GREMAN
matériaux microélectronique acoustique nanotechnologies

# Solid-state synthesis

Guillaume F. Nataf

EL NANO thematic school
11 – 16 June 2023

UMR 7347

# GREMAN laboratory

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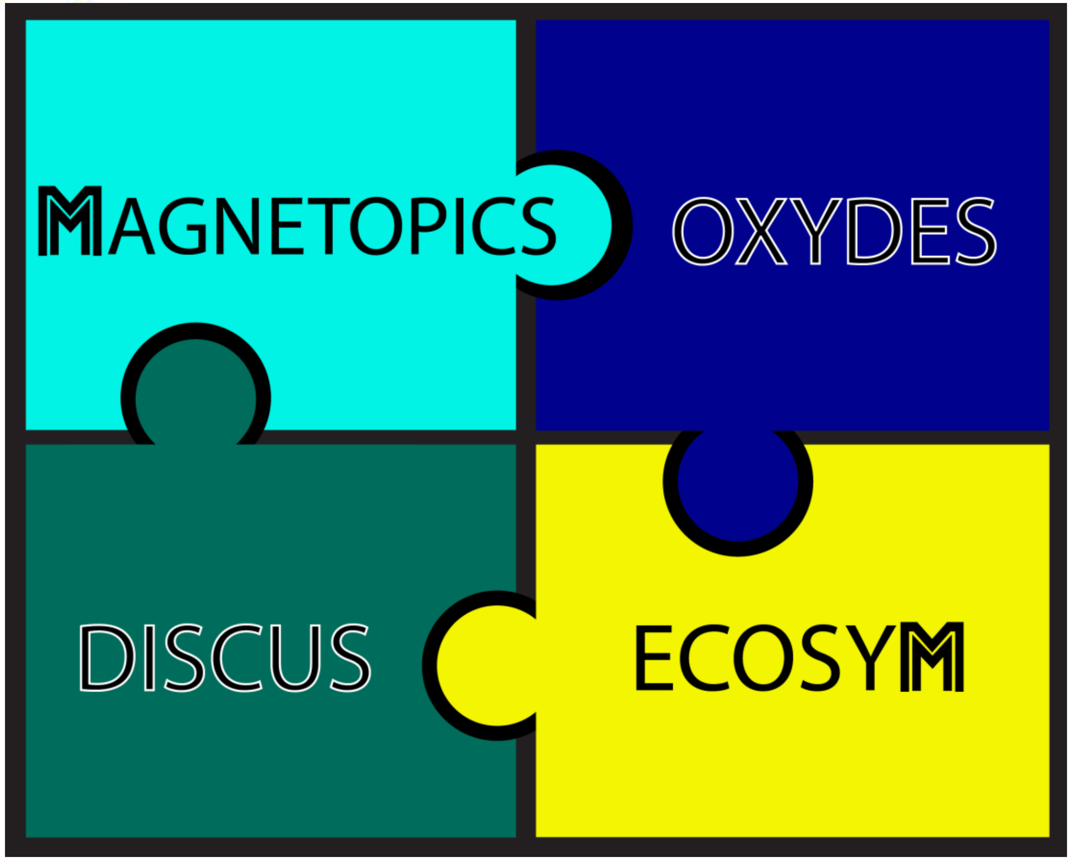
matériaux microélectronique acoustique nanotechnologies

magnetic and optical properties

oxides for energy efficiency




ultrasonic devices

energy, microelectronics

# This presentation would not exist without…

Fabien Giovannelli

Isabelle Laffez

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# Outline

- Basics of ceramics
- ZnO nanostructuring
- Nanocracks
- ZnO nanowires
- Spontaneous nanostructuration

Thermal conductivity

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# Outline

- Basics of ceramics
- ZnO nanostructuring
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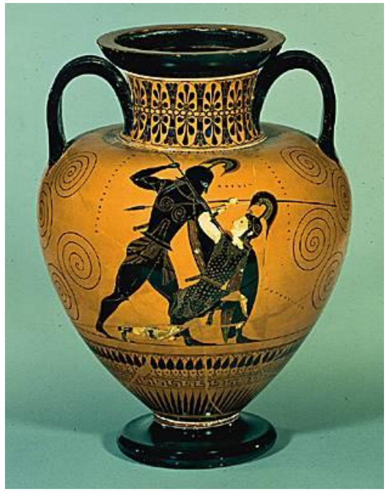
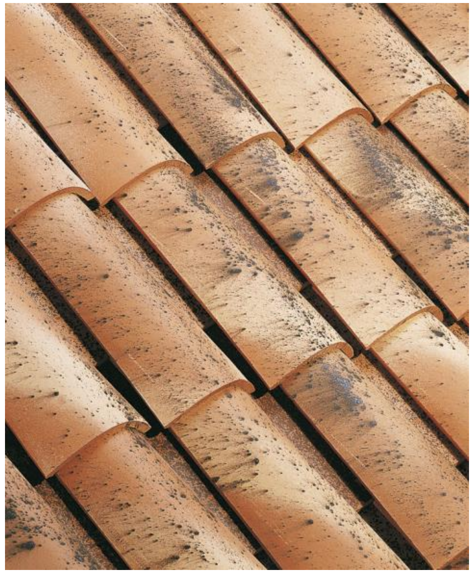
## Keramos (greek)



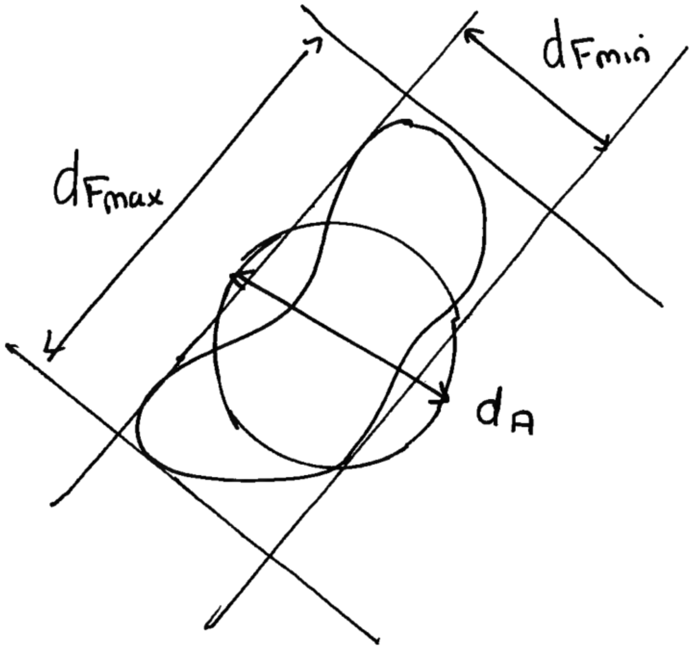
Pottery



Terracota

Ceramics

## What is the diameter of a particle?




$d_A$, **diameter of the projected area**: diameter of a spherical particle with the same projected area as the particle viewed in a direction perpendicular to the plane of the greatest stability of the particle

$d_F$, **Feret's diameter** (caliper diameter)

$d_V$, diameter of the sphere having the same volume

$d_S$, diameter of the sphere having the same equivalent specific surface

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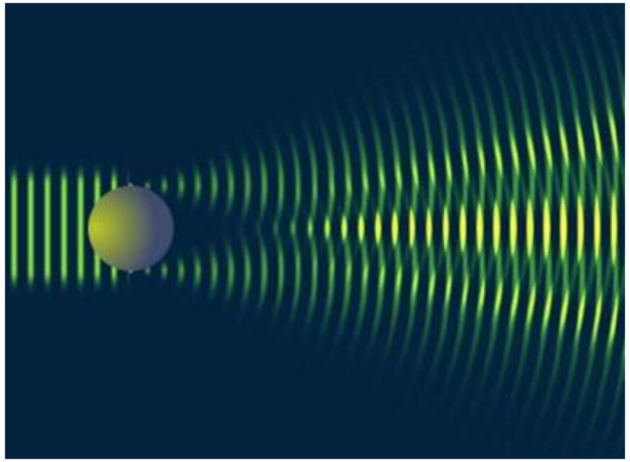
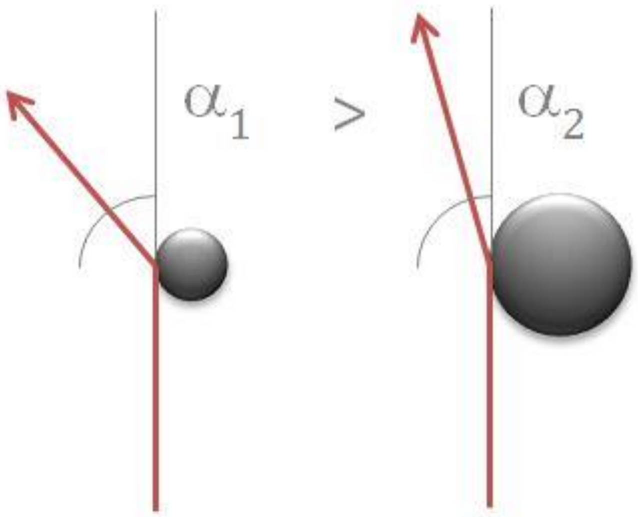
# How to measure grain sizes

| **Particle size** | **Measurement method** |
|---|---|
| > 100 µm | Dry sieving |
| > 30 µm | Wet sieving |
| 1 µm < $x$ < 100 µm | Sedimentometry |
| 0.1 µm < $x$ < 20 µm | Centrifugation |
| 0.02 µm < $x$ < 2 µm | Laser diffraction |
| 0.02 µm < $x$ < 1 mm | Microscopies |

# How to measure grain sizes: diffraction

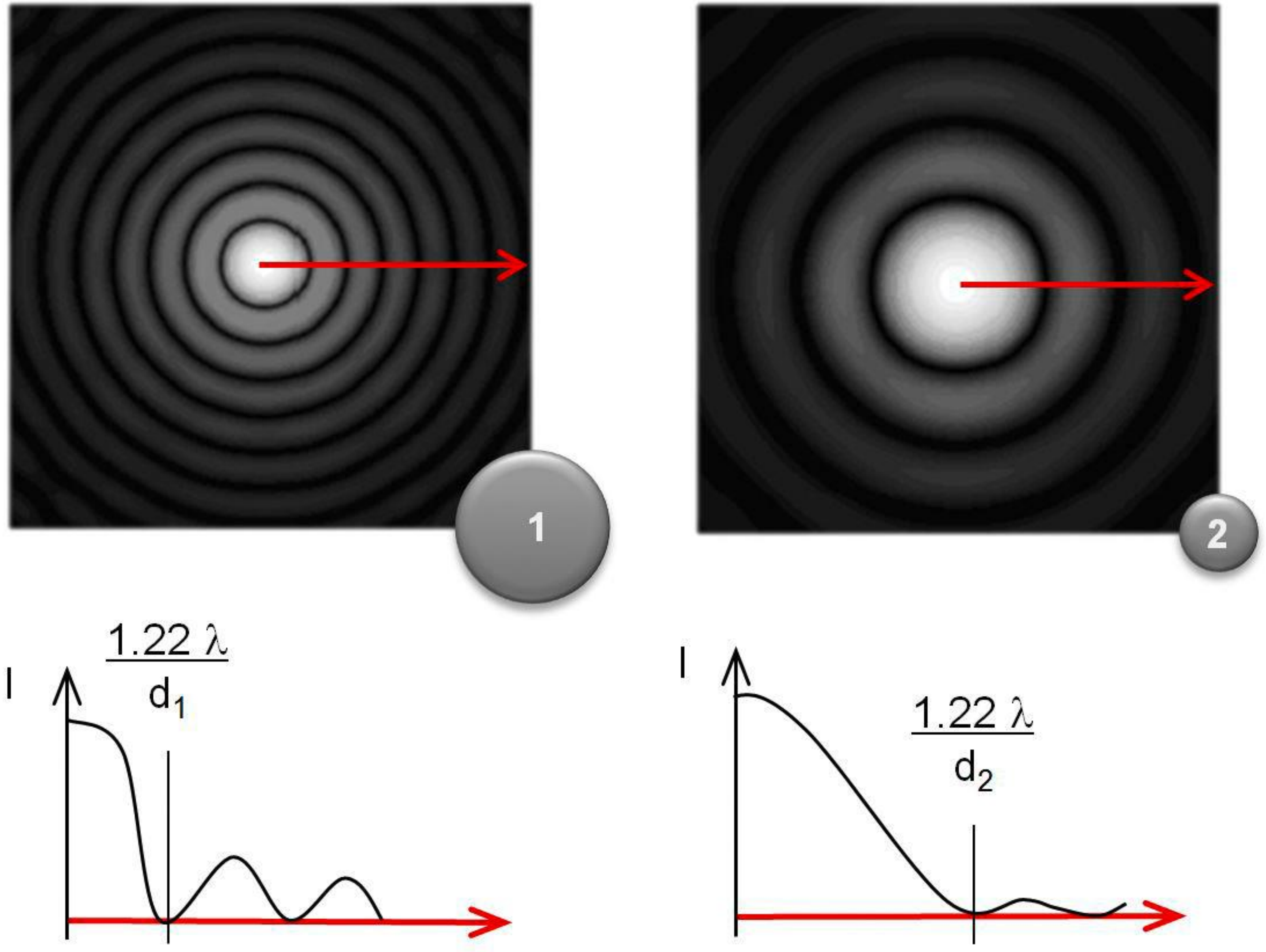


Each randomly moving particle in a **medium** (water, alcohol, etc.) absorbs, diffracts, refracts, reflects or scatters light at an angle that depends on its **size**




The diffraction angle of small particles ($\alpha_1$) is bigger than the diffraction angle of bigger particles ($\alpha_2$)

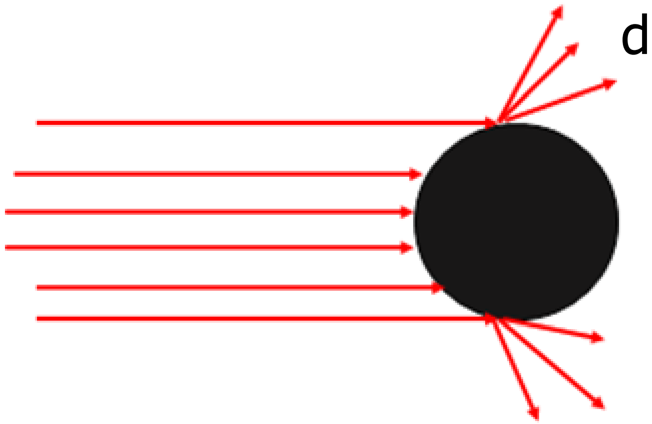
# How to measure grain sizes: Airy pattern




$d_1 > d_2$

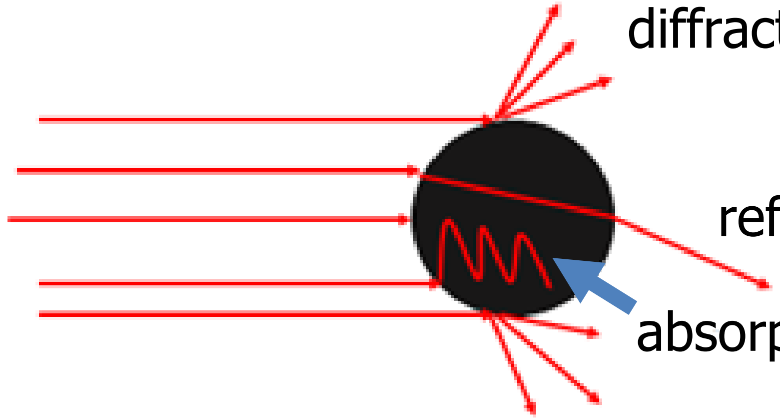
# How to measure grain sizes: laser granulometry

## Fraunhofer diffraction theory




- Spherical and opaque particles
- Diameter of the particles > $\lambda$ of the beam
- Particles far from each other
- Particles move randomly

## Mie scattering theory




- Spherical particles
- Homogeneous particles
- Particles far from each other
- Refractive indices of the particles and the medium are known

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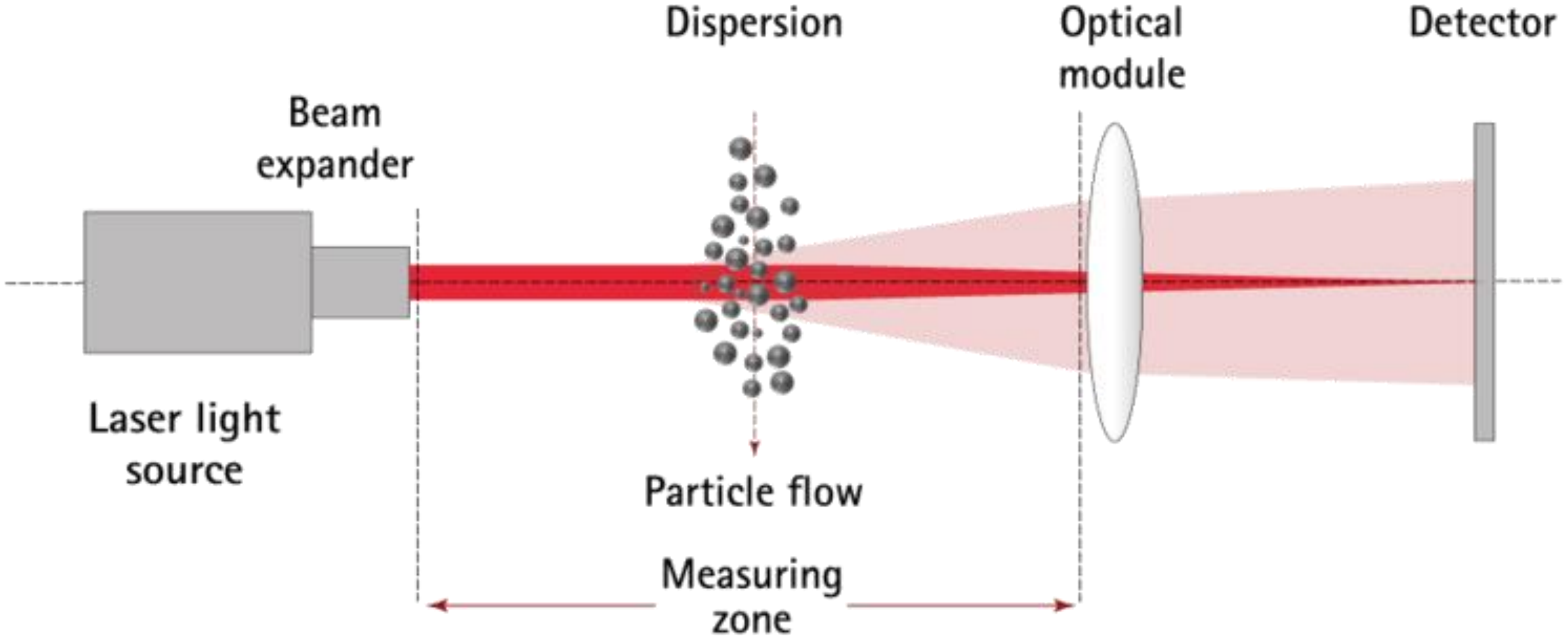
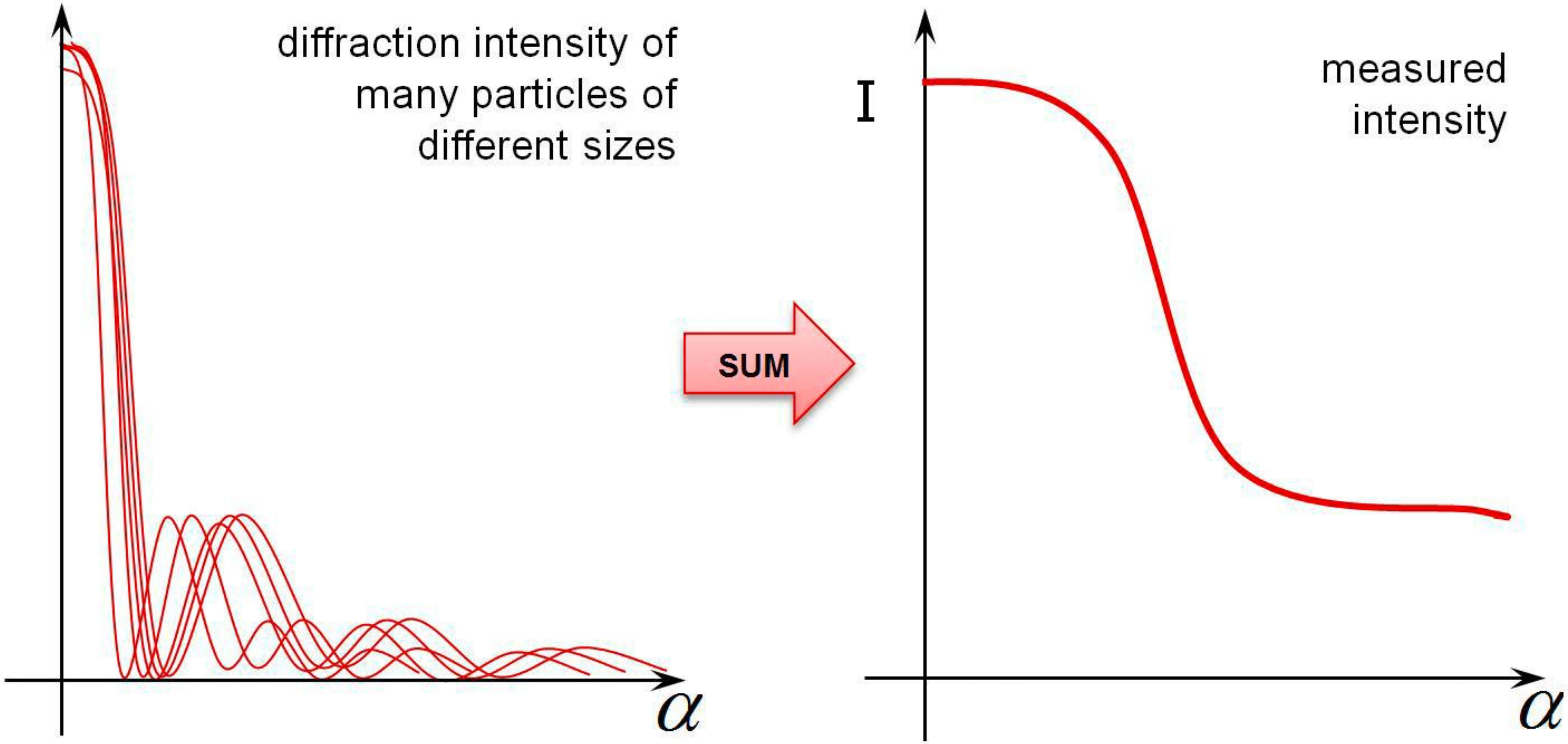
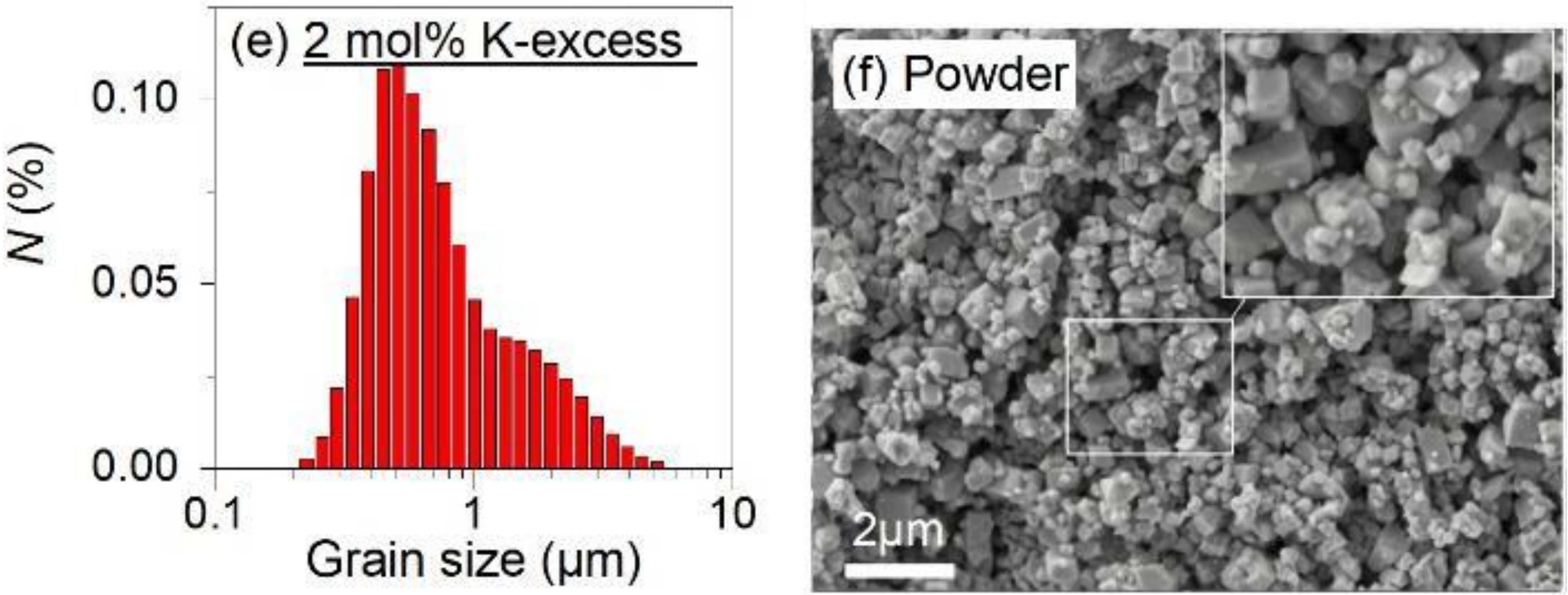
# How to measure grain sizes: laser granulometry



# How to measure grain sizes: laser granulometry



# Laser granulometry: an example



# Dynamic Light Scattering (DLS)

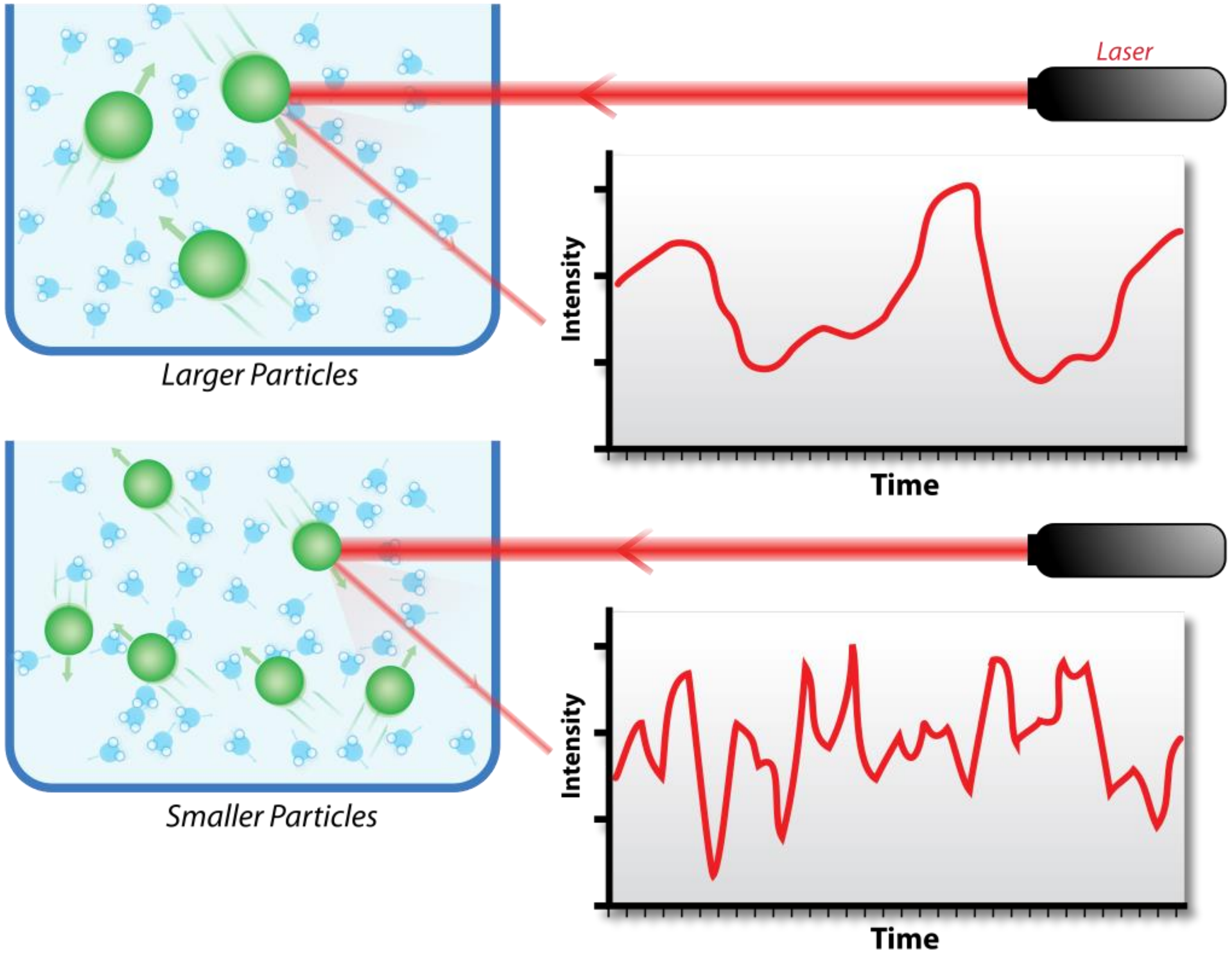
## For nanoparticles (1 – 500 nm)

All particles in the solution are hit by the light and all of them **diffract the light in all directions**.

