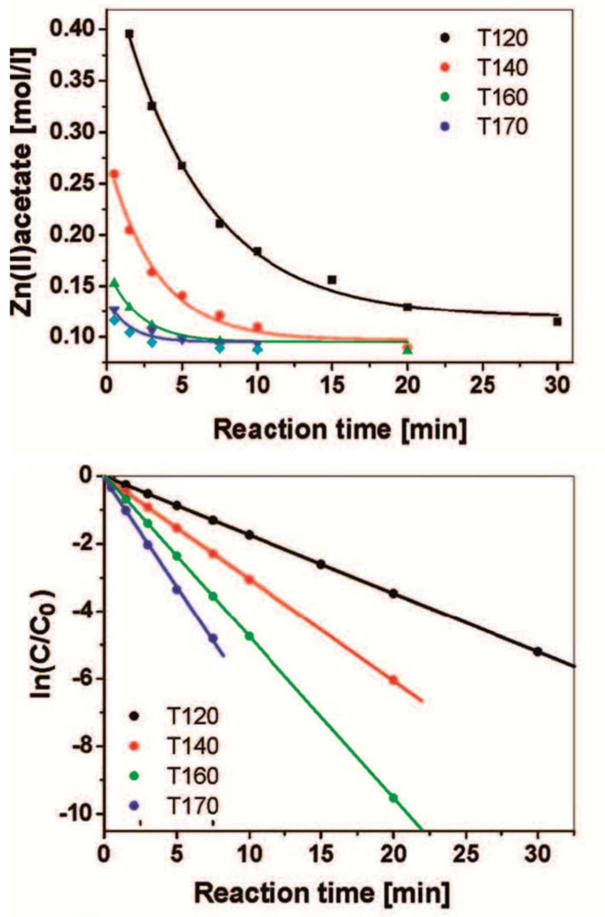




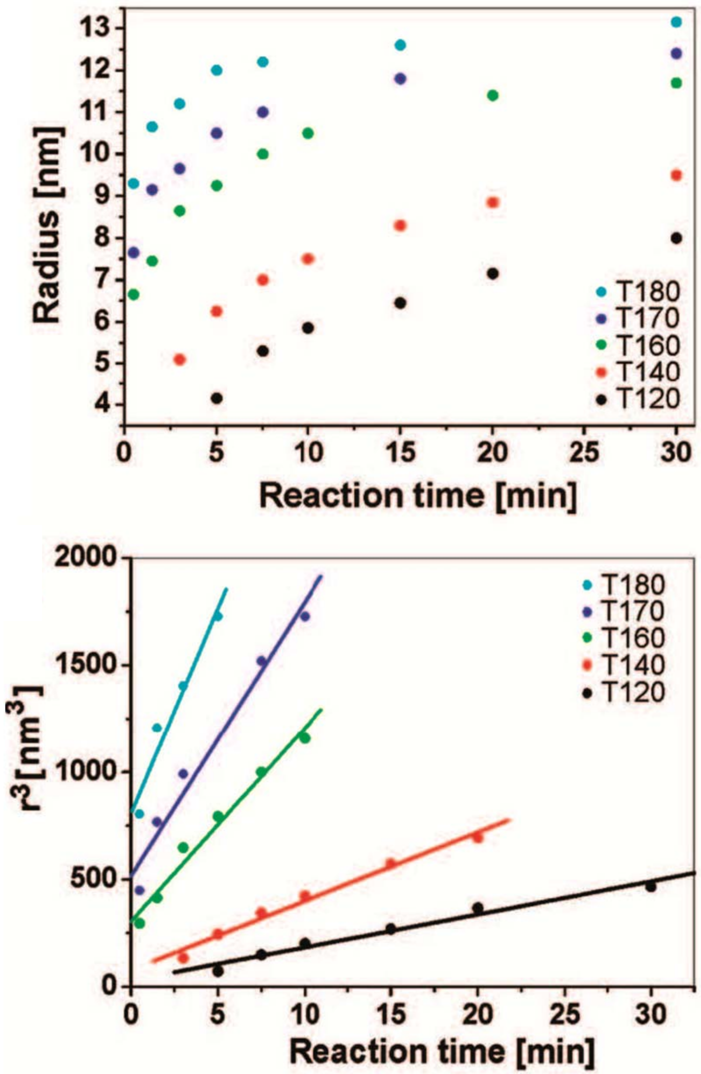
TEM image of ZnO after 3 min @ 120 ºC

I. Bilecka *et al*., *ACS Nano*, **2009**, 3 (2), 467-477

ZnO – Results (II)