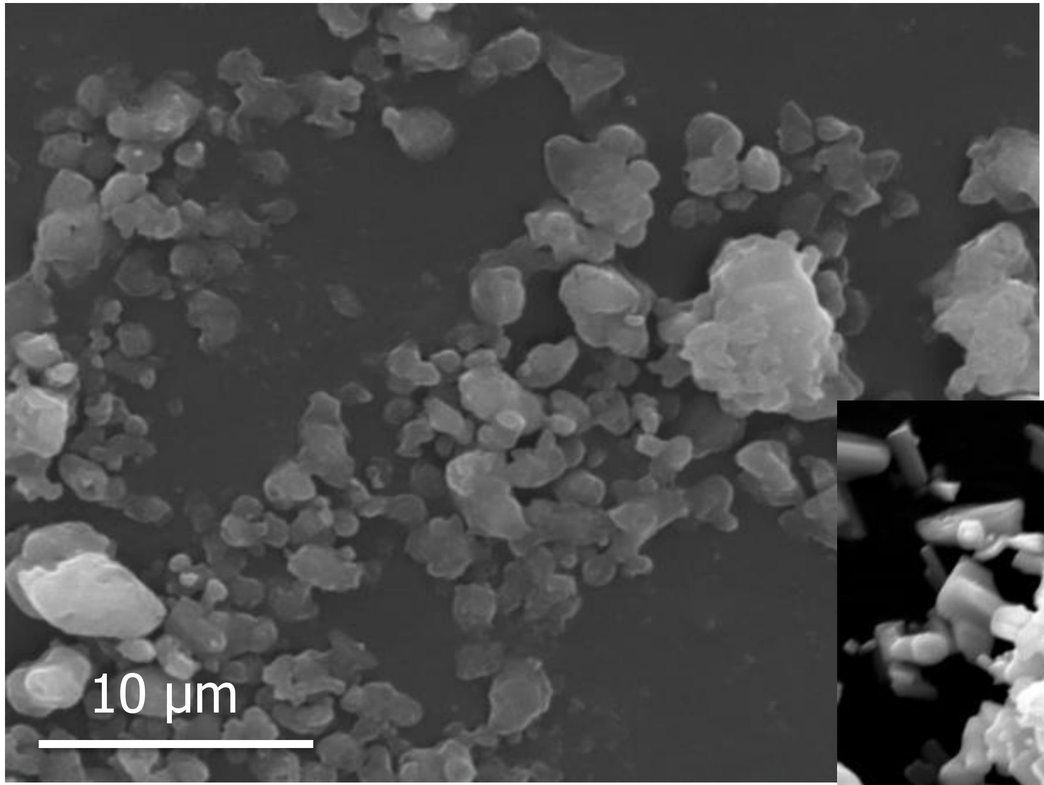
The diffracted light interfere either **constructively** (light regions) or **destructively** (dark regions).

Information is contained about the time scale of **movement** of the scatterers.

Autocorrelation of the intensity trace
→ diameter

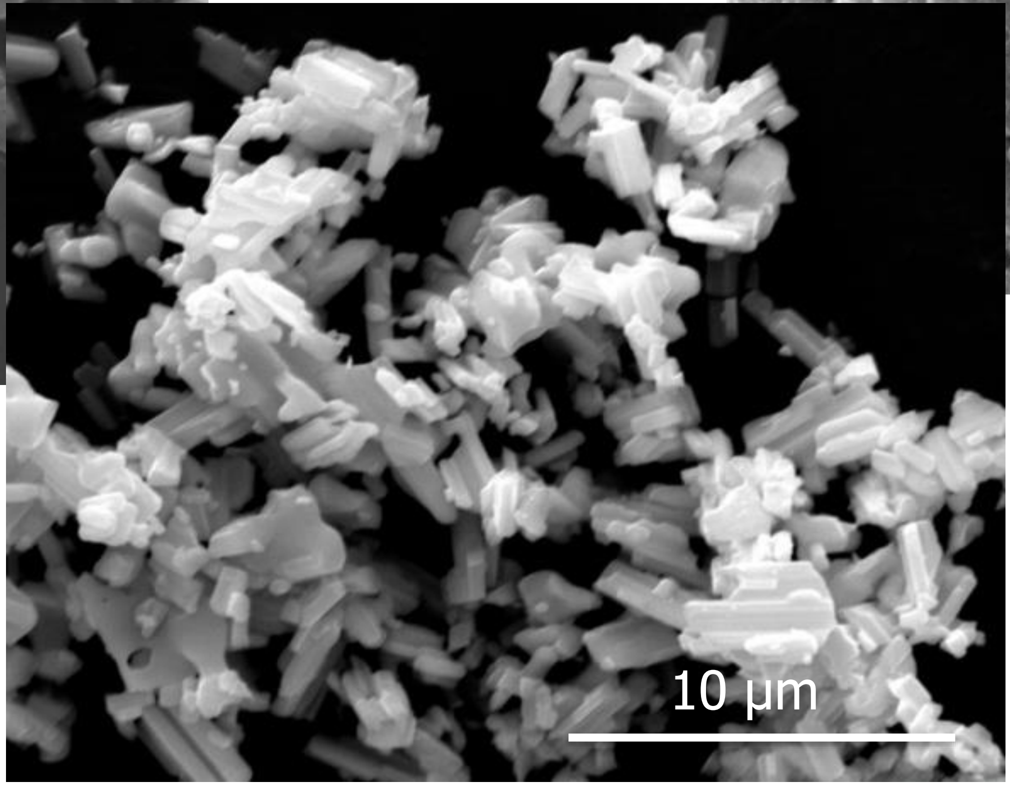


## Scanning electron microscopy

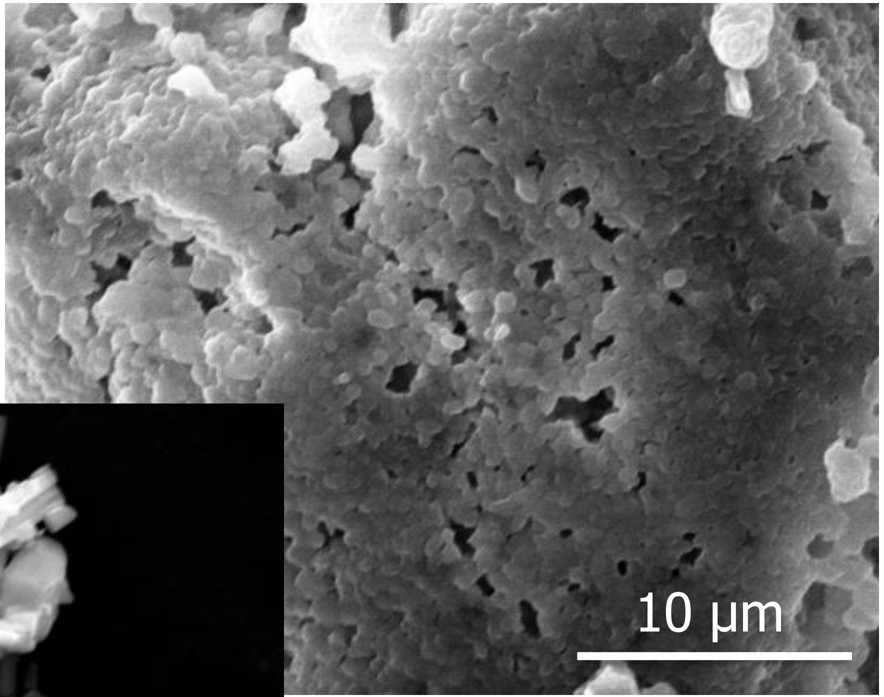



$K_2CO_3$

$Nb_2O_5$

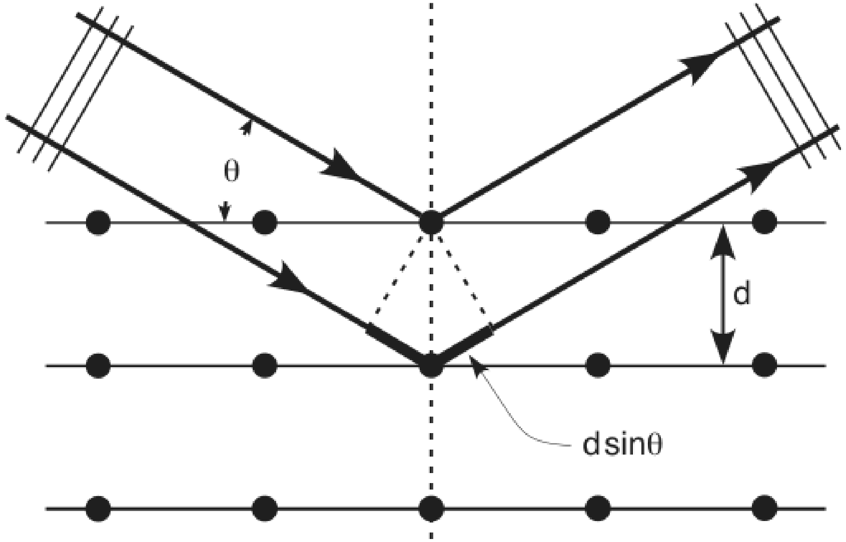



$Na_2CO_3$

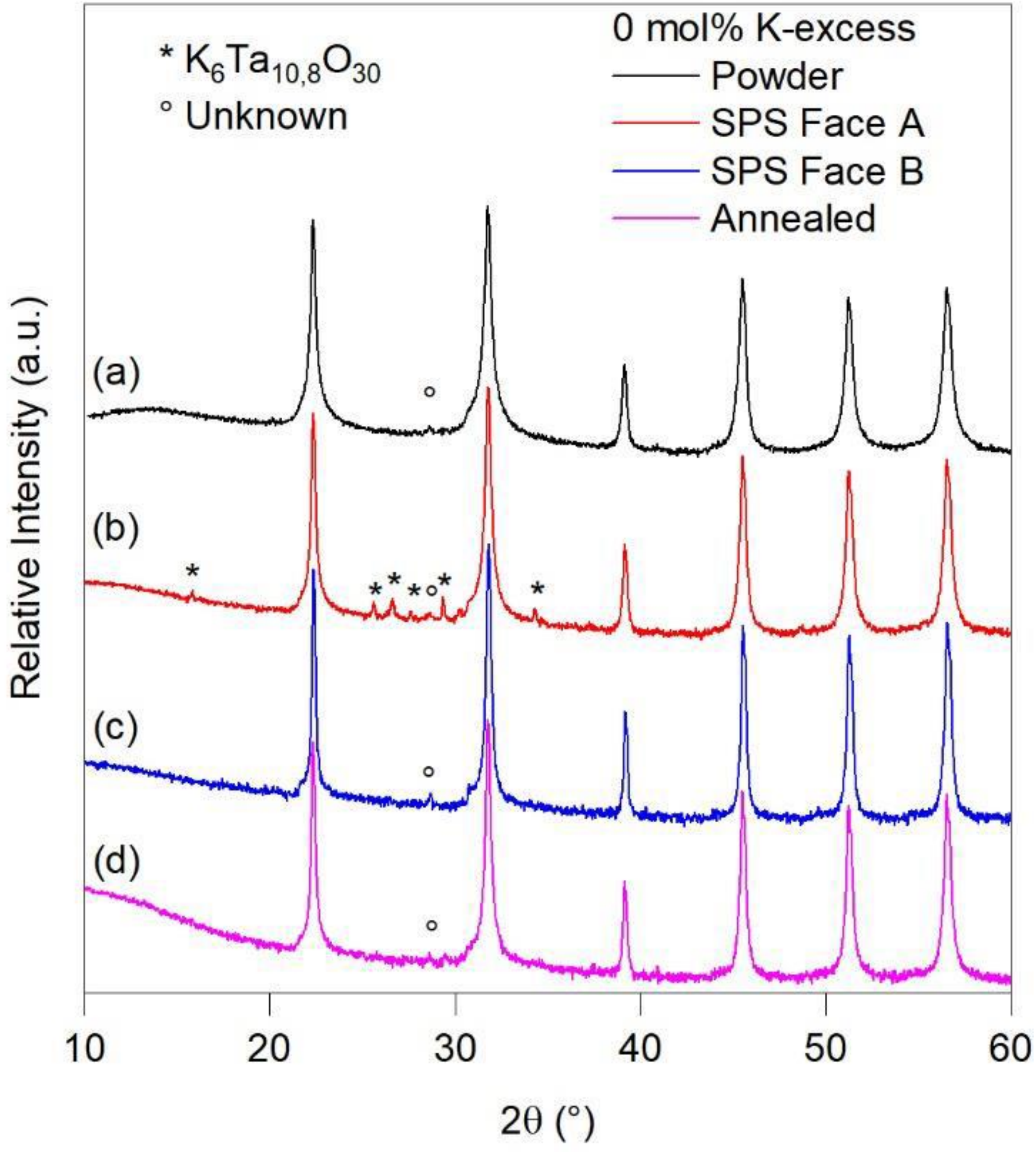


# Purity and crystal structure

## X-ray diffraction




Bragg's law: $\lambda = 2d \sin\theta$

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# Process to obtain a ceramic

selection and storage
of raw materials

↓

grinding


↓

calcination

chemical synthesis

grinding

↓

shaping

↓

sintering

↓

polishing

synthesis

ceramic

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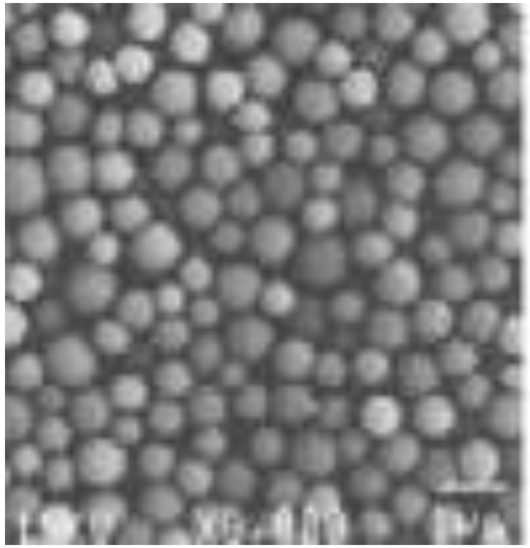
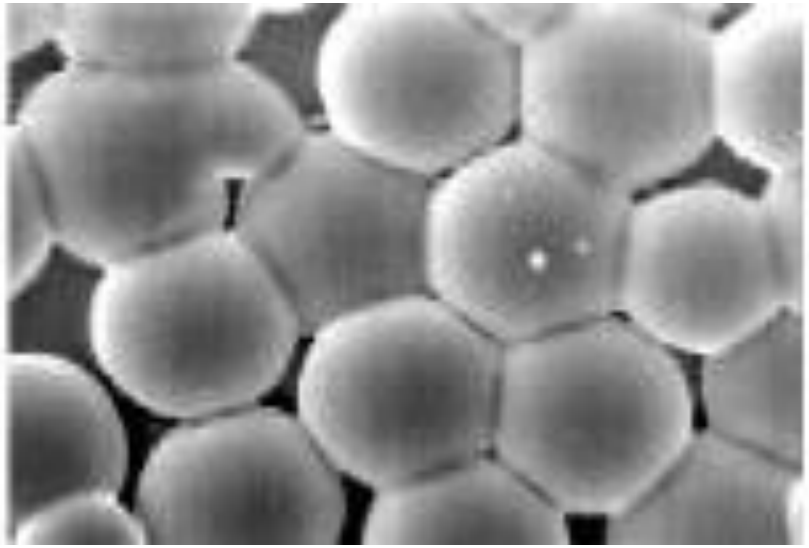
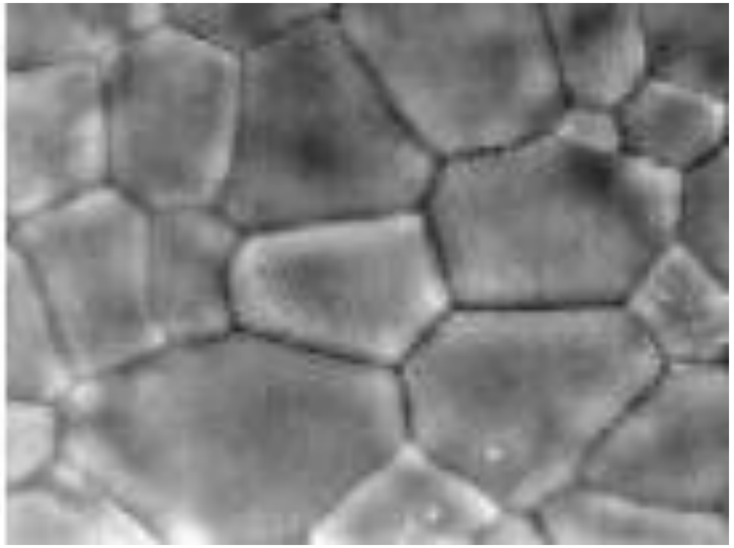
# Sintering



Powder material



Thermal cycle



Solid, dense, granular, polycristalline material = a ceramic!

**To obtain "good" ceramics, you need first "good" precursors**

"good" ceramics = relevant properties

"good" precursors = known size, shape and structure

# Outline

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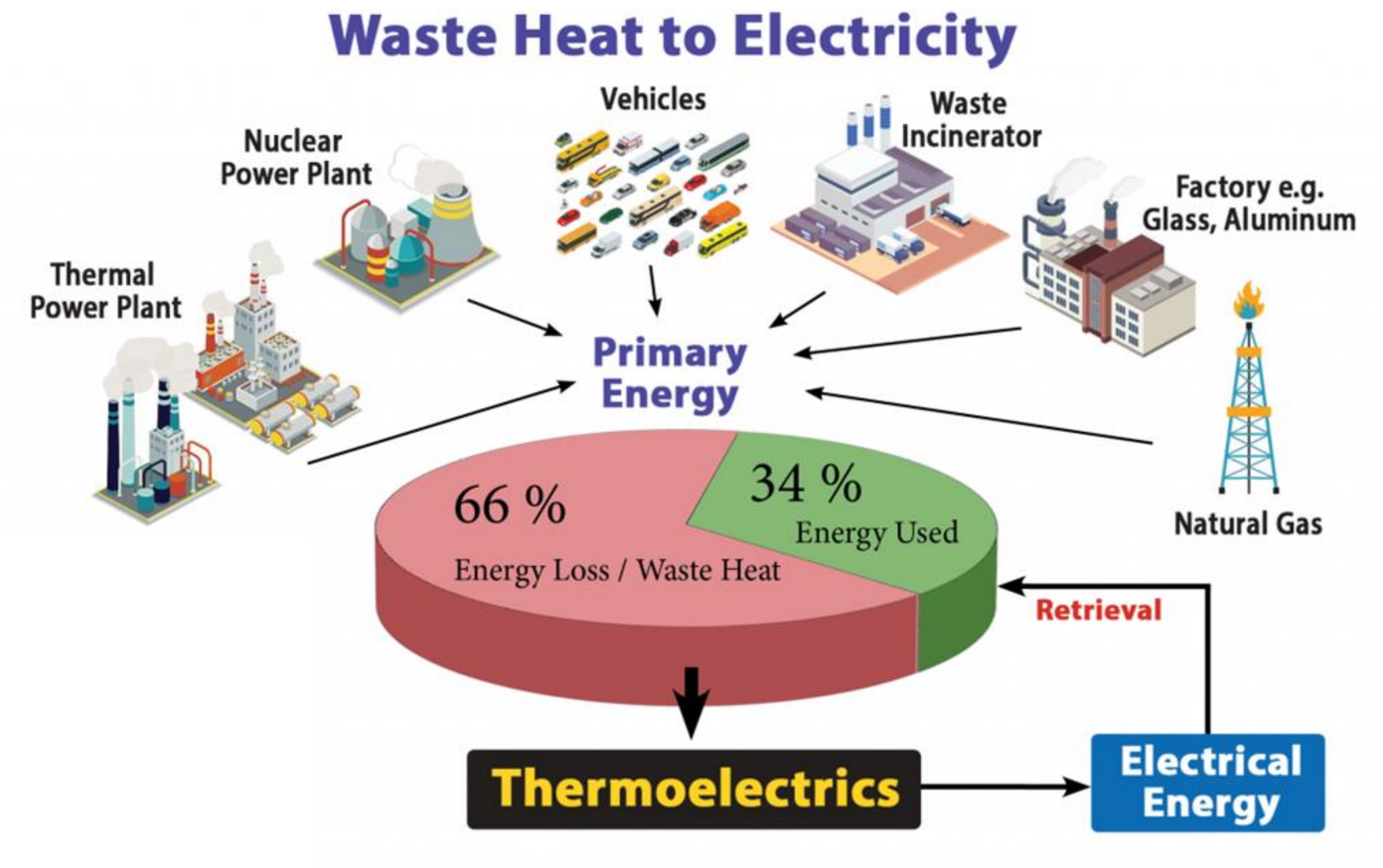
# What can we do with waste heat?