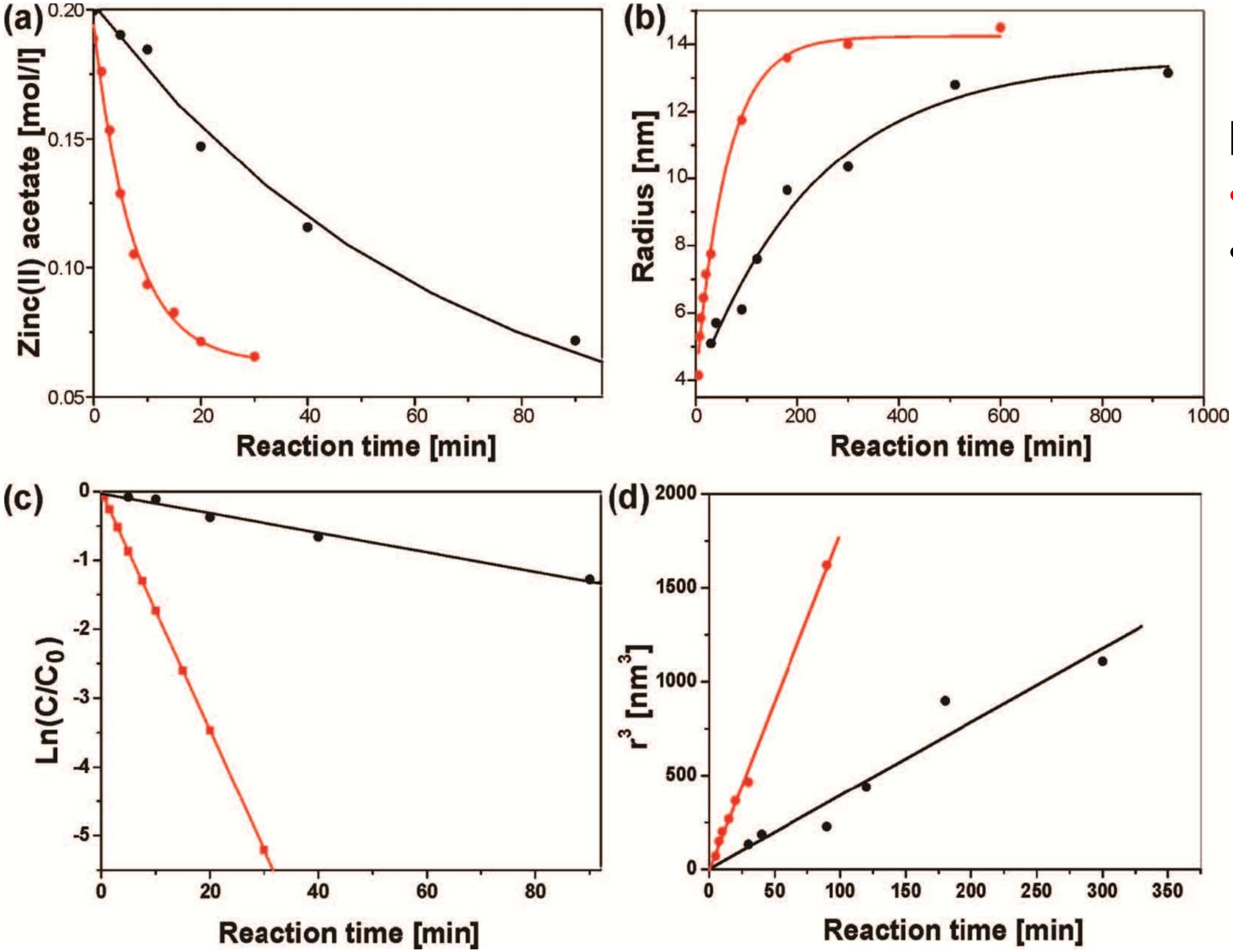


$$ln(C/C_0) = -k_{esterification} \cdot t$$



I. Bilecka *et al.*, *ACS Nano*, **2009**, 3 (2), 467-477

ZnO – Results (III) – Conventional vs MW



Legend:

- Microwave
- Conventional

I. Bilecka *et al.*, *ACS Nano*, **2009**, 3 (2), 467-477

Sintering

Hybrid Sintering:

- Microwave Oven
- Conventional

➡

- Clear effect MWs observed?
- Effect on final density

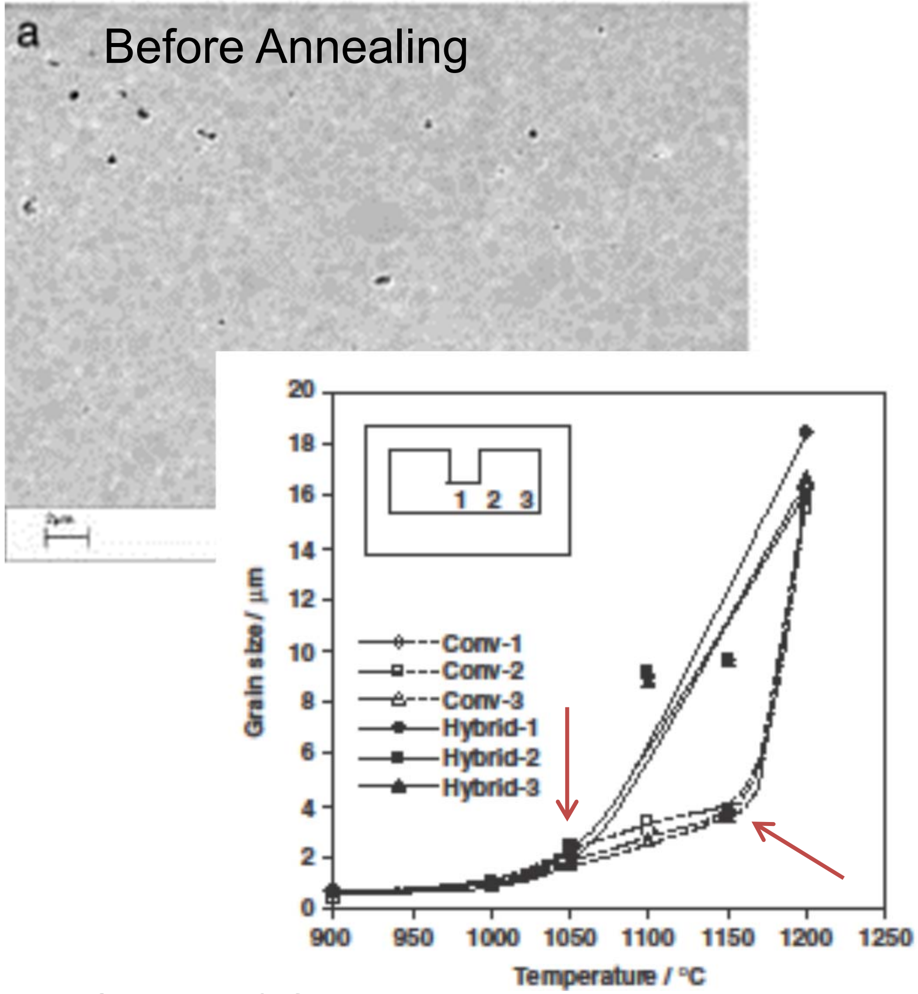
Procedure:

- ZnO pallets (13 x 5 mm) – pre-annealed at 850 ºC
- Sintering at 900 ºC – 1200 ºC (heat/cool 20 ºC/min)
- Dwell time 1, 3 or 5 hours
- Conventional, Microwave (max. 1000 W) and Hybrid heating

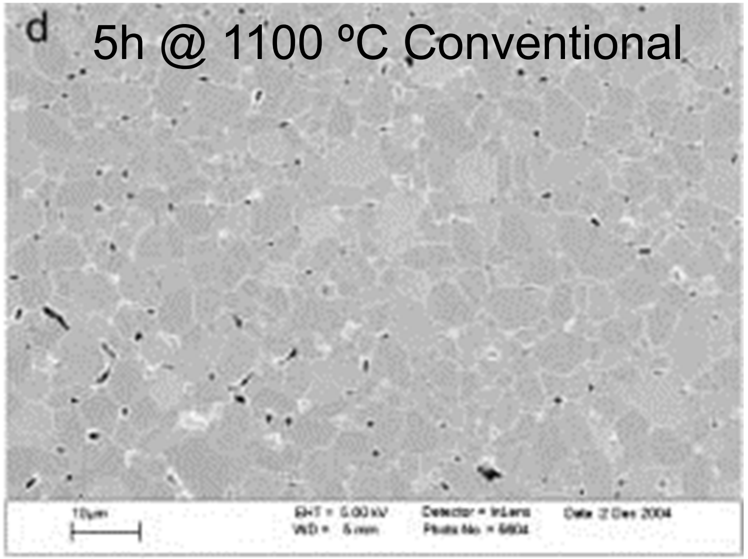
J. Wang *et al*., *Thin Solid Films*, **2008**, 516, 5996-6001

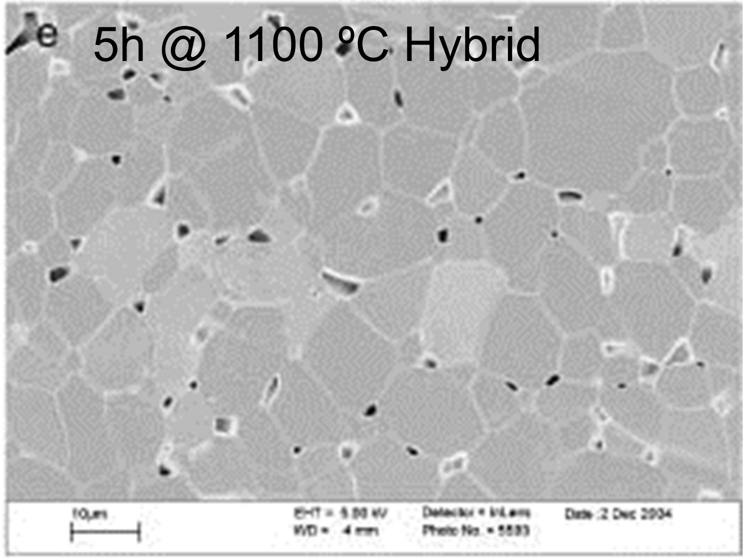
J. Binner *et al*., *J. Am. Ceram. Soc.*, **2007**, 90 (9), 2693-2697

Sintering – Results (I)