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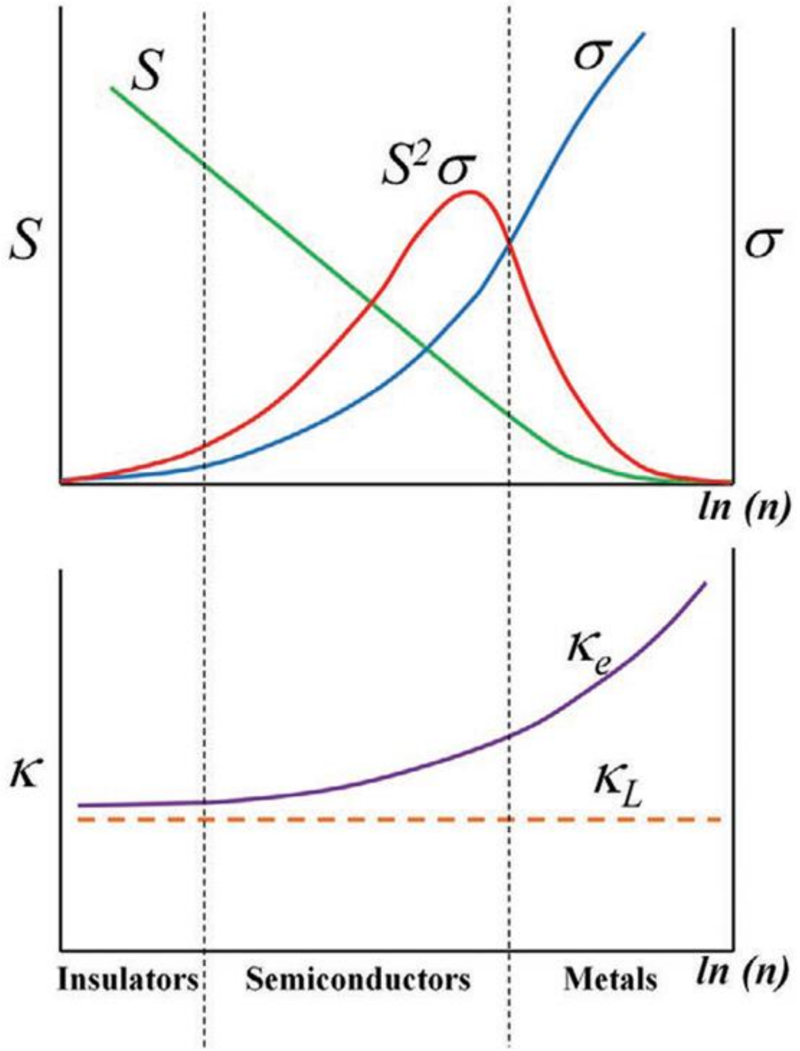
# Efficiency of a thermoelectric material




$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}$$

Temperature difference

Dimensionless Figure of Merit

**ZT = T $S^2/\rho\kappa$ = T $S^2\sigma/\kappa$**

High Seebeck coefficient

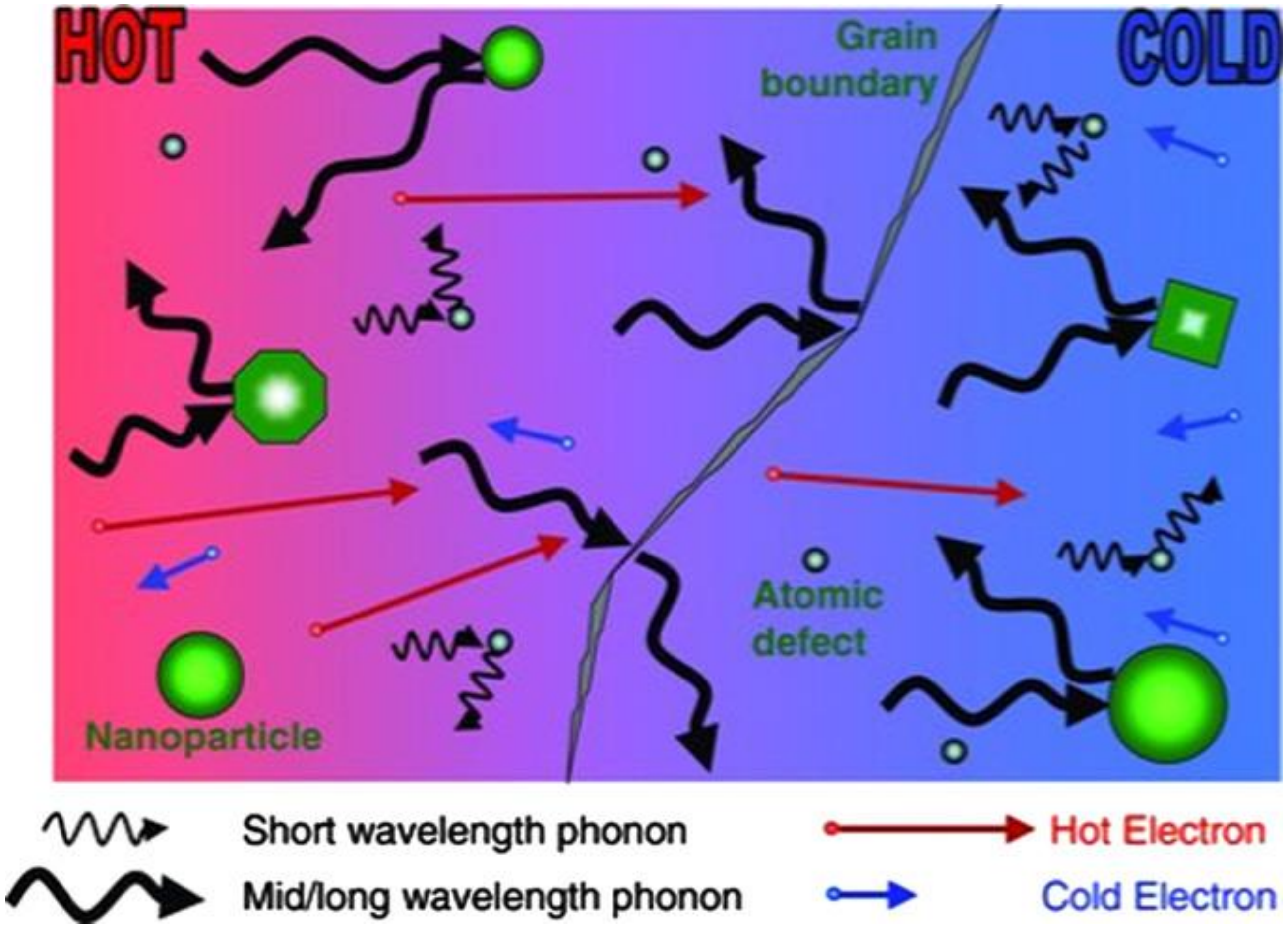
High electrical conductivity

Low thermal conductivity

# Phonon scattering in thermoelectrics

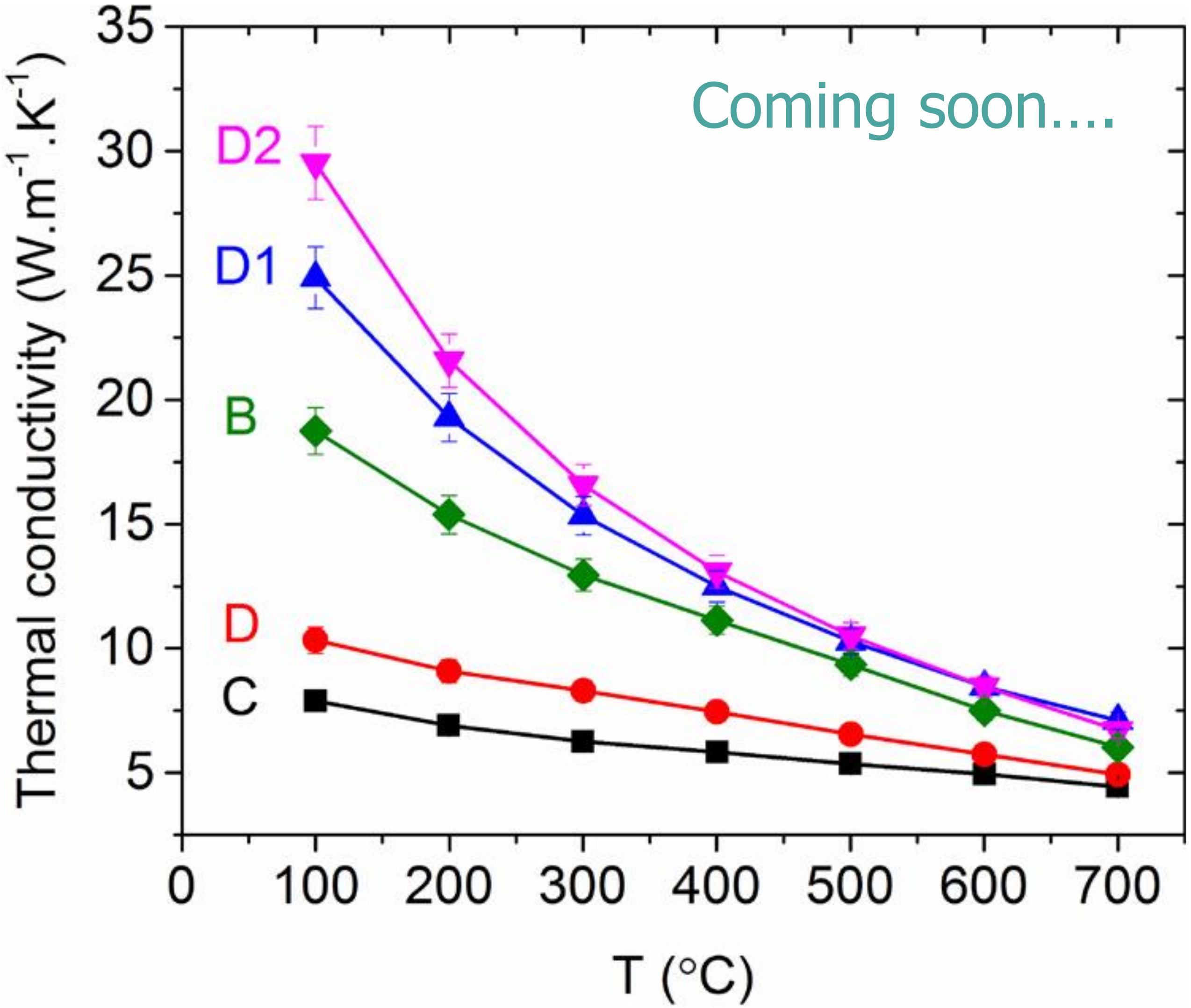
short wavelength phonons
→ atomic defects

mid- and long-wavelength phonons
→ nanoparticles, grain boundaries




Vineis *et al. Adv. Mater.* **22** (2010).

# ZnO: thermal conductivity

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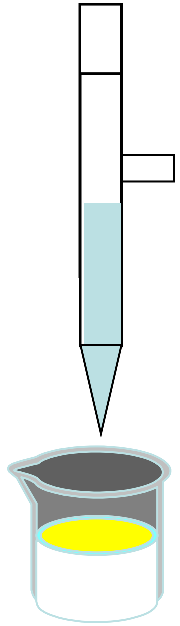
Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

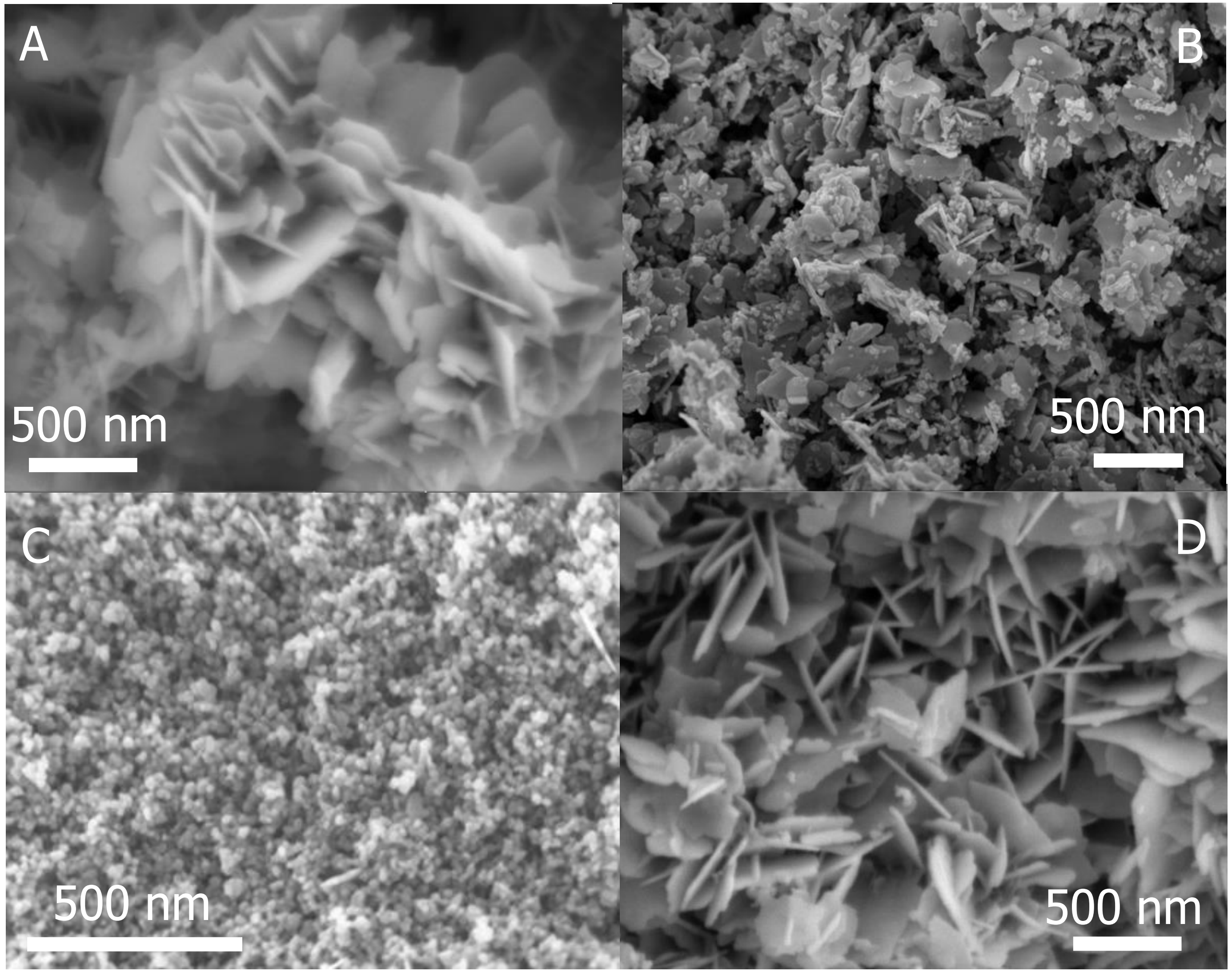
# ZnO: controlled precipitation in aqueous solution



125 mL
4 M NaOH

100 mL
1 M $Zn(NO_3)_2 \cdot 6H_2O$
(+ 2% $AlCl_3$)

Dropwise addition, stirring, 20°C
Centrifugation (4000 rpm - 5 min)
Washing 4 times




Giovannelli *et al.* Powder Technol. **262** (2014).

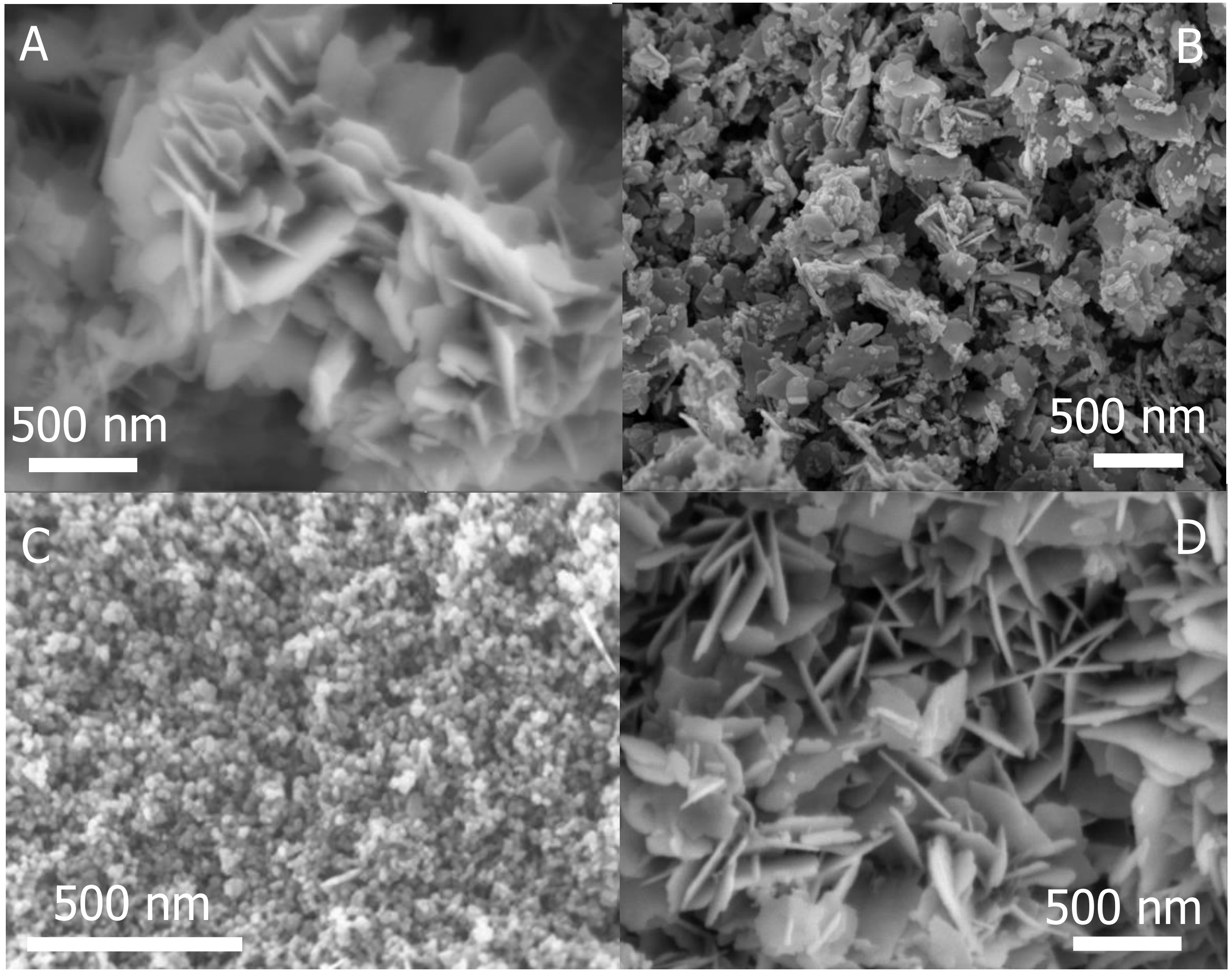
# ZnO: different starting morphologies

A Pure ZnO, 20°C
→ sand rose morphology

B Al-doped ZnO, 20°C
→ platelets and nanoparticles

C Al-doped ZnO, 60°C
→ isotropic nanoparticles

D Al-doped ZnO, 20°C
(90% water + 10% ethanol)
→ sand rose morphology

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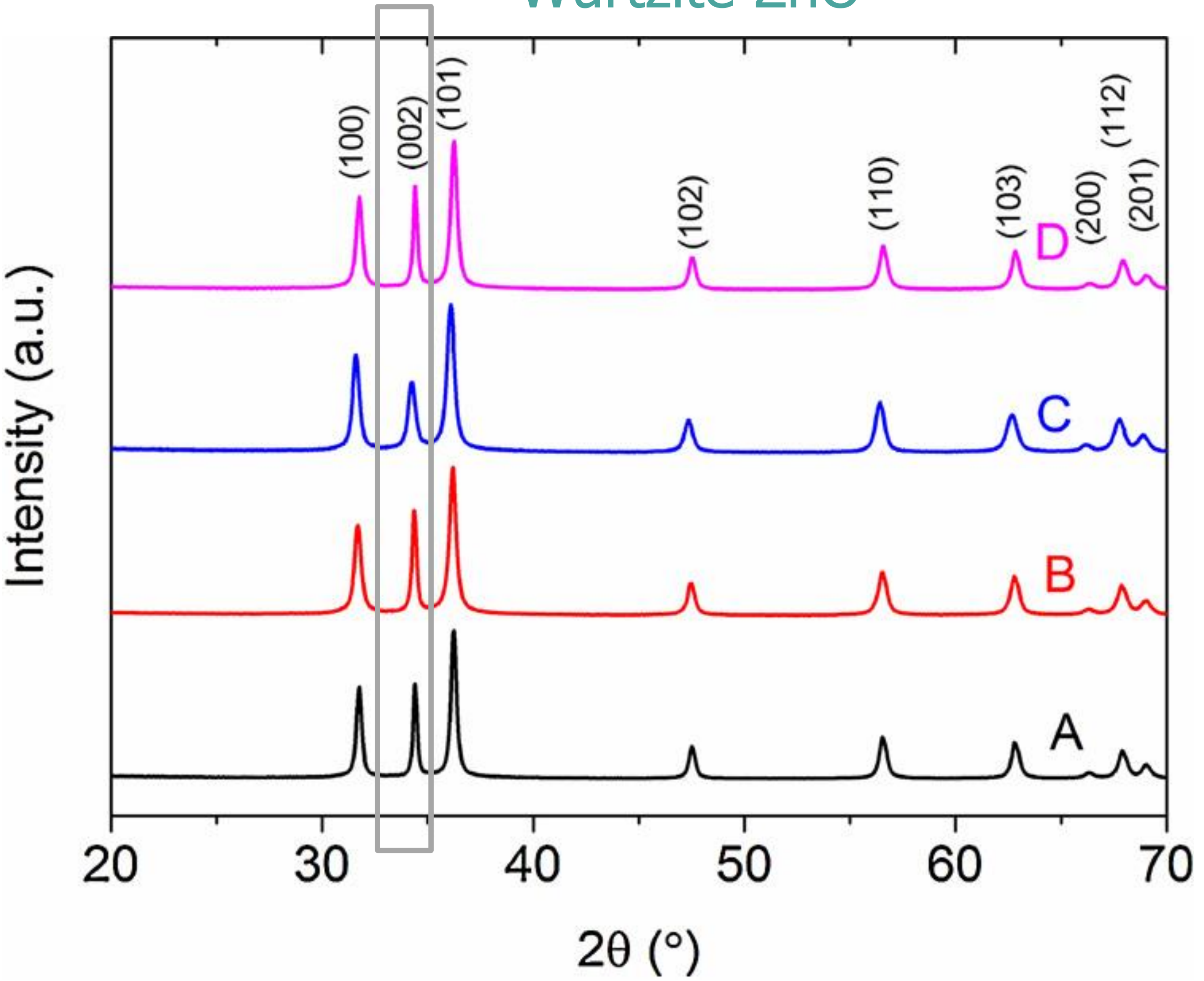
Wurtzite ZnO

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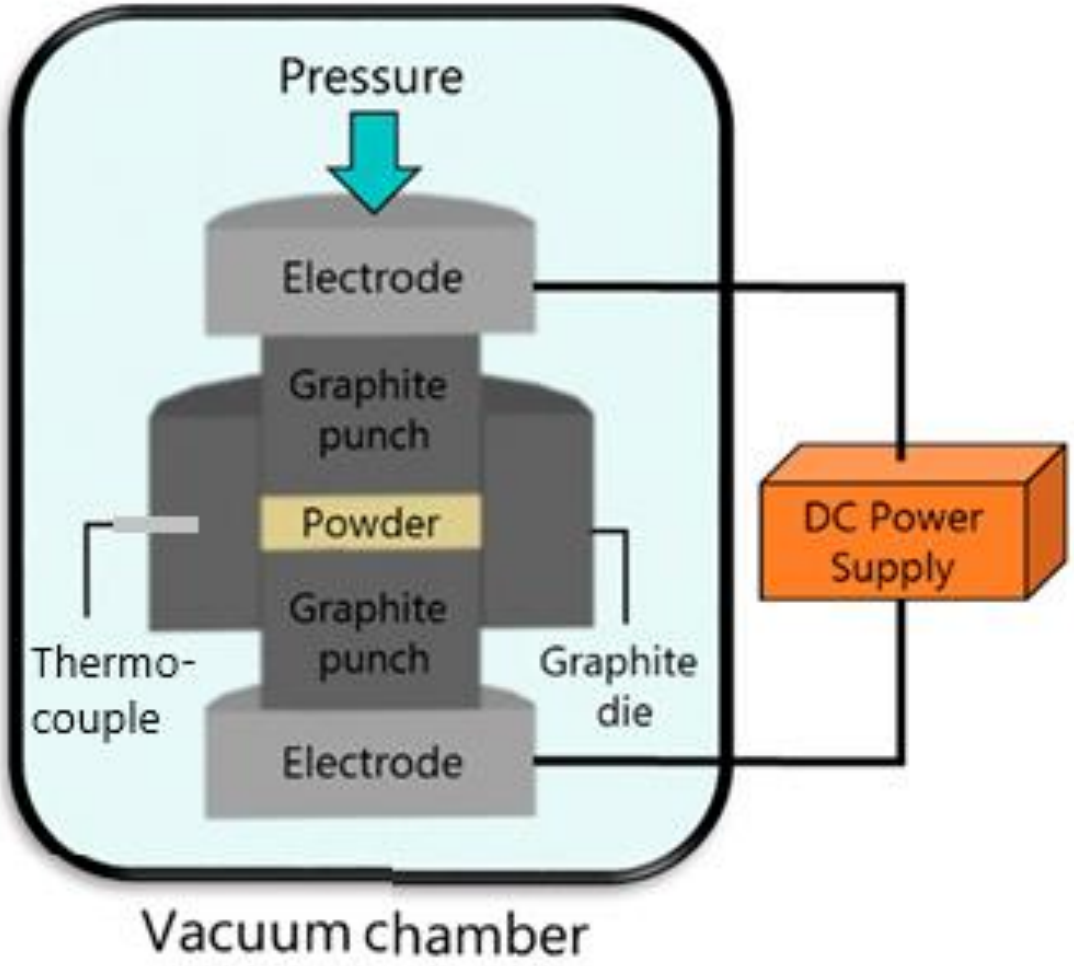
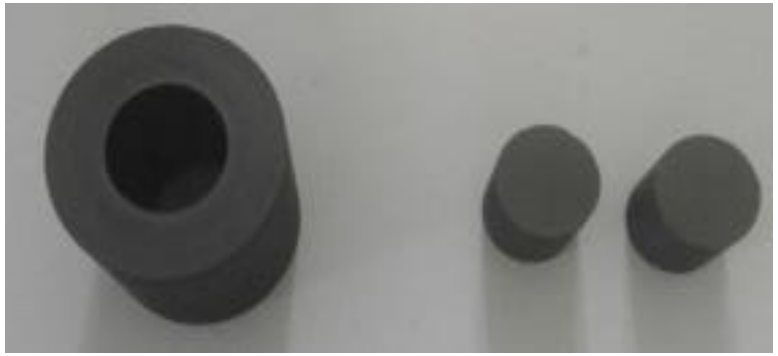
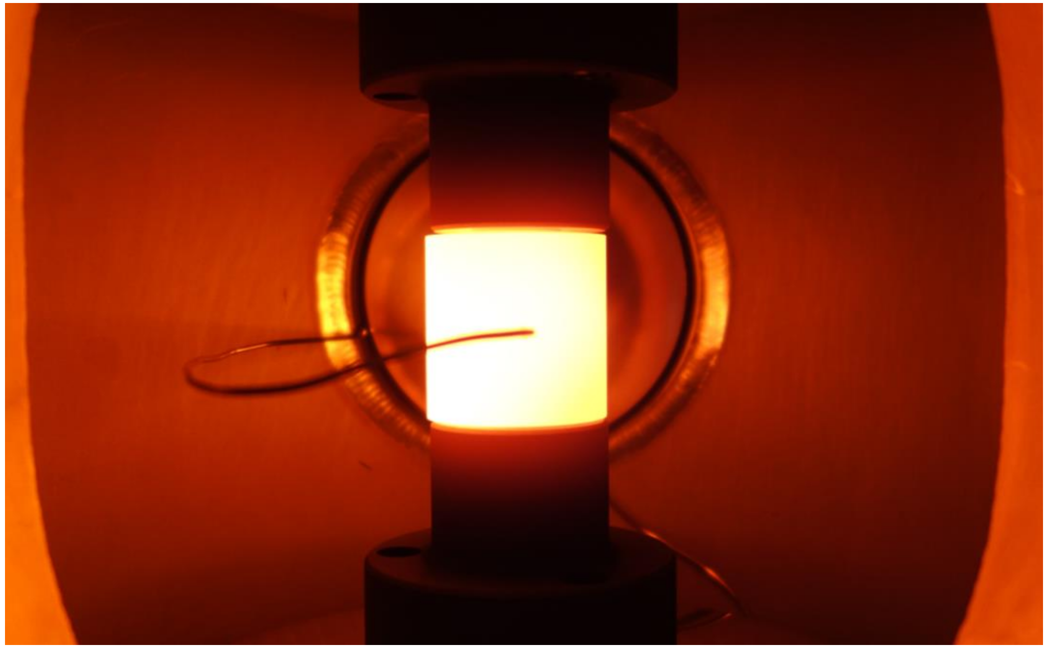
Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# Spark plasma sintering

Advantages: fast, limited grain growth, limited evaporation, high densities
Drawbacks: carbon contamination, reducing environment, sintering process unclear

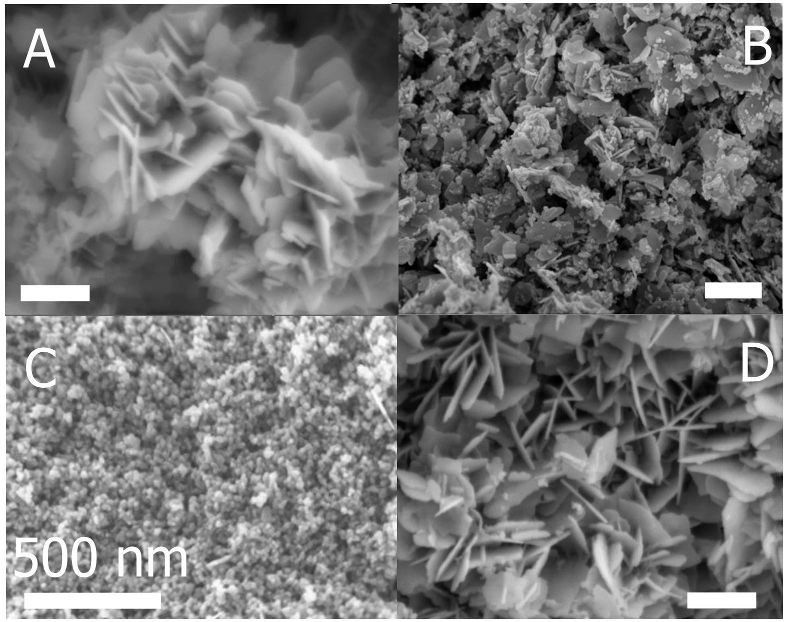




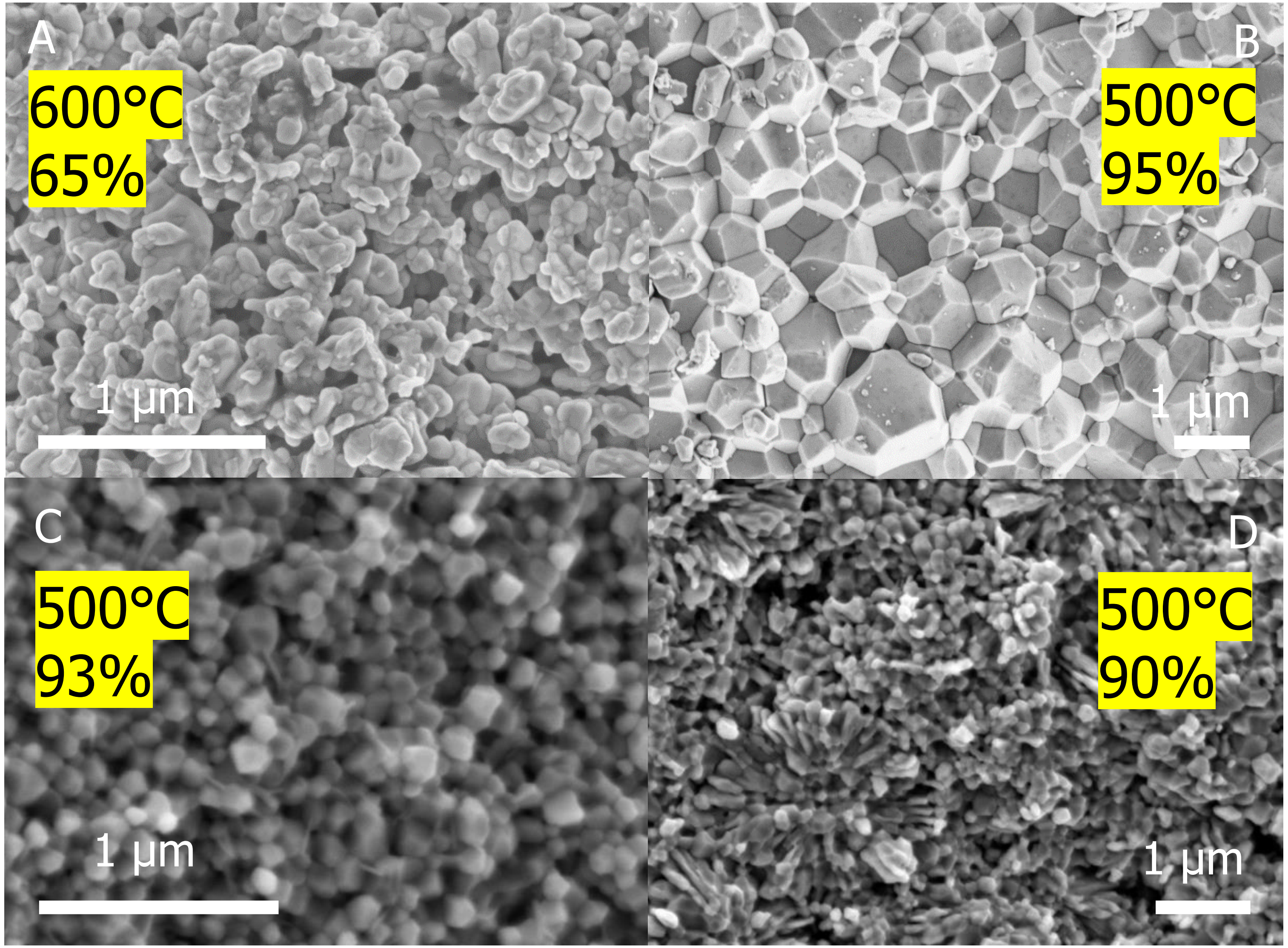
Phuah *et al. Materials* **13** (2020).

# ZnO: after spark plasma sintering




100 Mpa, 100 K min$^{-1}$, 5 min

A porous
B micron-size grains
C 100 nm grains
D isotropic grains (150 nm)
& anisotropic grains (500 nm)

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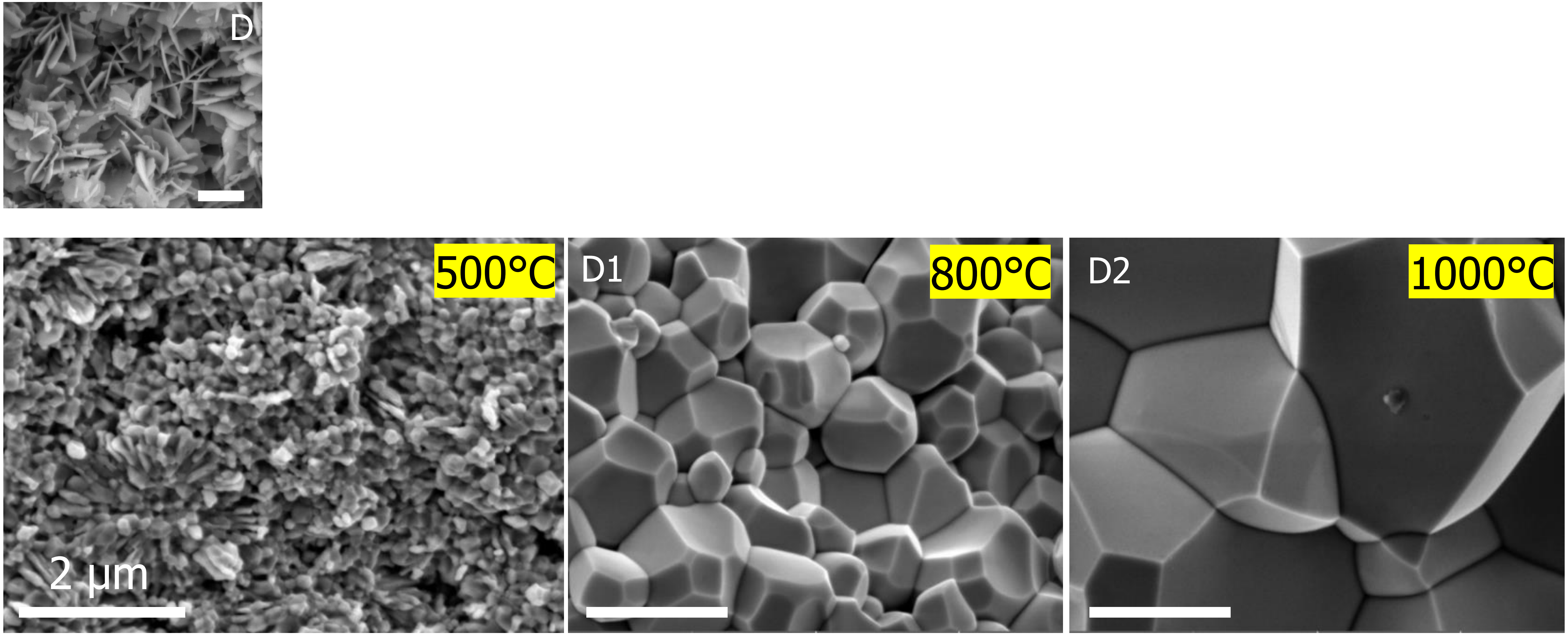
Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: grain growth

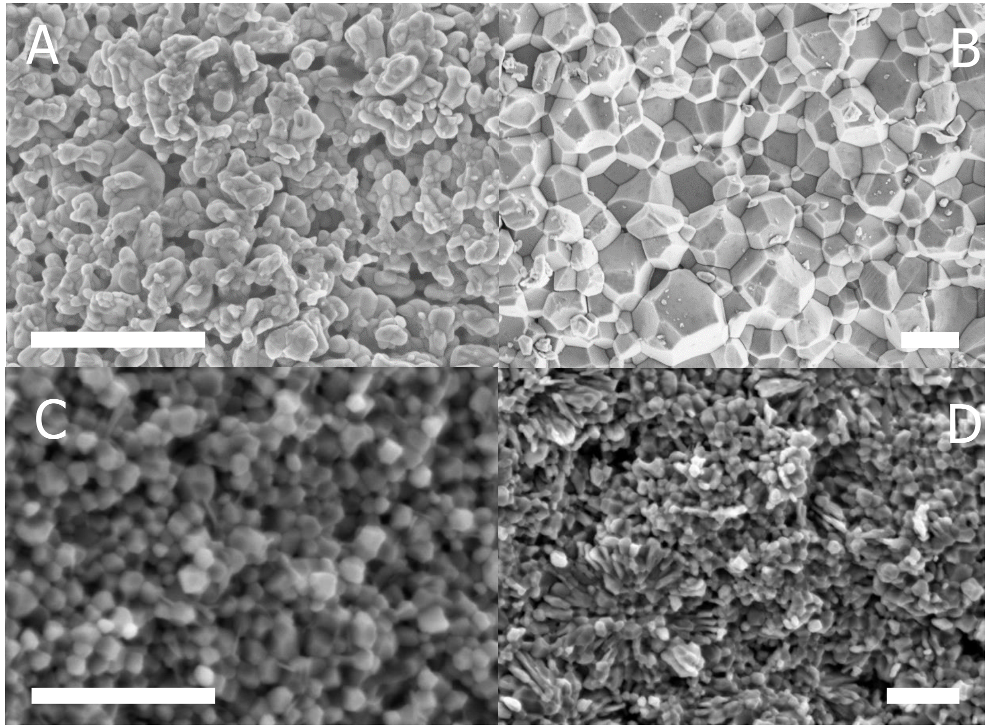


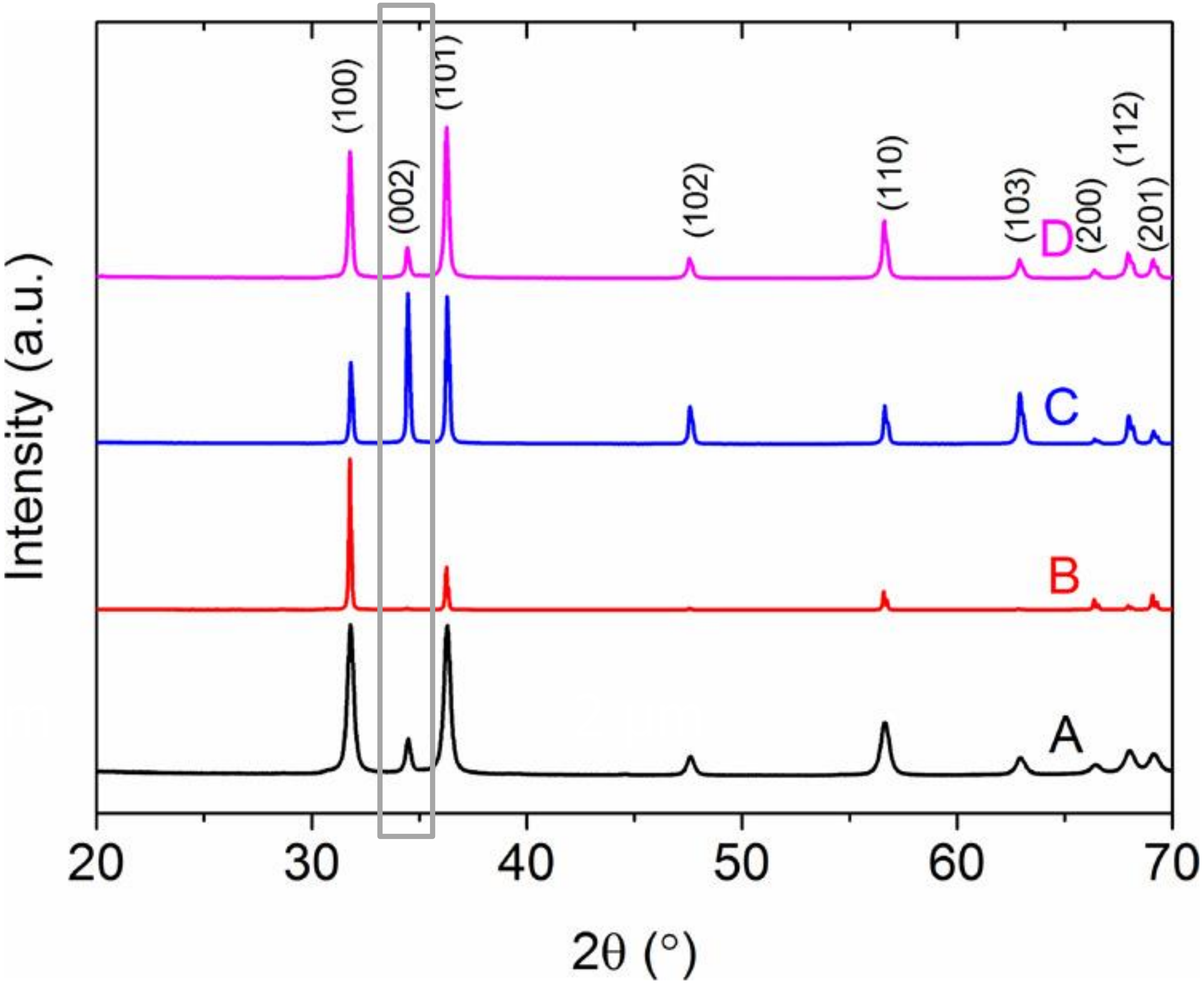

Higher sintering temperature → grain growth

Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: texturation

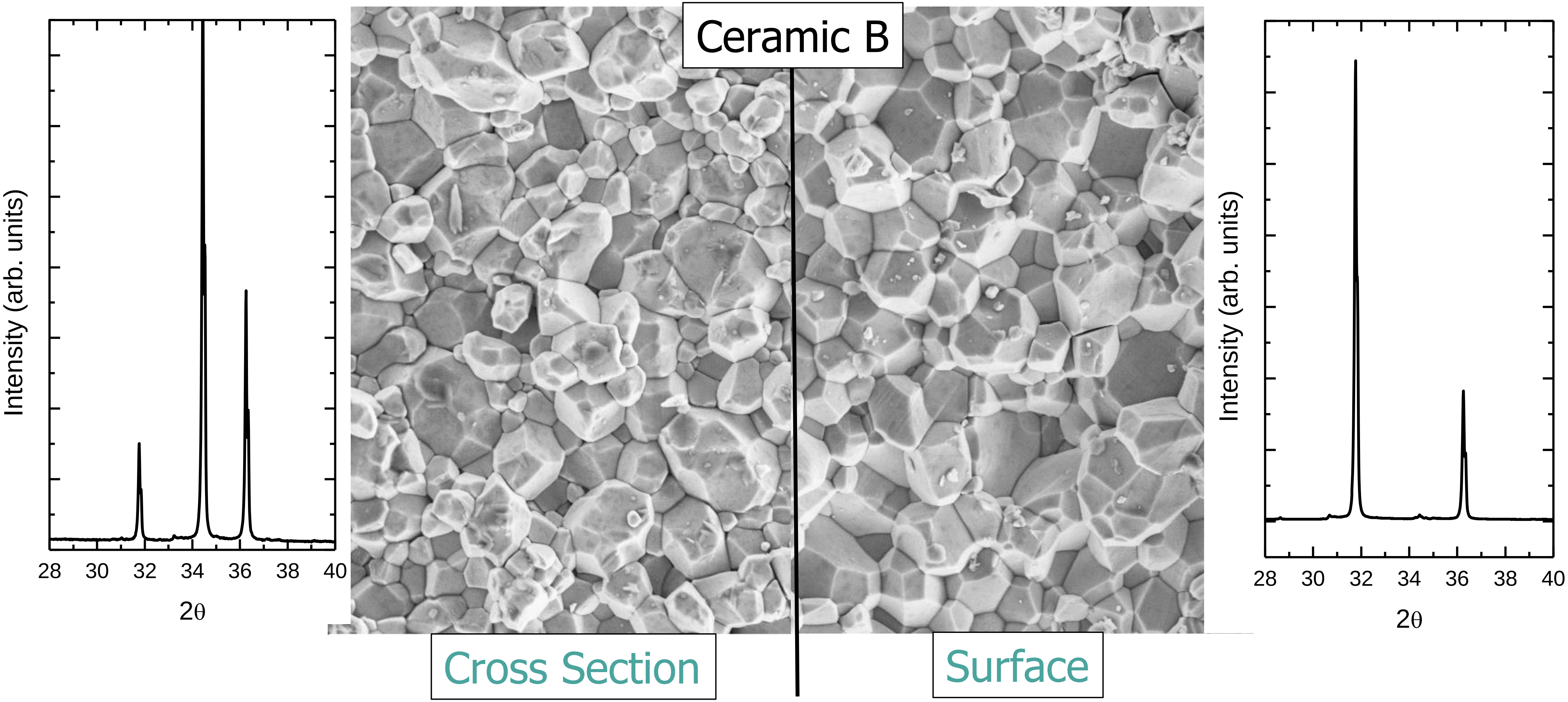
Powders
A sand rose morphology
B platelets and nanoparticles
C isotropic nanoparticles
D sand rose morphology



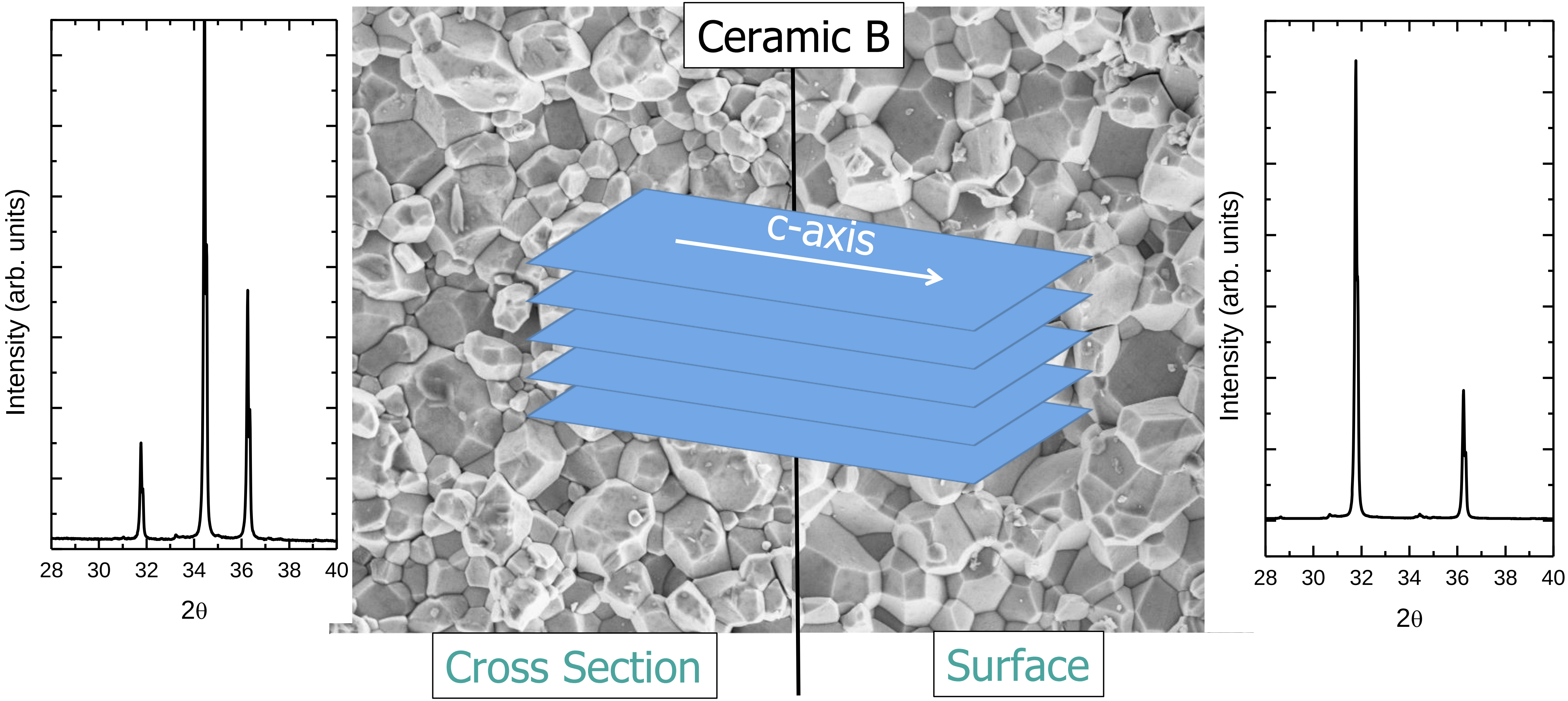

Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: texturation




Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: texturation

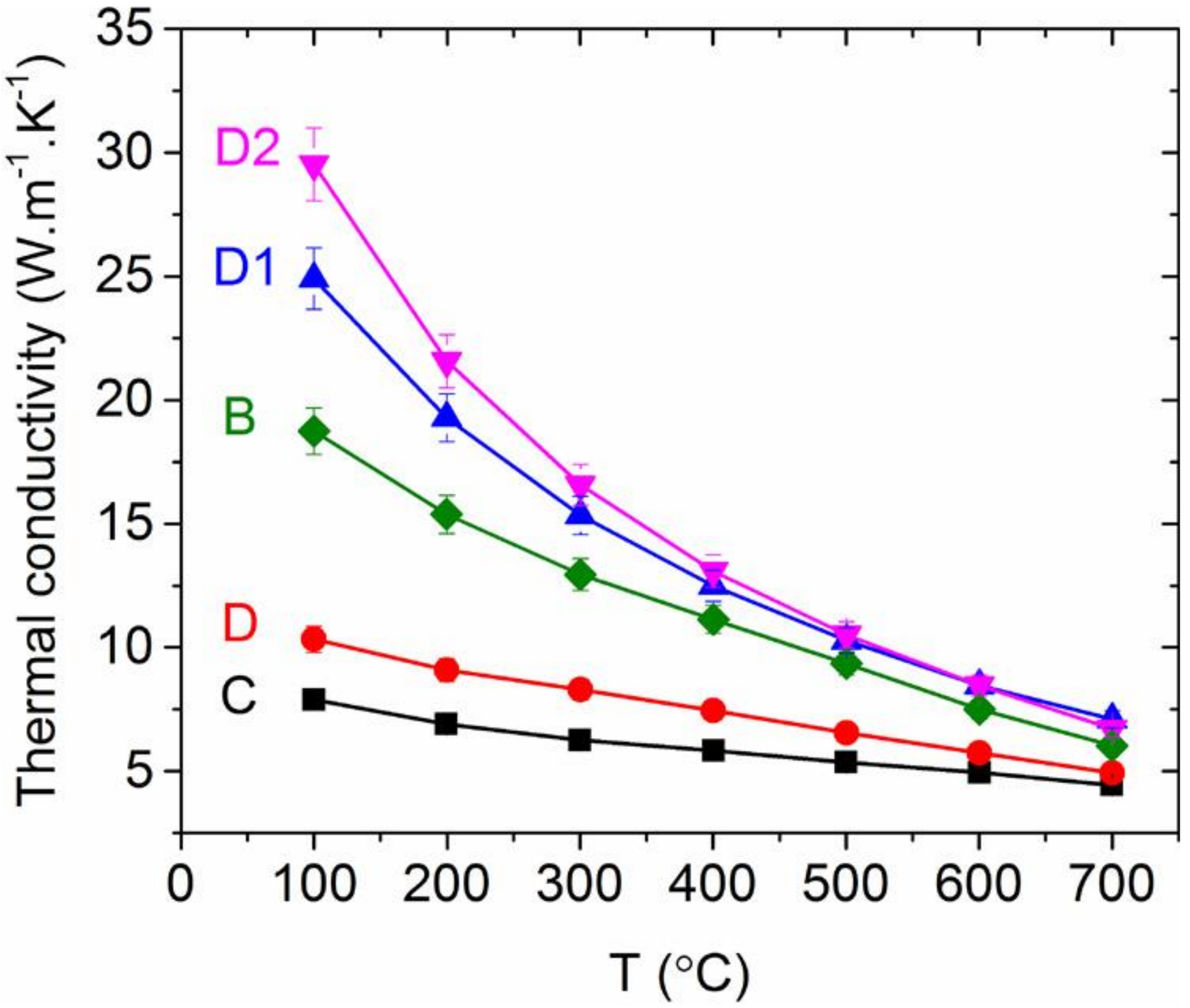



Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: thermal conductivity

| Sample | Average grain size (nm) |
|---|---|
| D2 | 5000 |
| D1 | 1100 |
| B | 700 |
| D | 150/400-700 |
| C | 110 |