Onset of Growth



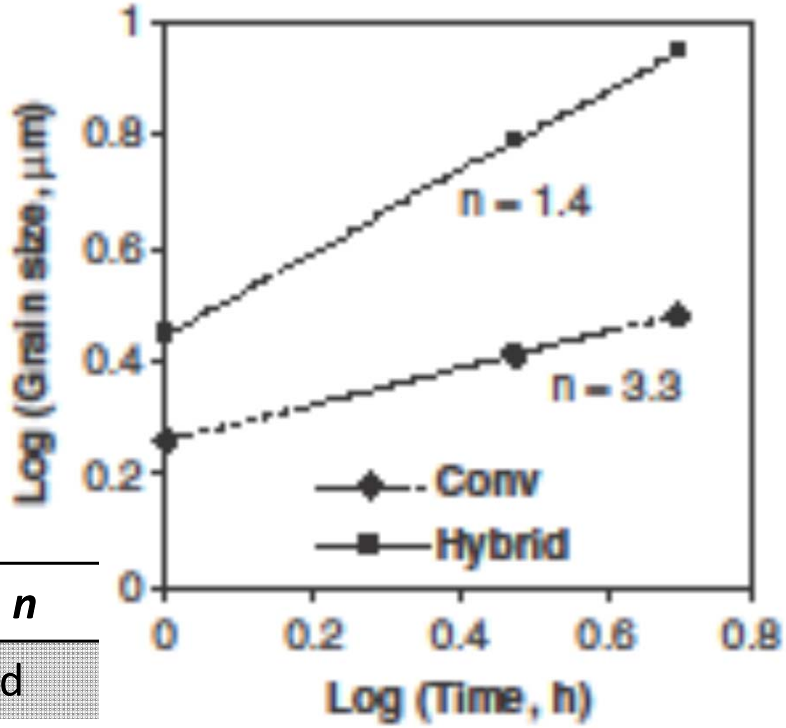


J. Binner *et al.*, *J. Am. Ceram. Soc.*, **2007**, 90 (9), 2693-2697

Sintering – Results (II)

$$\left.\begin{array}{l} G^n - G_0^n = k \cdot t \\ k = k_0\, exp\left(-\dfrac{Q}{RT}\right) \end{array}\right\} G^n = k_0\, exp\left(-\dfrac{Q}{RT}\right) \cdot t$$

$$\Rightarrow log\, G = \frac{1}{n} log\, k + \frac{1}{n} log\, t$$



	Grain Growth Exponent, *n*	
Annealing Temperature	Conventional	Hybrid
1100 ºC	~ 3.3	~ 1.4
1150 ºC	~ 3.3	~ 1.4
1200 ºC	~ 1.6	~ 1.5

Lower Value of *n* = Faster Grain Growth

All Densities are > 98.0 %

J. Binner *et al.*, *J. Am. Ceram. Soc.*, **2007**, 90 (9), 2693-2697

S.J. Bennison and M.P. Harmer, *J. Am. Ceram. Soc.*, **1983**, 66 (5), C90-2

Rapid Thermal Annealing

Characteristics:

- Fast heating (dielectric loss)
- Enhanced densification behavior
- Less particle growth

What can be expected?

- Higher densities
- Smaller particle sizes
- Different properties of the prepared thin films / powders

MW-effect???

MW-Effect

Microwave-assisted chemistry:

- Microwave-Matter interactions not yet fully understood
  - Enhanced reaction kinetics
  - Altered product distributions

  } "Specific MW-effect"

➡ Purely thermal/kinetic effects

- Super-heating of solvents
- Catalysts absorbing more MWs than less polar medium

Cannot be re-produced by conventional heating

➡ Heated debates in scientific community

Conclusions / Outlook

Microwave-technology in Materials Science:

- Fast / reproducible technique for annealing / synthesis
- High purity materials are obtained
- Different effects are observed compared to conventional heating

Outlook:

- Significant increase in publications over the last years
- Broader application of the technique
- More research on so-called “MW-effect”

Propositions

1. Because of the financial crisis AND the knowledge within our group, PLD-targets should be made ourselves instead of ordered.

2. Although not every effect of microwave-technology on samples is understood, it decreases sample preparation time, and thus increases the productivity.