The thermal conductivity decreases with decrasing grain size

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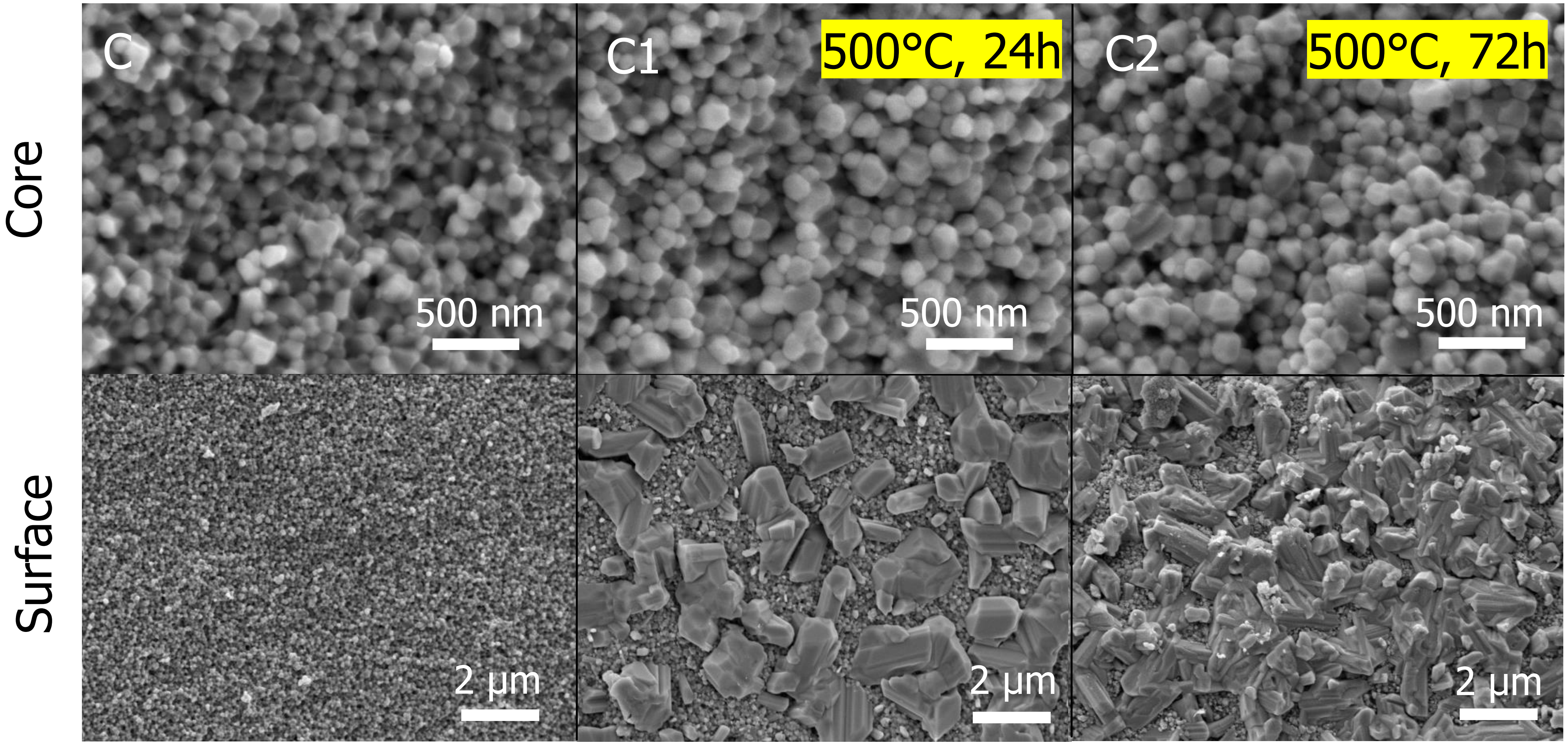
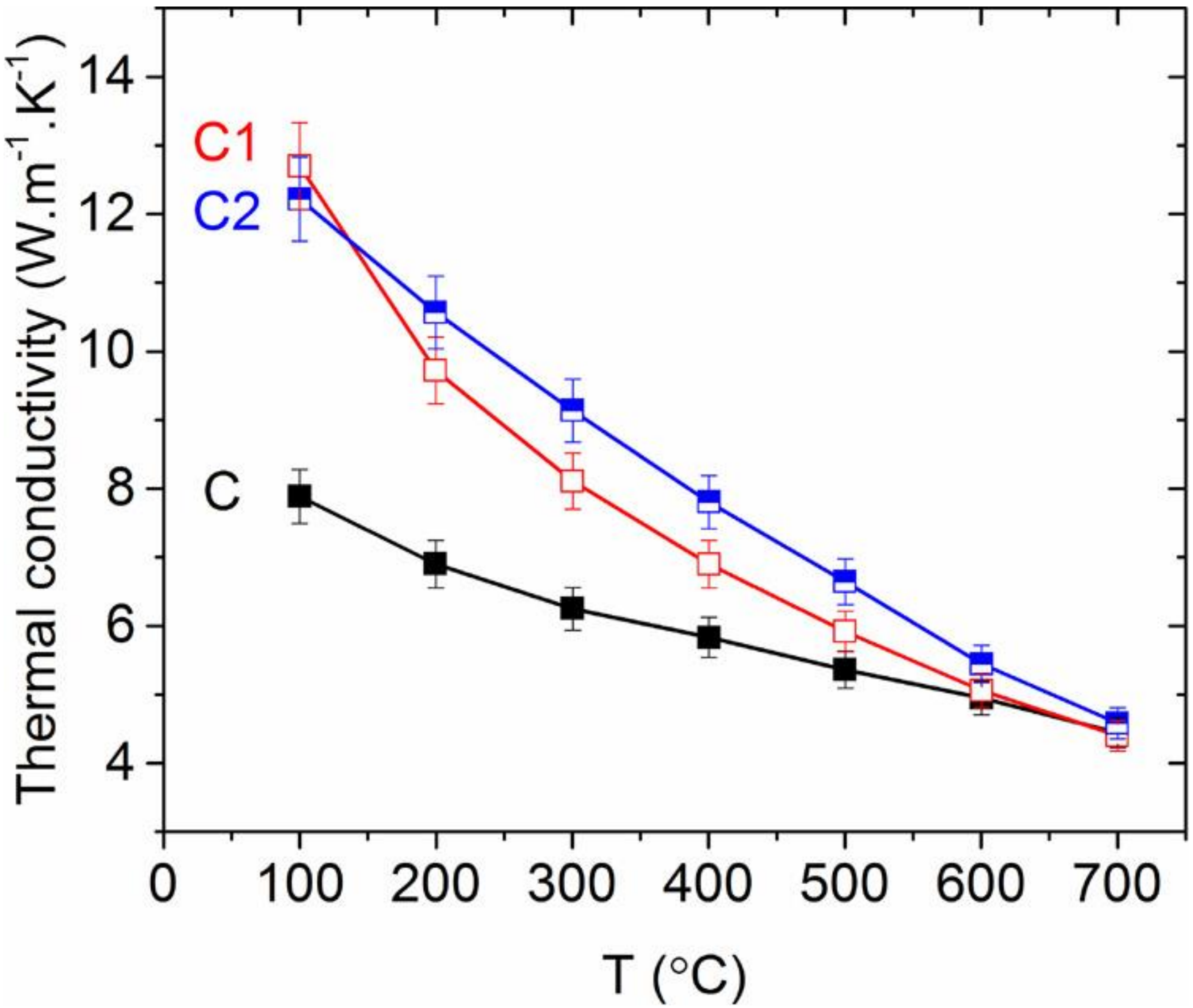
Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: annealing times




Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# ZnO: thermal conductivity

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Giovannelli *et al. J. Eur. Ceram. Soc.* **38** (2018).

# Take home message

The size of the grains in ceramics depends on the size and morphology of the particules in the precursors.

The thermal conductivity decreases with decreasing grain sizes.

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- Basics of ceramics
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- ZnO nanowires
- Spontaneous nanostructuration

Thermal conductivity

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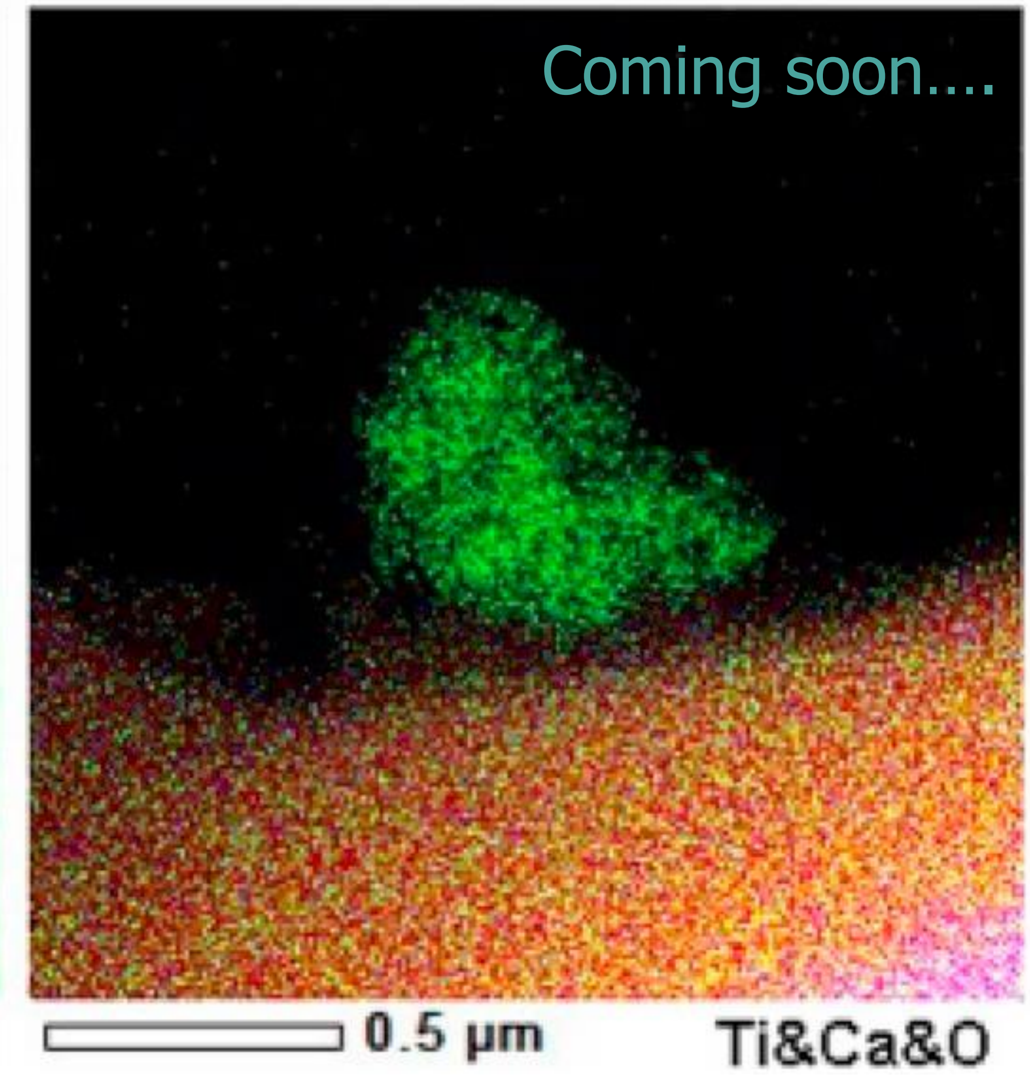
# Exsolution



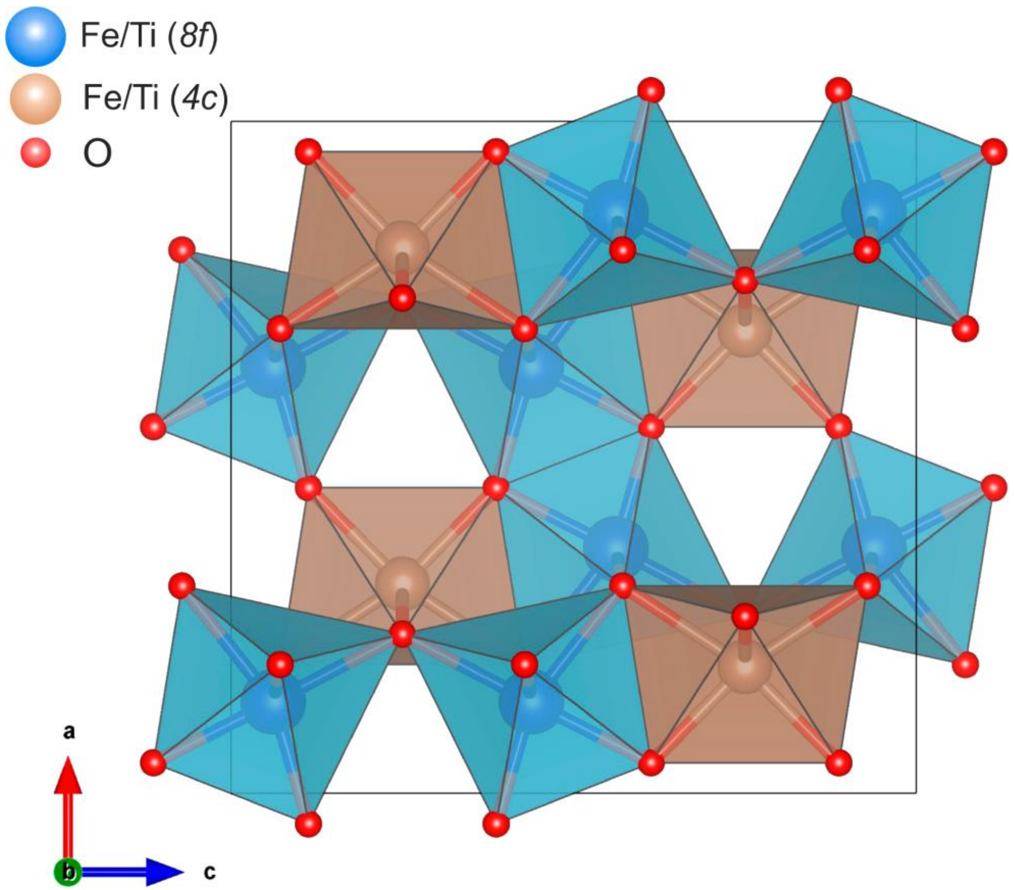

Chen *et al. Materials Characterization* **149** (2019).

# Pseudobrookite

$Fe_2TiO_5$

Orthorhombic (Bbmm space group)
Fe preferentially occupies 4c position
n-type semiconductor

High values of Seebeck coefficients:
-100 to -320 µV $K^{-1}$ [286-1000 K]

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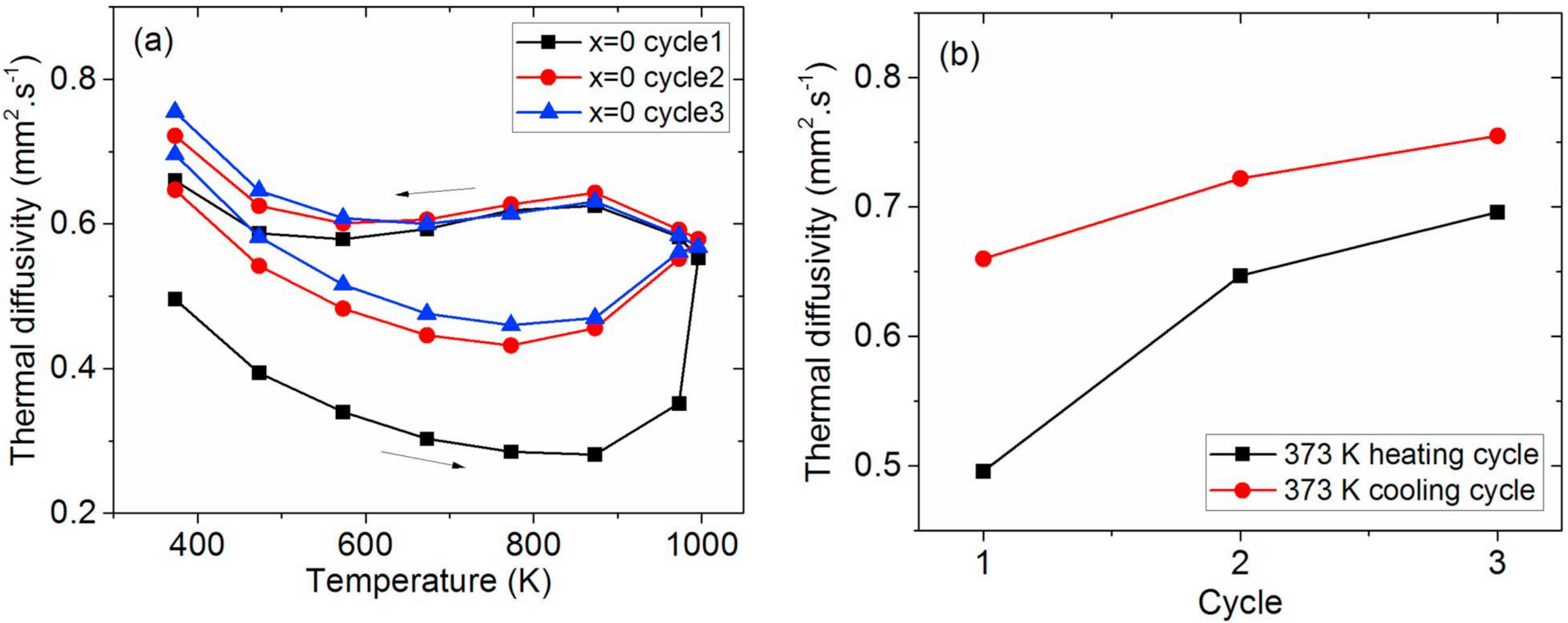
Seitz *et al. Inorg. Chem.* **55** (2016). Cleveland *et al. J. Am, Ceram* **478** (1978).

# Thermal diffusivity upon cycling

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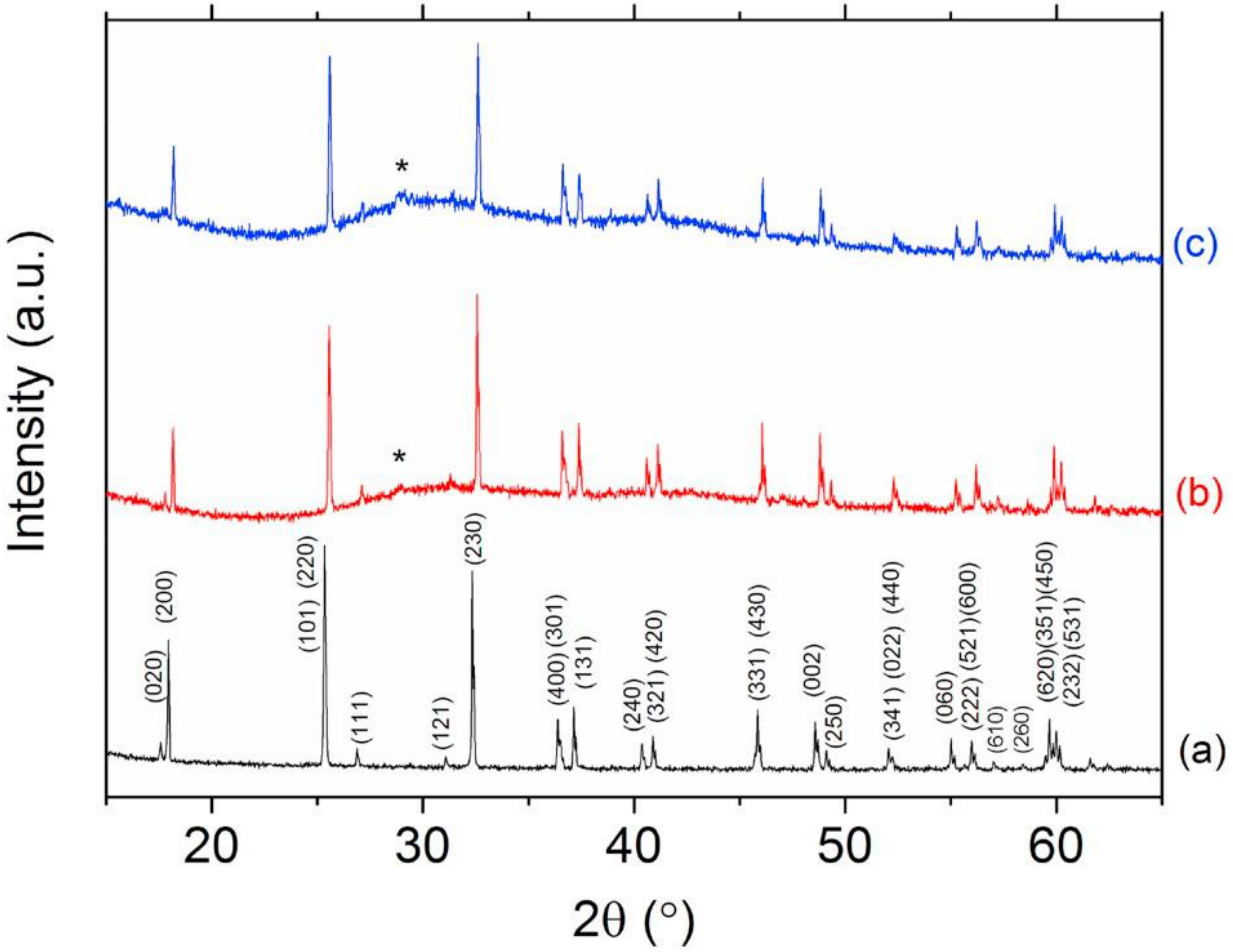
Chen *et al.* *Materials Characterization* **149** (2019).

# X-ray diffraction after cycling

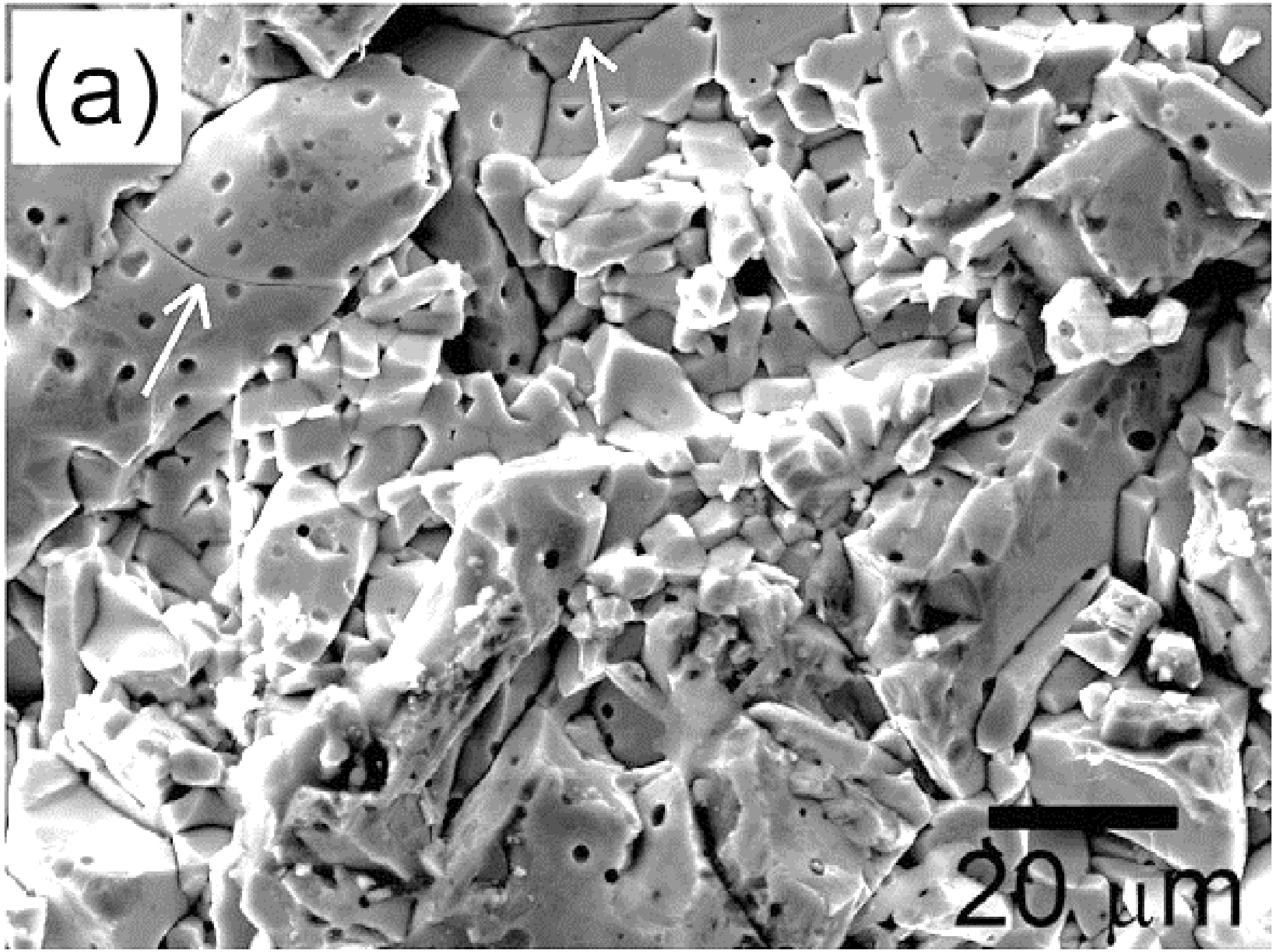



after 3 cycles

initial

Chen *et al. Materials Characterization* **149** (2019).

# Thermal diffusivity: influence of cracks

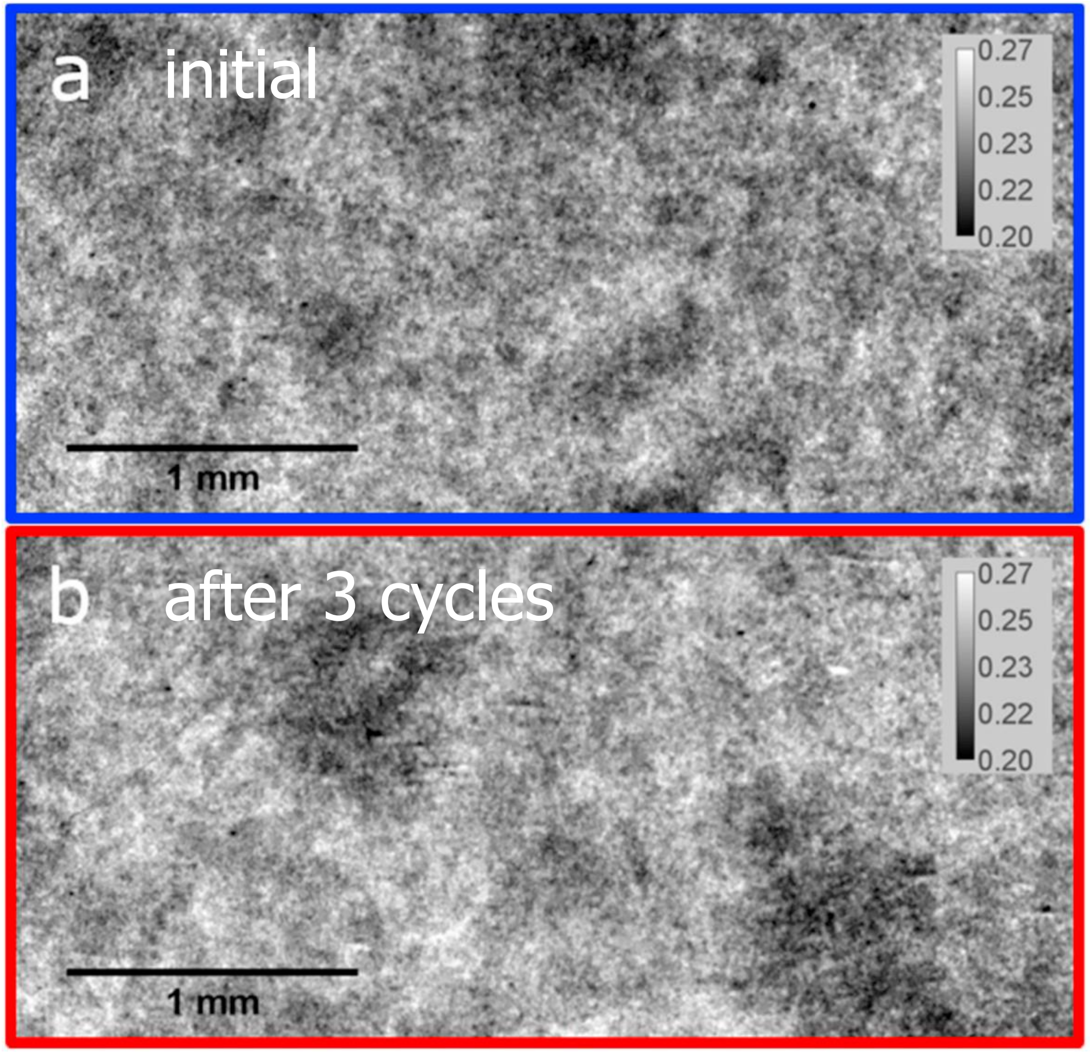


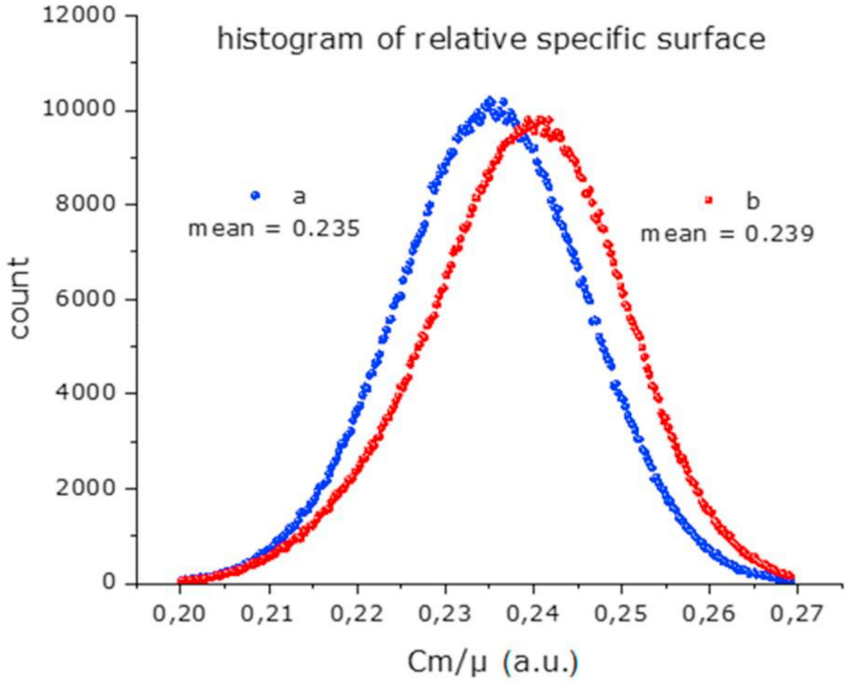

High degree of anisotropy in thermal expansion → formation of microcracks during cooling

Chen *et al. Ceram. Int.* **44** (2018).

# X-ray refraction radiographs

## Relative specific surface

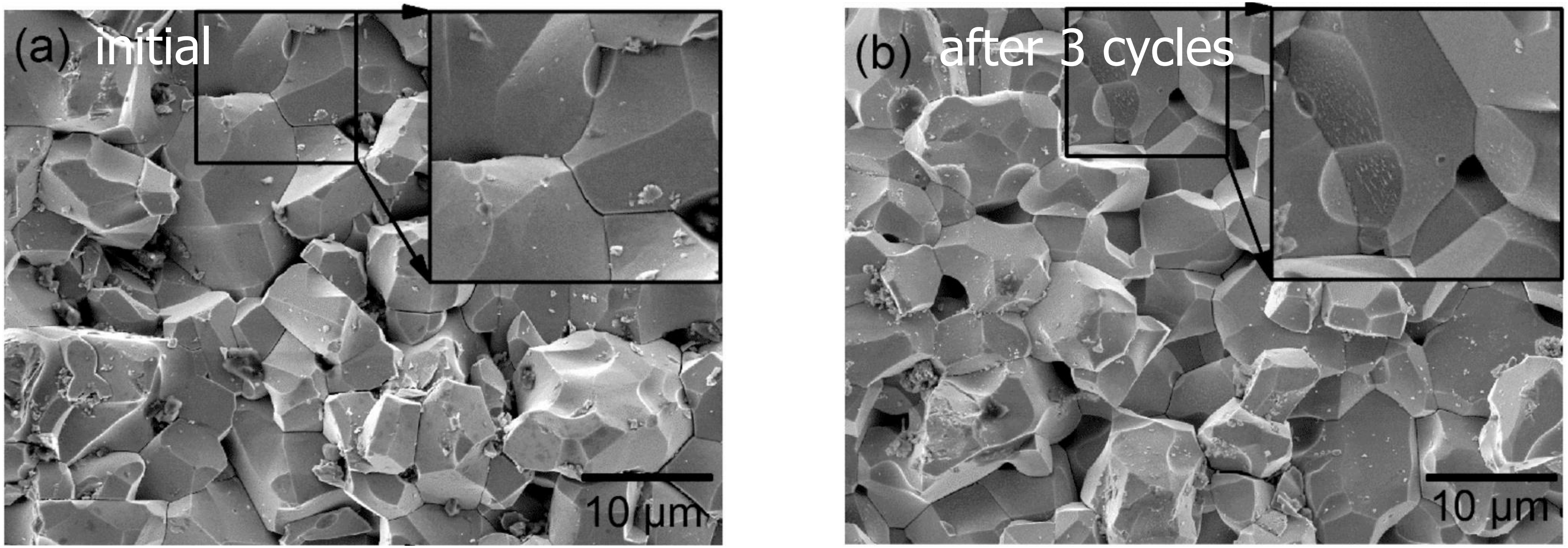



Increase of specific surface during cycling

Chen *et al. Materials Characterization* **149** (2019).

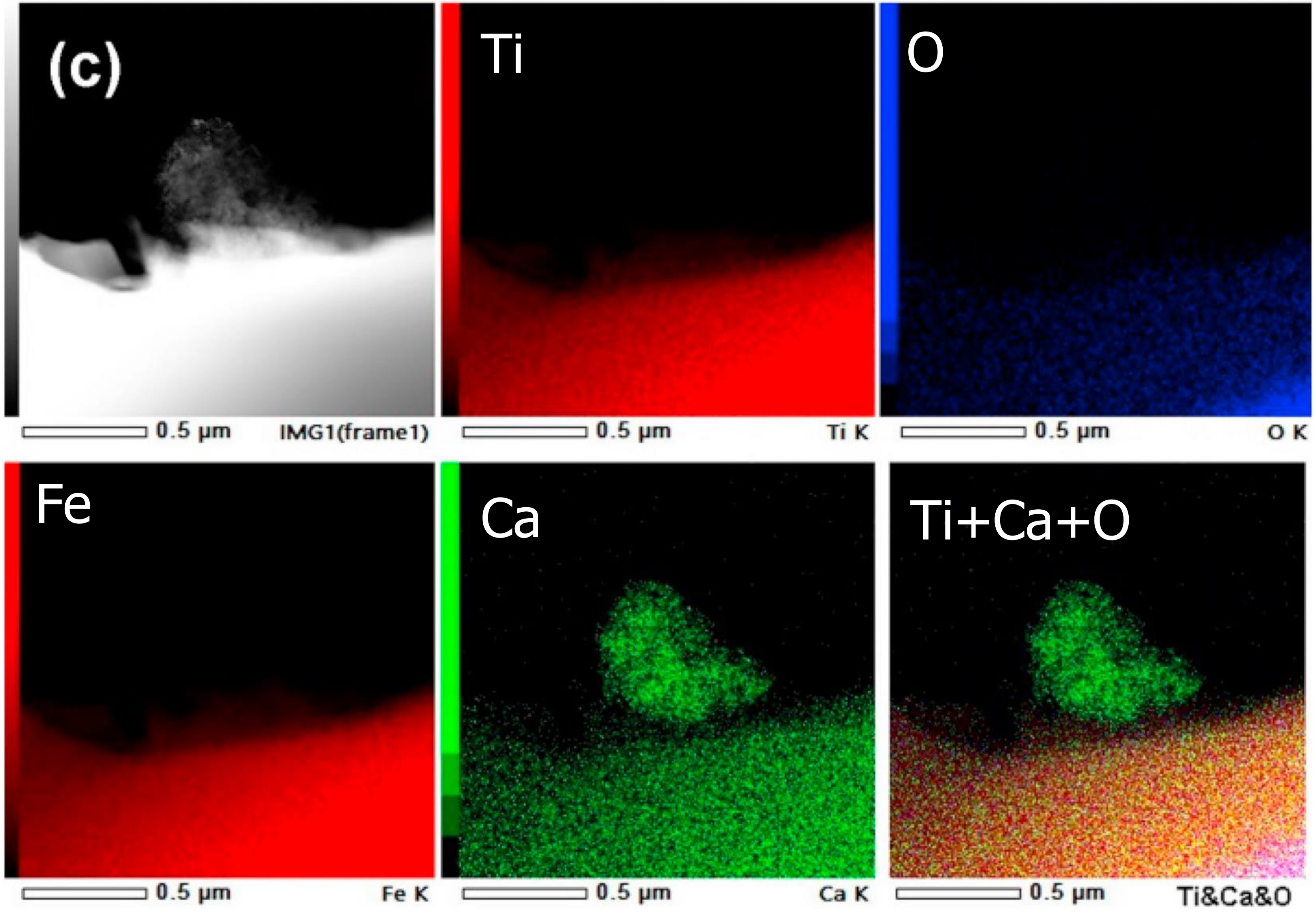
# X-ray refraction radiographs




nanocrystals at grain boundaries

Chen *et al. Materials Characterization* **149** (2019).

# Transmission Electron Microscopy images




$Fe_2TiO_5$ with higher purity and better crystallinity is then obtained
→ higher thermal diffusivity



Chen *et al. Materials Characterization* **149** (2019).

# Take home message

Stop blaming all the time the cracks!

Never trust X-ray diffraction to assess the purity of a compound!

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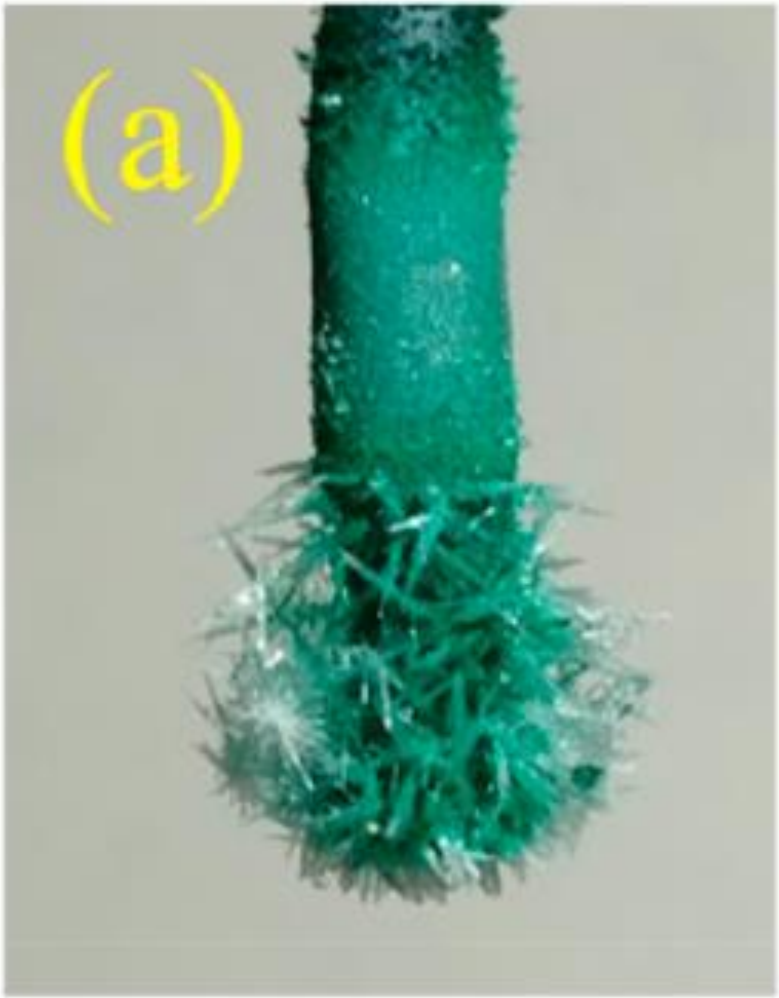
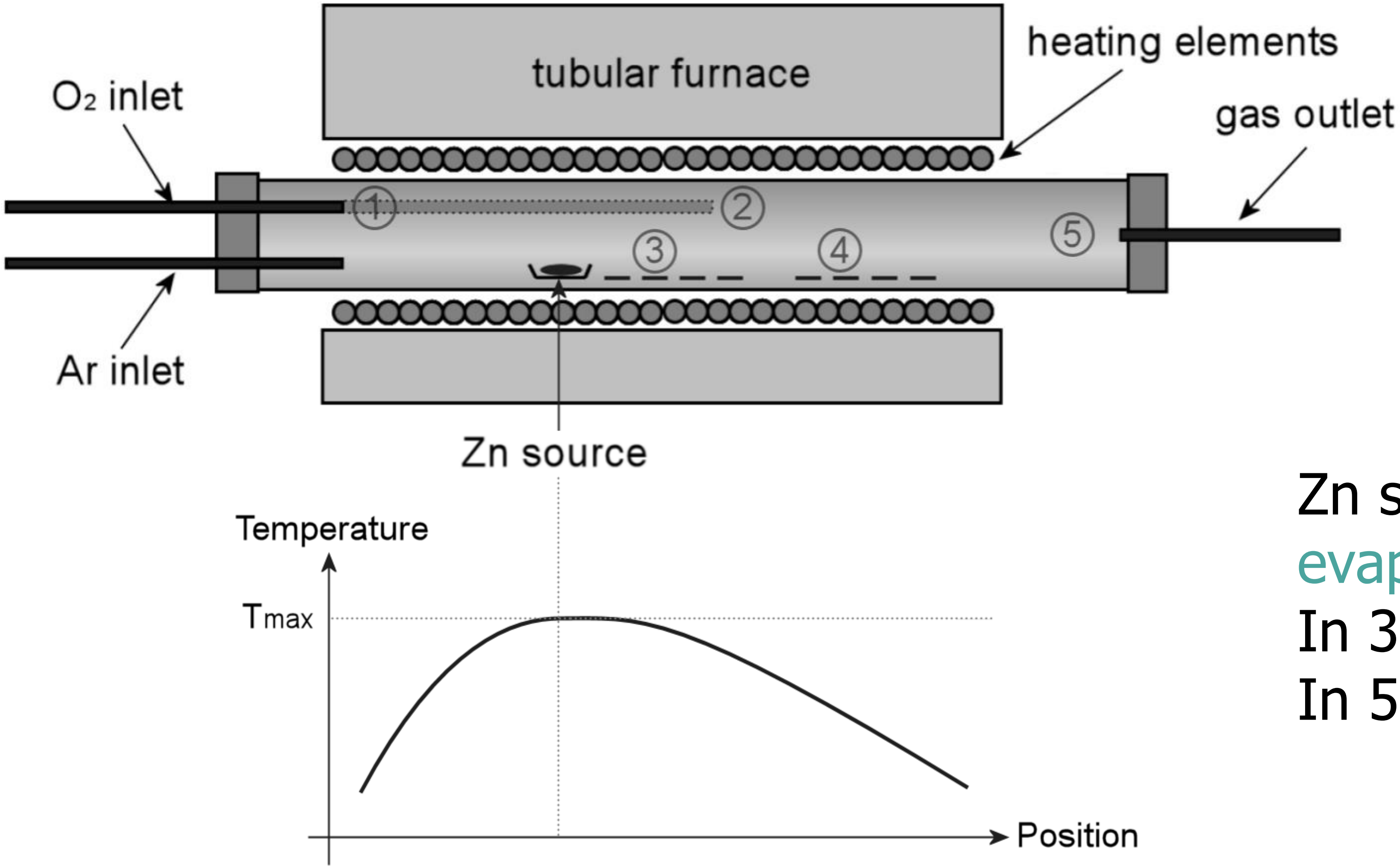
# Doped ZnO wires by…




Coming soon….

Giovannelli *et al. J. Phys. Chem. Solids* **158** (2021).

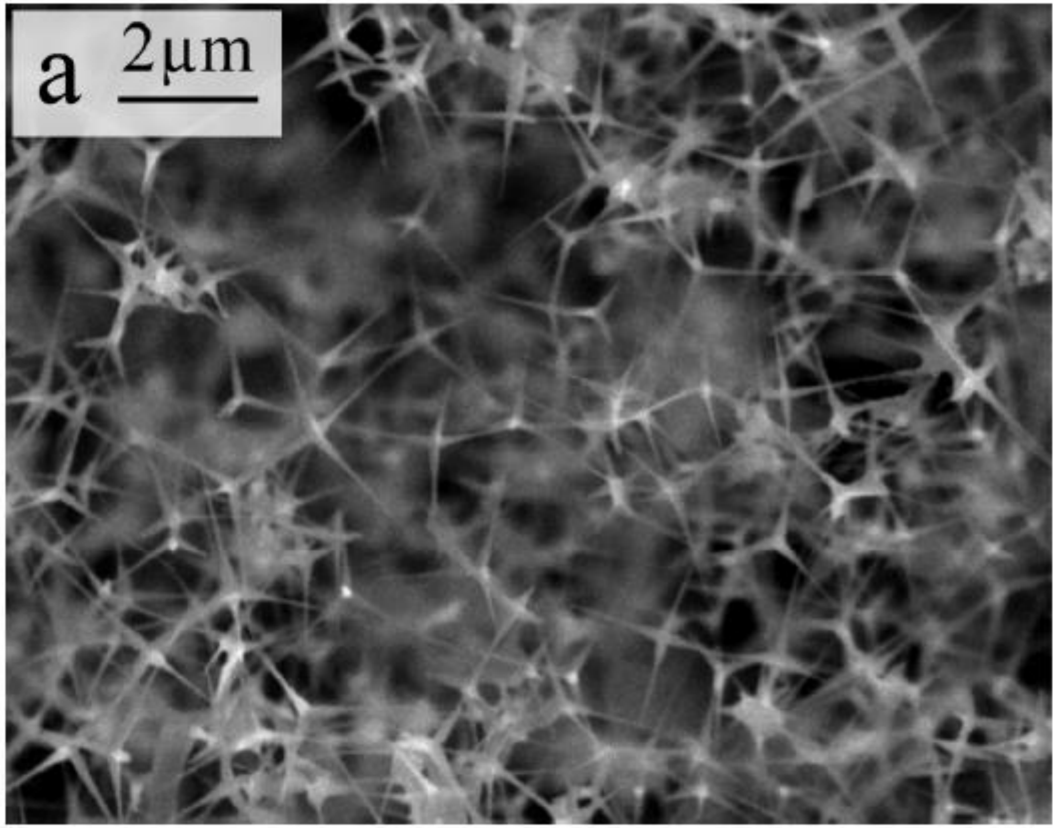
# ZnO wires: standard growth reactor



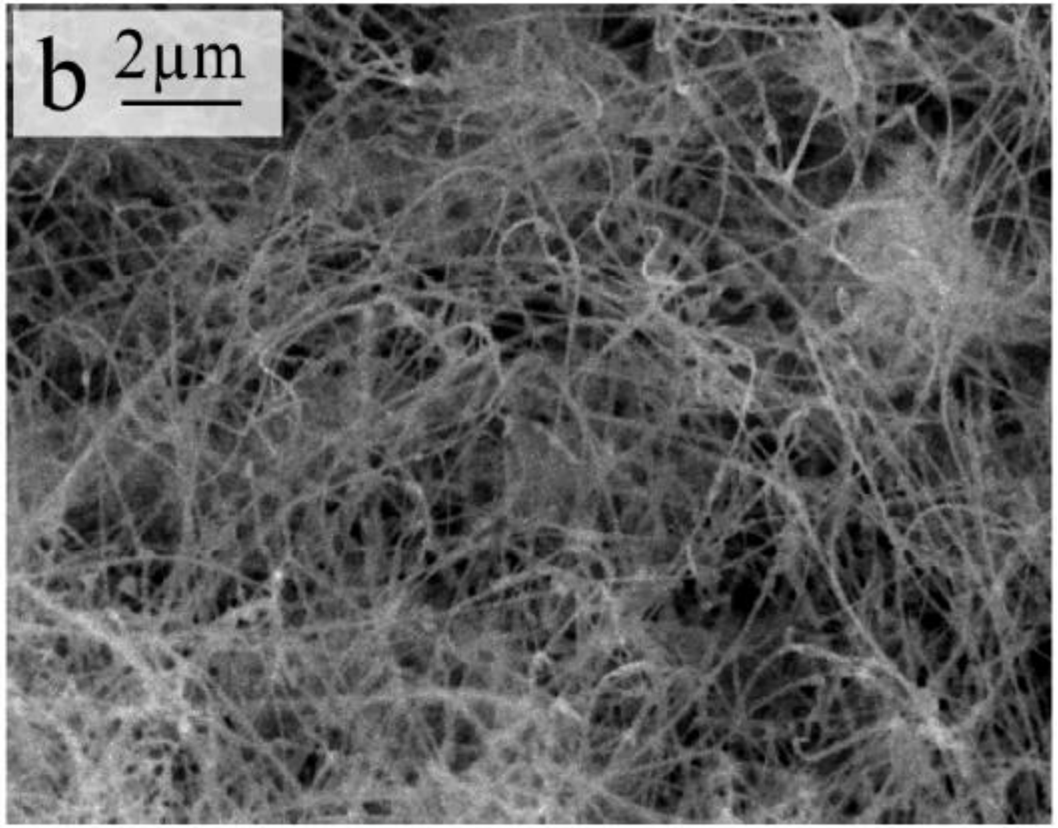

Zn source: polycristalline evaporation
In 3: nanowires
In 5: tetrapods

Calestani *et al. MRS Proc.* **1174** (2009).

# ZnO wires: standard growth reactor



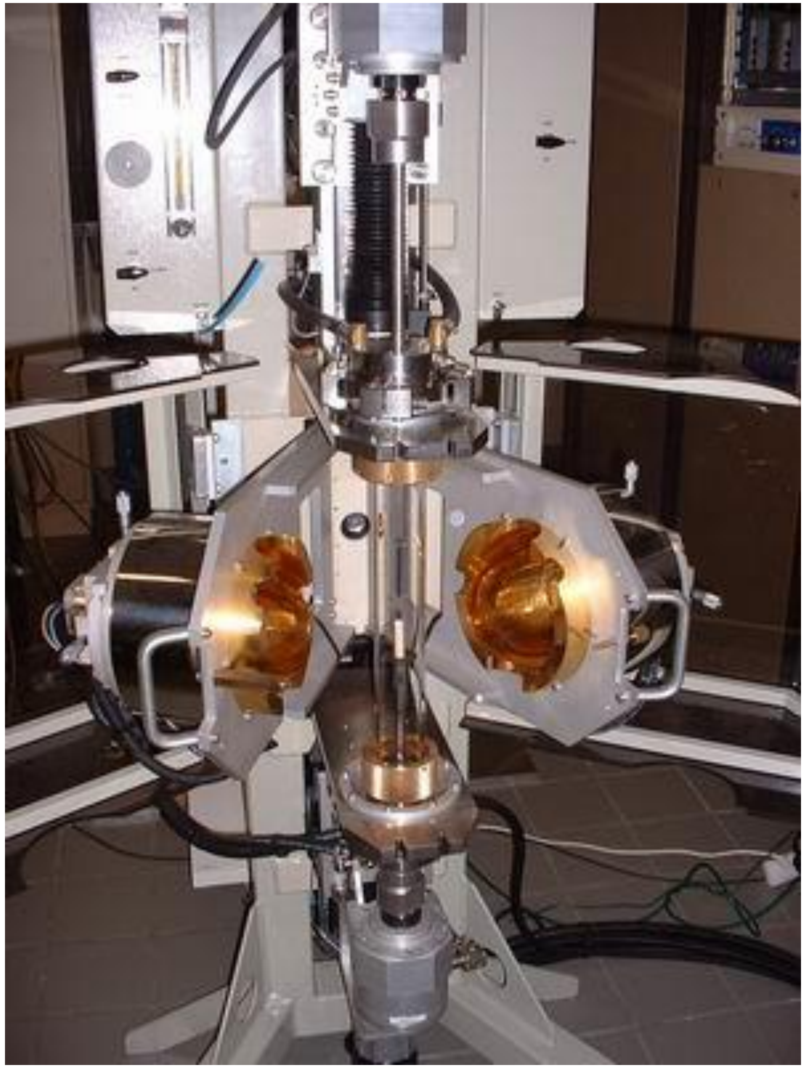

Tetrapods

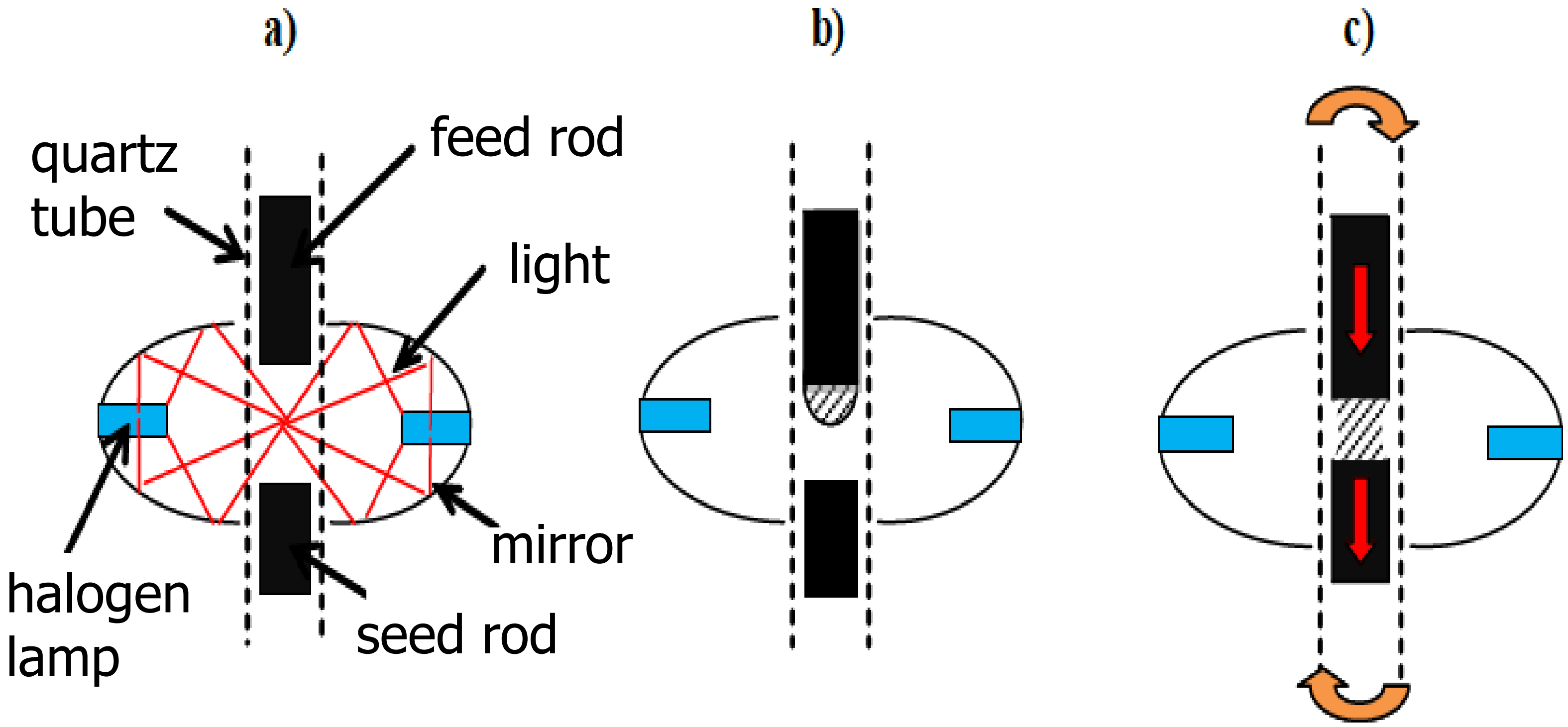



Nanowires

Calestani *et al. MRS Proc.* **1174** (2009).

# Optical furnace






focus → melting of the rod → contact → crystal growth

- power of the lamps
- diameter of the rod

- quality of the seed
- stable melted zone

- speed of rotation and translation

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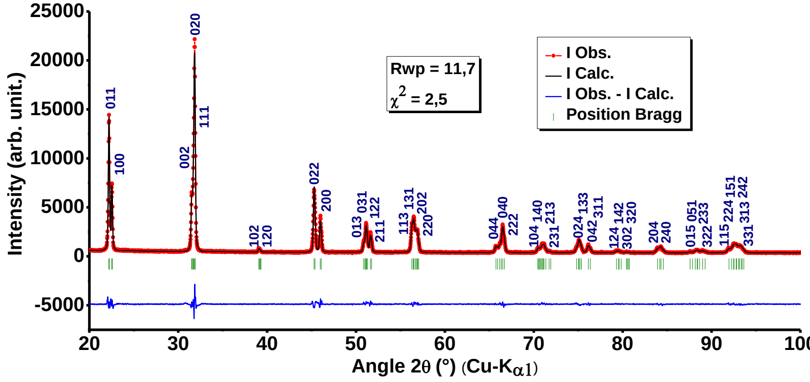
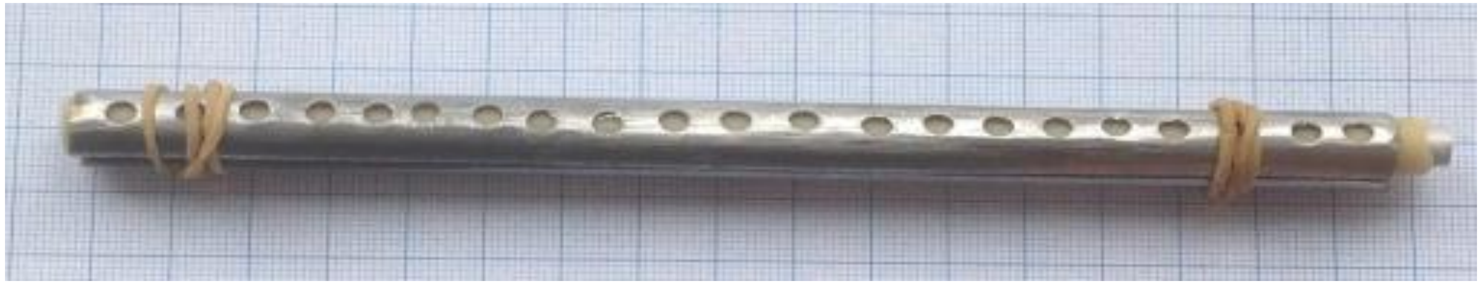
Keck *et al. Phys. Rev.* **39** (1953). Revcolevschi *et al. Progress in Materials Science* **42** (1997).

# Optical furnace: before the growth

## Synthesis of the phases

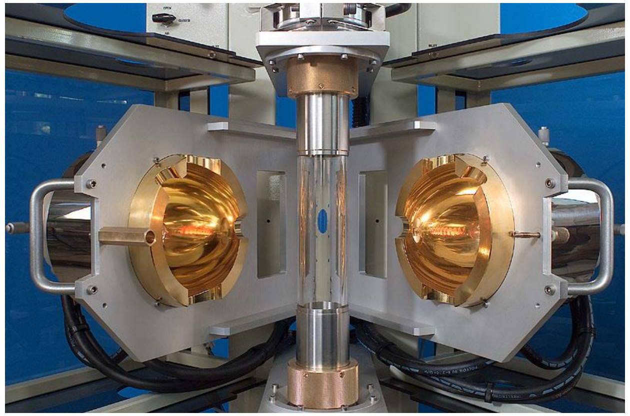


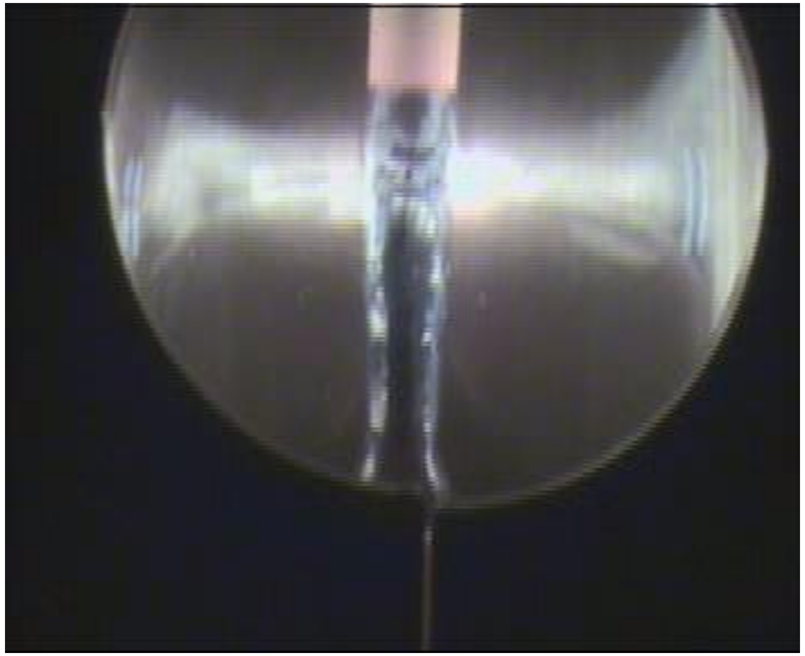

## Shaping: isostatic pressing of the rods (diameter: 6 mm)

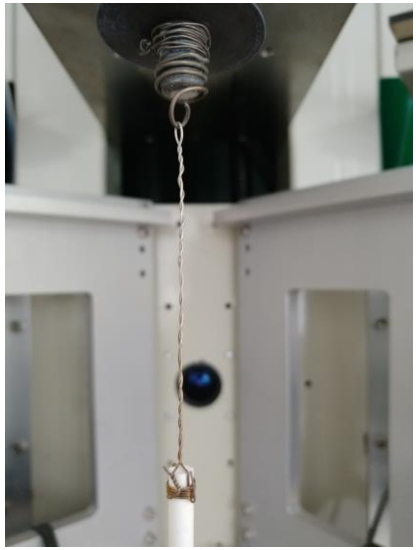


## Sintering → homogeneous structures

# Optical furnace: experimental setup







feed rod:
free to move

seed rod: fixed
with ceramic paste

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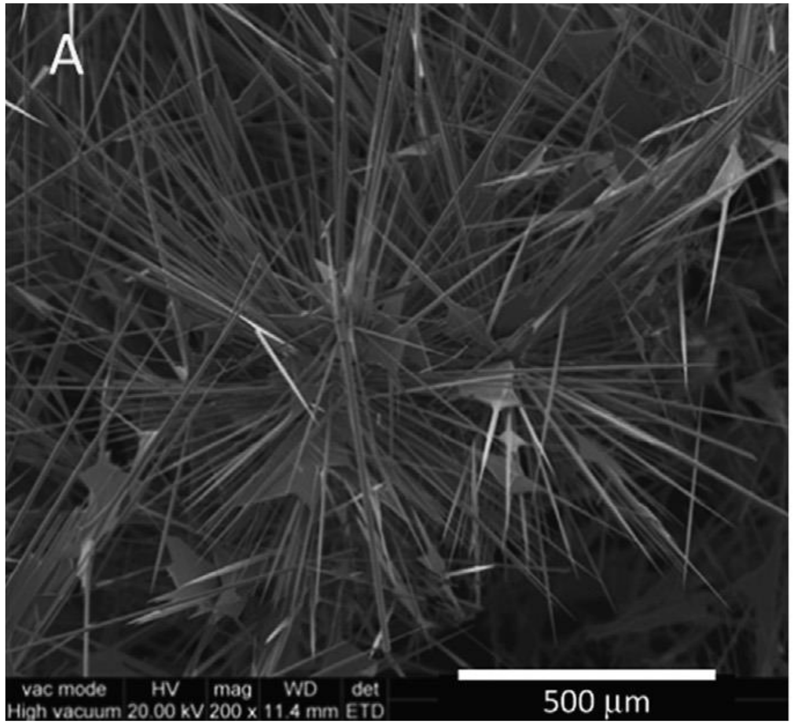
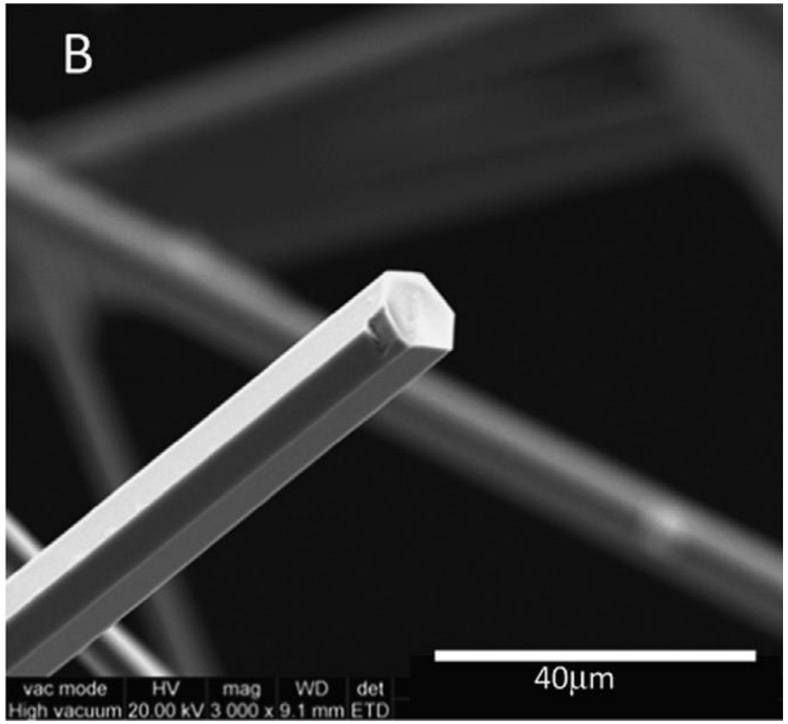
# ZnO wires


## In 10 minutes

ZnO (ceramics) → Zn (g) + ½ $O_2$ (g) → ZnO (wires)

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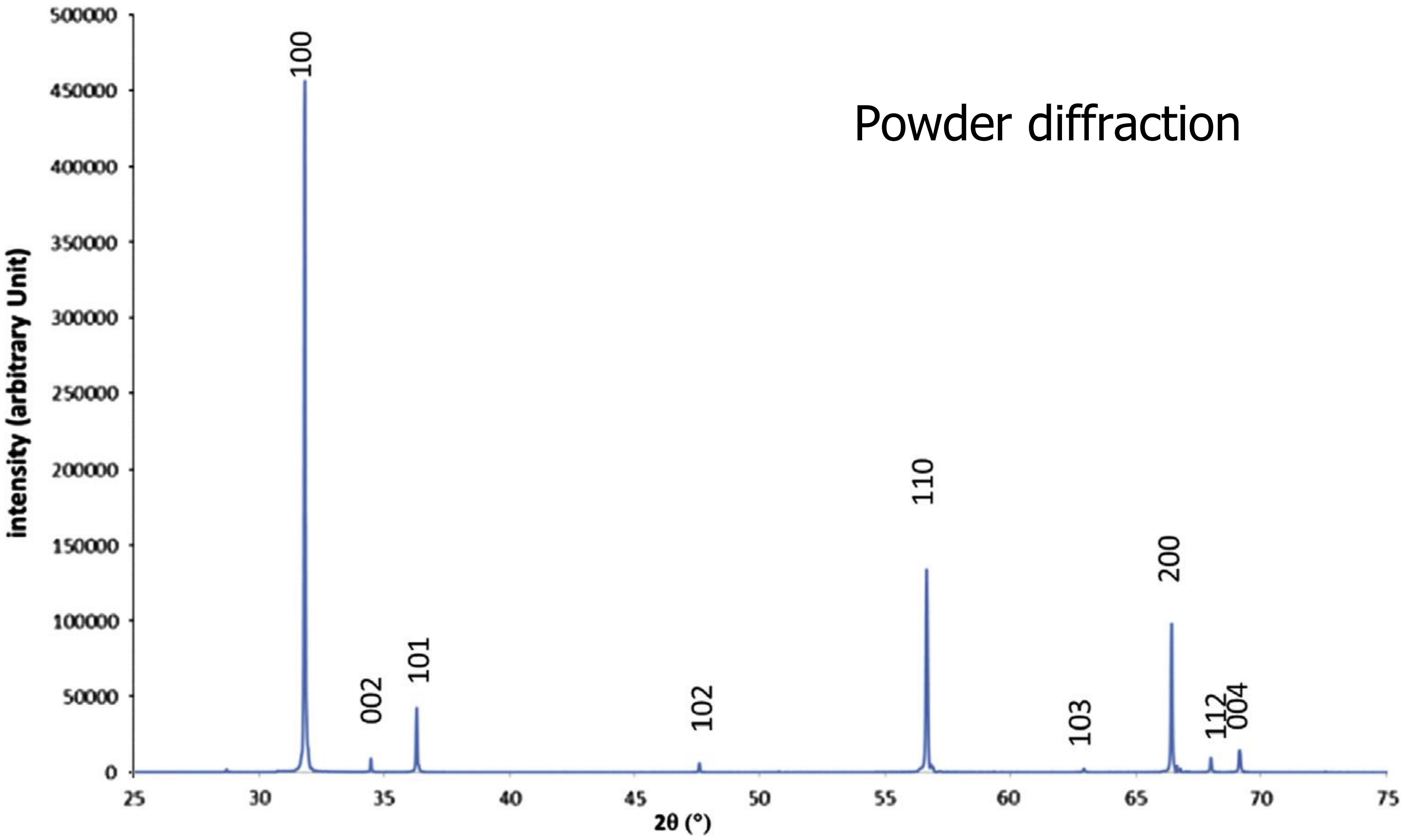
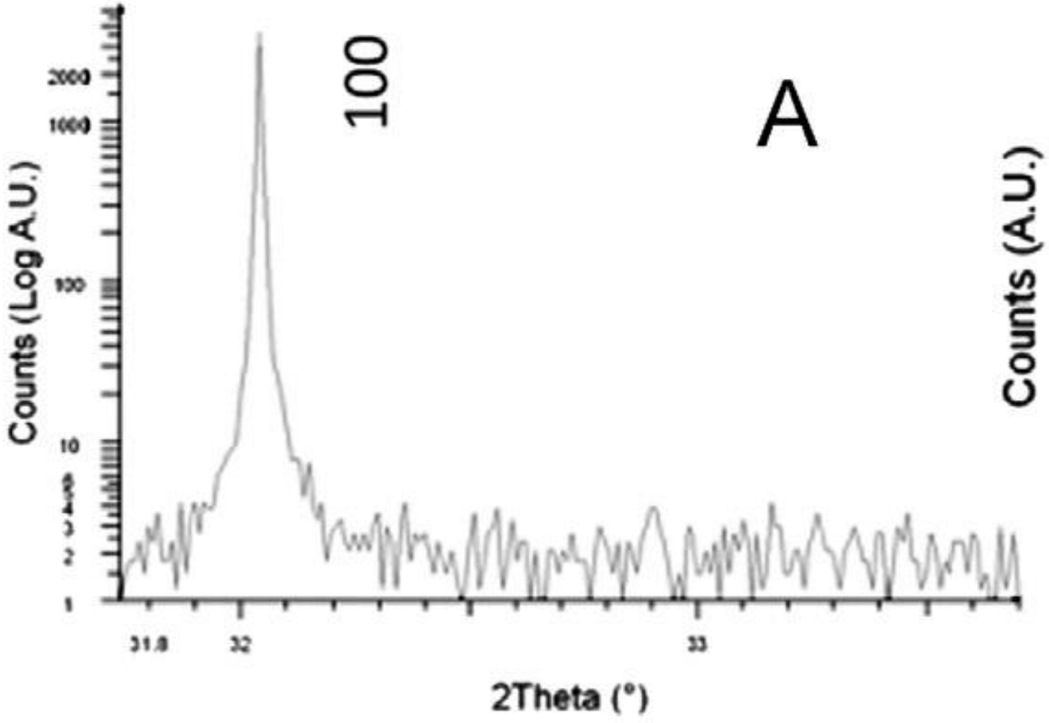
Giovannelli *et al. Mater. Lett.* **107** (2013).

# ZnO wires: X-ray diffraction

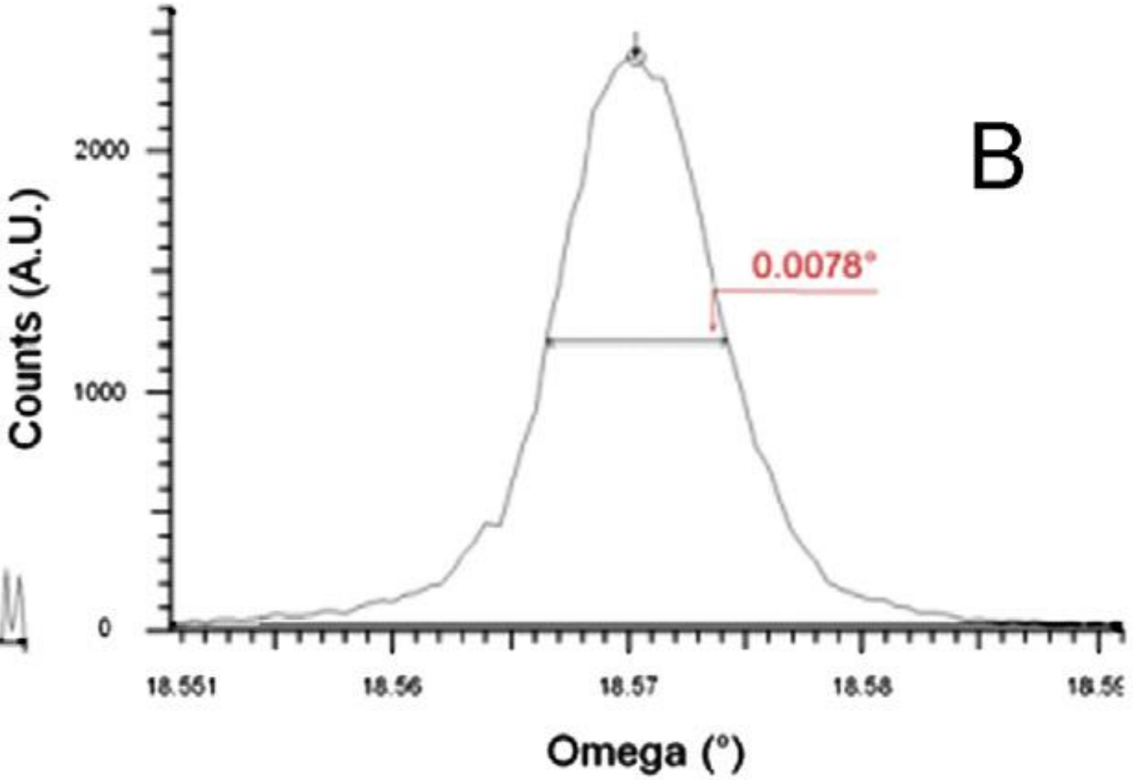



Giovannelli *et al. Mater. Lett.* **107** (2013).

# ZnO wires: high crystallinity




Micro-diffraction

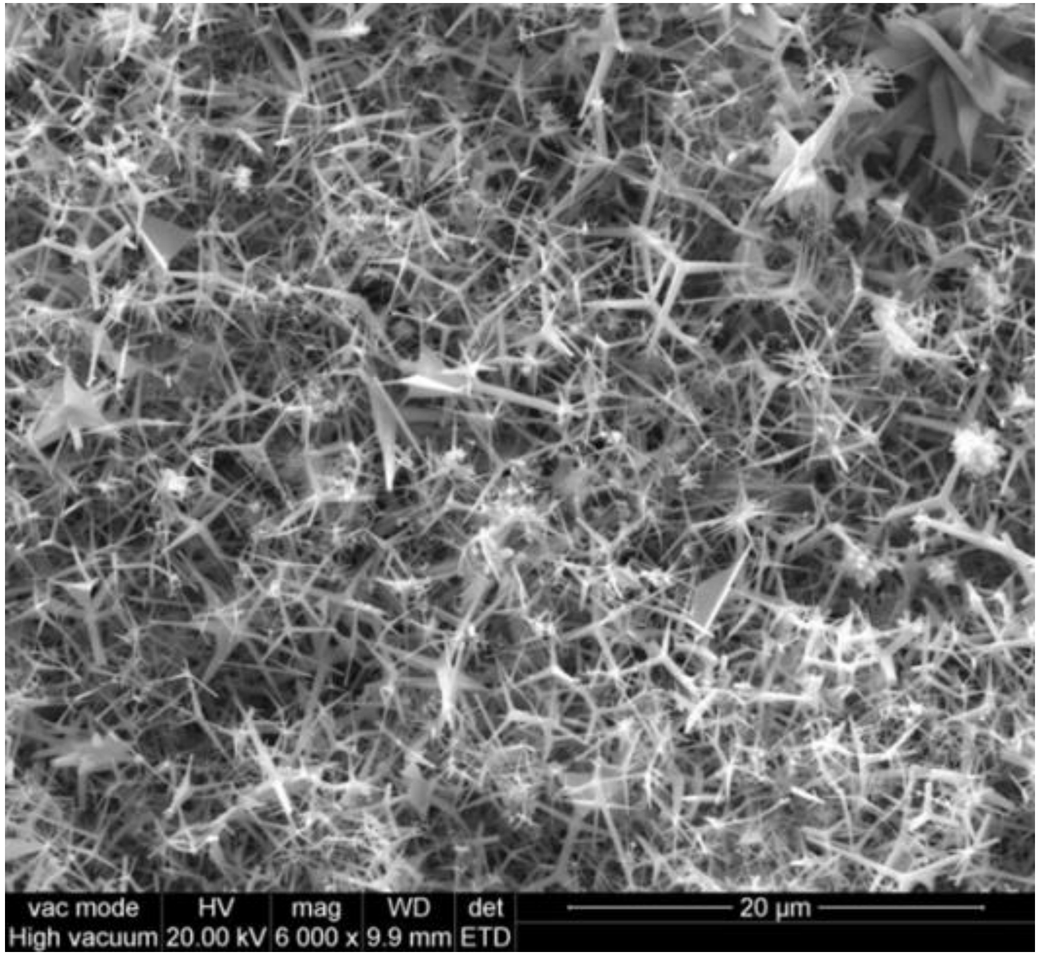


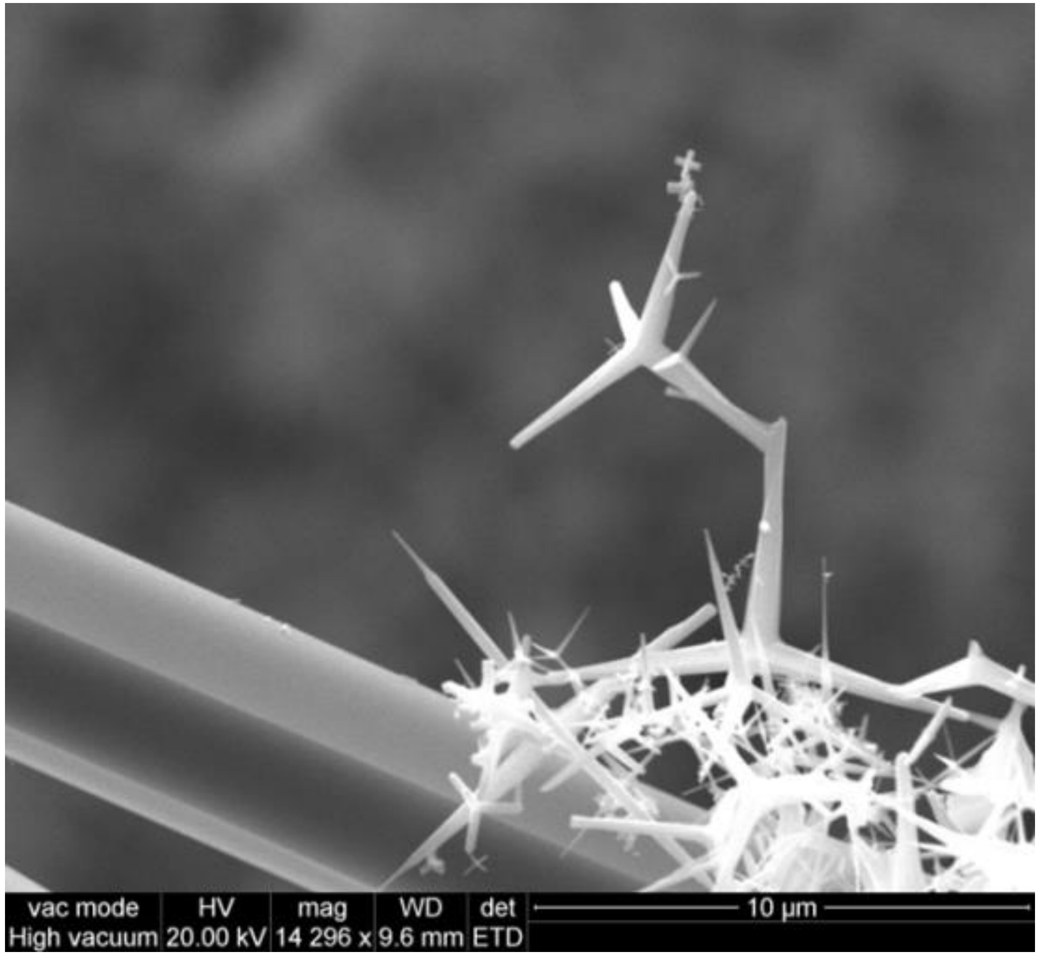

Rocking curve

Giovannelli *et al. Mater. Lett.* **107** (2013).

# ZnO tetrapods

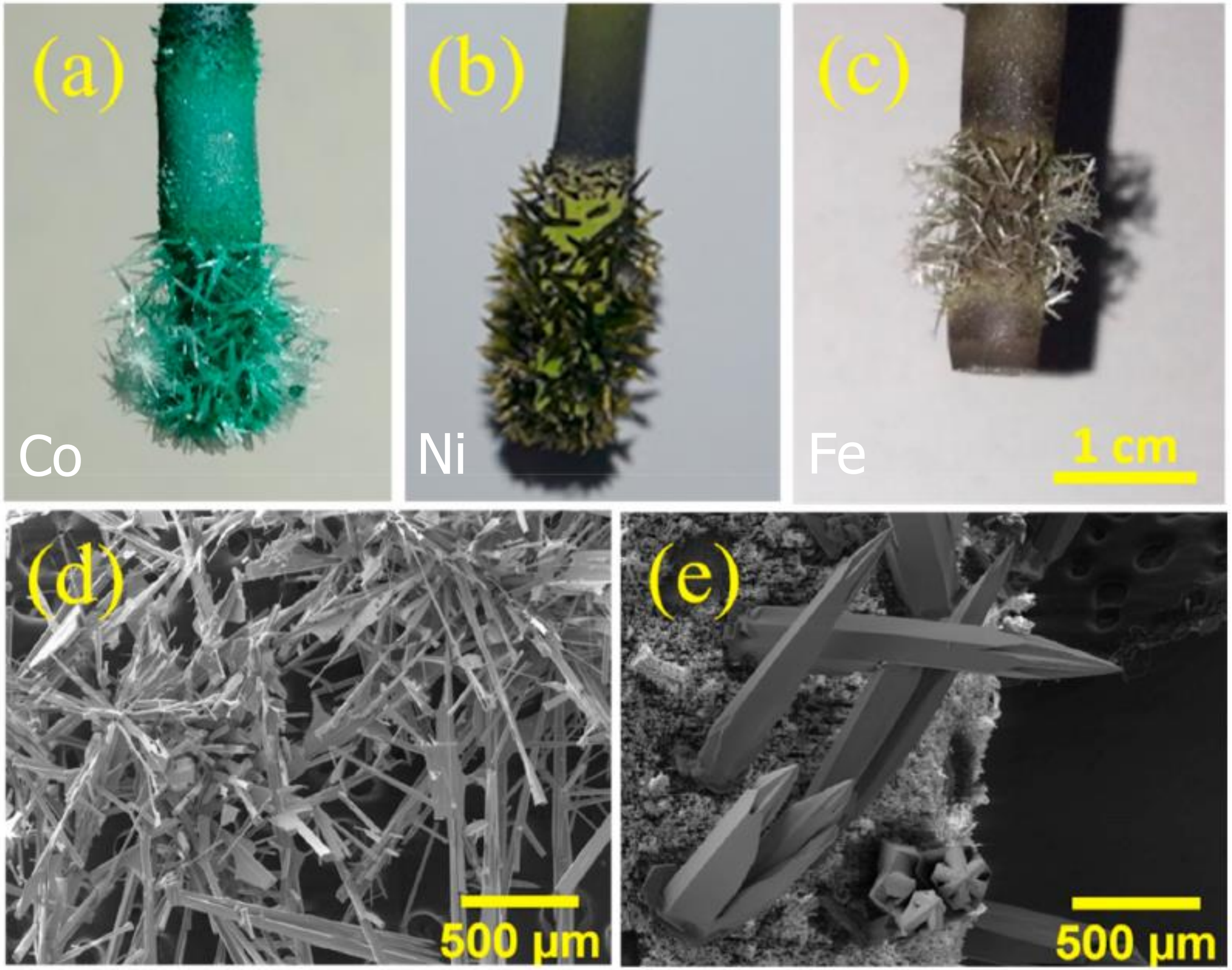
## Higher temperatures (higher lamp power)



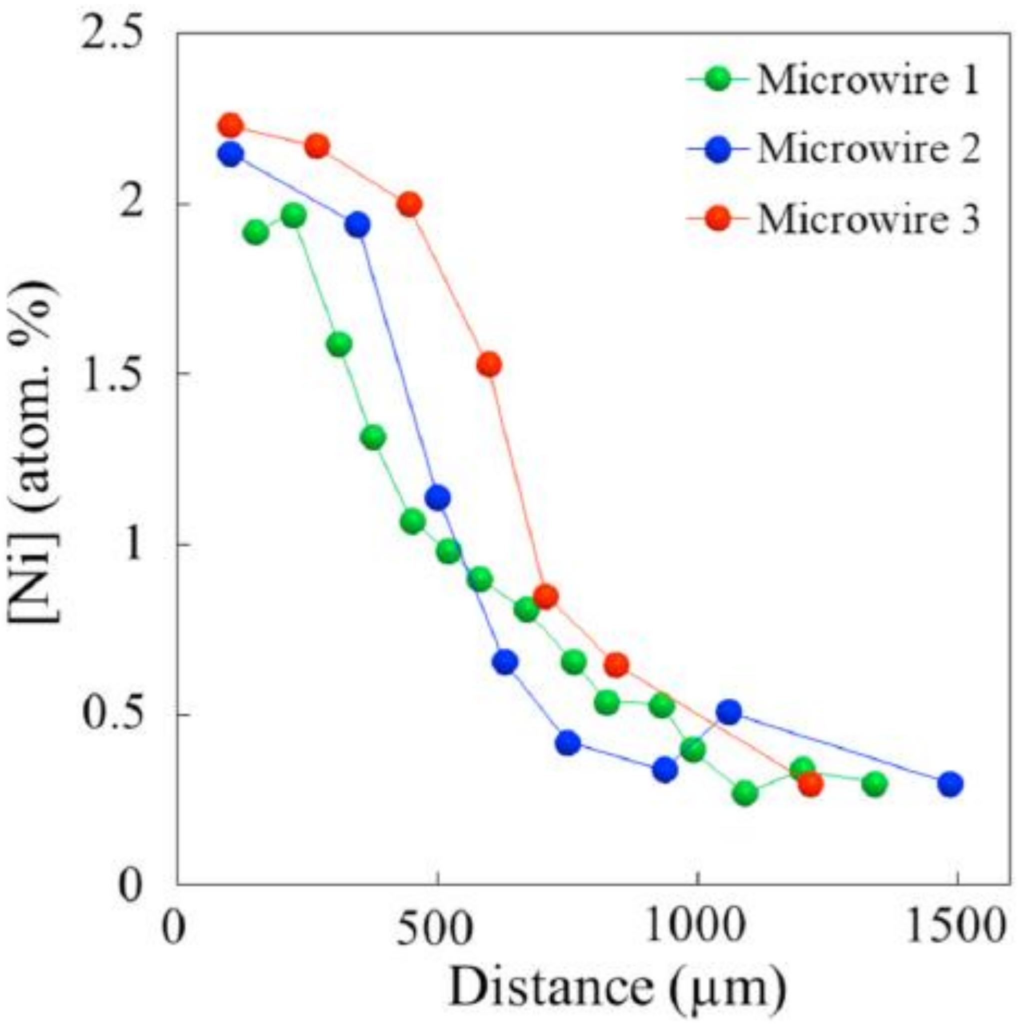

Giovannelli *et al. Mater. Lett.* **107** (2013).

# Doped ZnO wires




Giovannelli *et al. J. Phys. Chem. Solids* **158** (2021).

# Doped ZnO wires: diffusion process




Energy-dispersive X-ray spectroscopy (EDX) measurements

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Giovannelli *et al. J. Phys. Chem. Solids* **158** (2021).

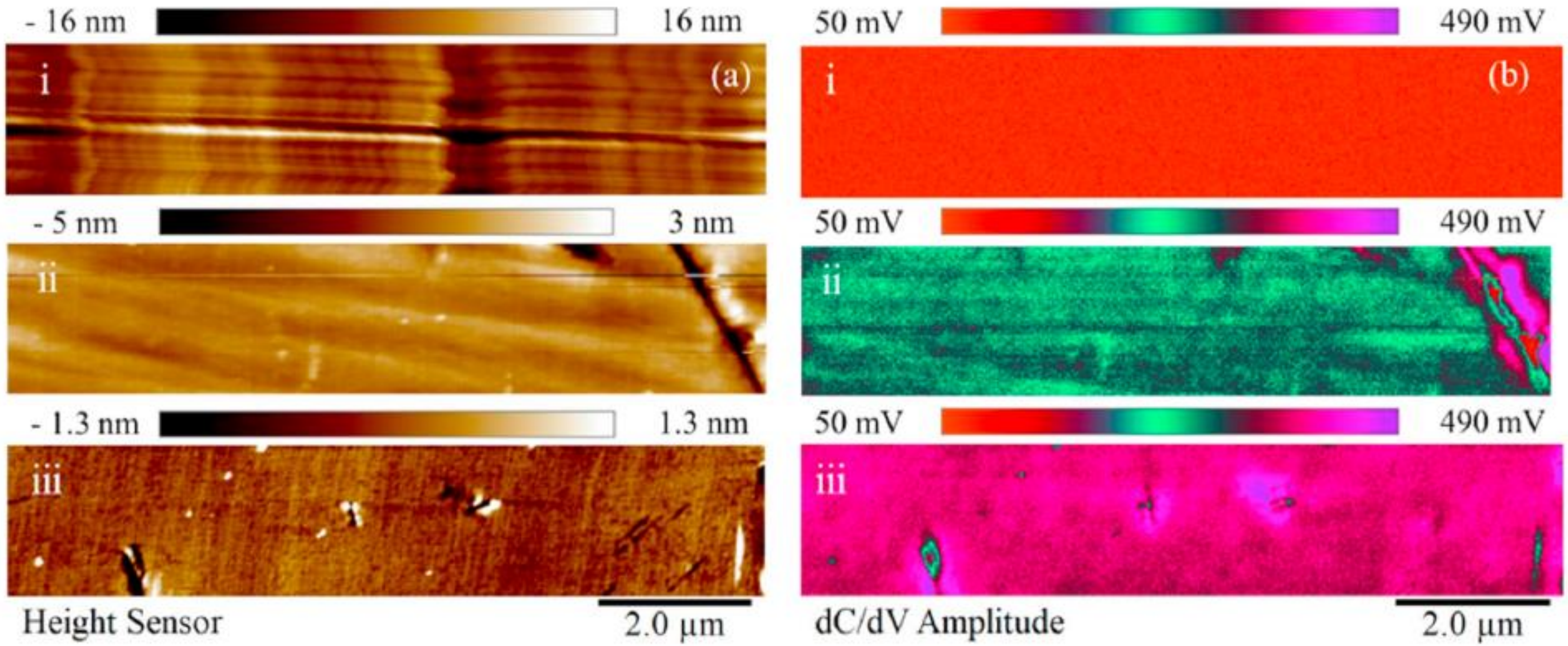
# Doped ZnO wires: diffusion process

Scanning capacitance microscopy measurements

base

middle

tip

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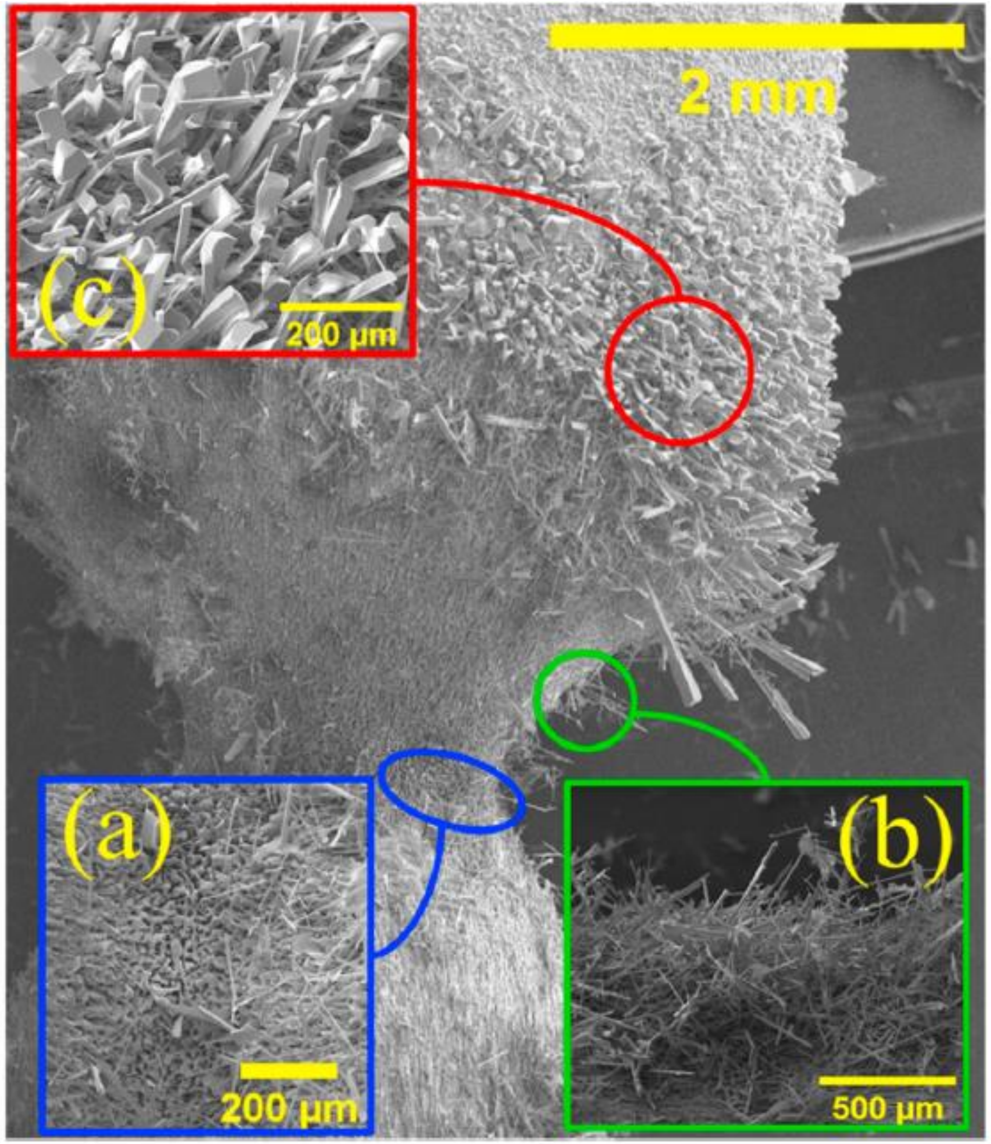
Giovannelli *et al. J. Phys. Chem. Solids* **158** (2021).

# Crystallization of $SnO_2$




$SnO_2$ (ceramics) → SnO (g) + ½ $O_2$ (g)

< 100 µm: no crystallization

100 µm - 800 µm: microwires (diameter: 10 µm)

800 µm - 3 mm: microwires (diameter: 50 µm)

Giovannelli *et al. J. Phys. Chem. Solids* **158** (2021).

# Take home message

It is possible to make nanostructures with techniques designed for macroscopic samples.

# Outline

- Basics of ceramics

- ZnO nanostructuring

- Nanocracks

- ZnO nanowires

- Spontaneous nanostructuration

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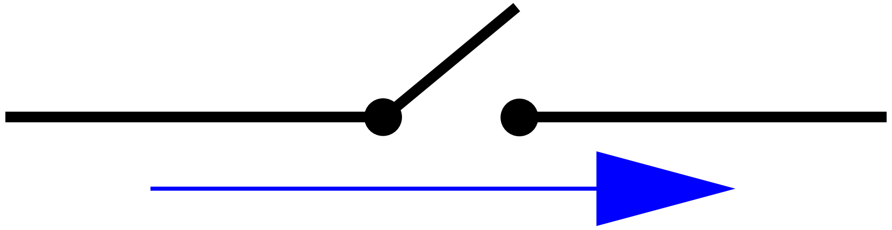
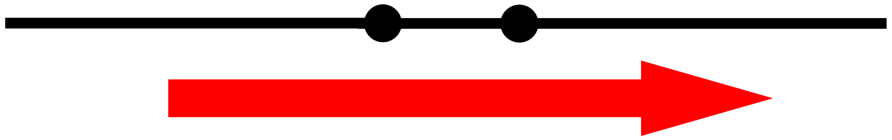
# Is it possible to control heat flows as easily as electricity?



Low thermal conductivity



High thermal conductivity

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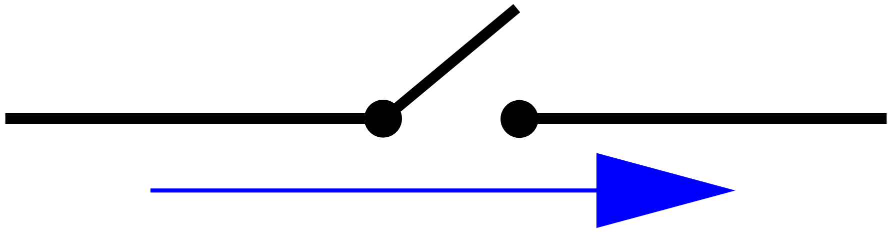
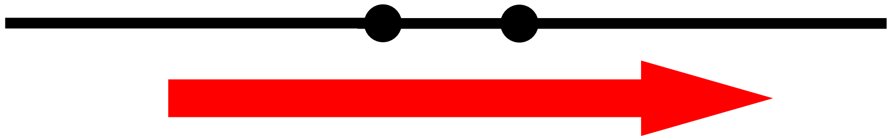


Low thermal conductivity



High thermal conductivity

Not yet….

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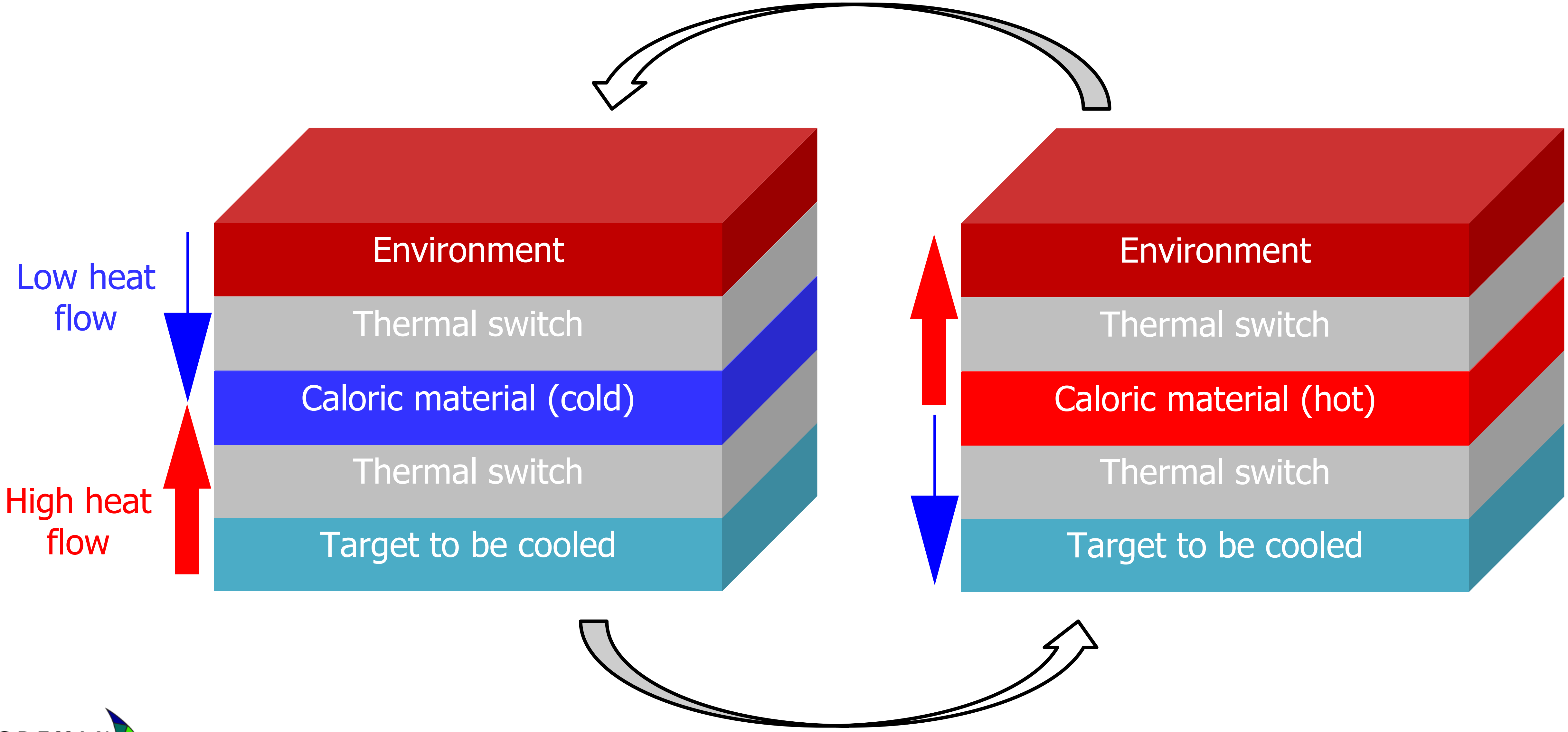
# What could be achieved with thermal switches?

Environment friendly refrigeration

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# The ideal thermal switch


Environment friendly

Easily manufactured

$R = k_H / k_L$ ~ 10

Cyclable $10^9$ times

No moving parts

Switch fast < 20 ms

Close to room temperature

Operate with small temperature gradients < 4 K

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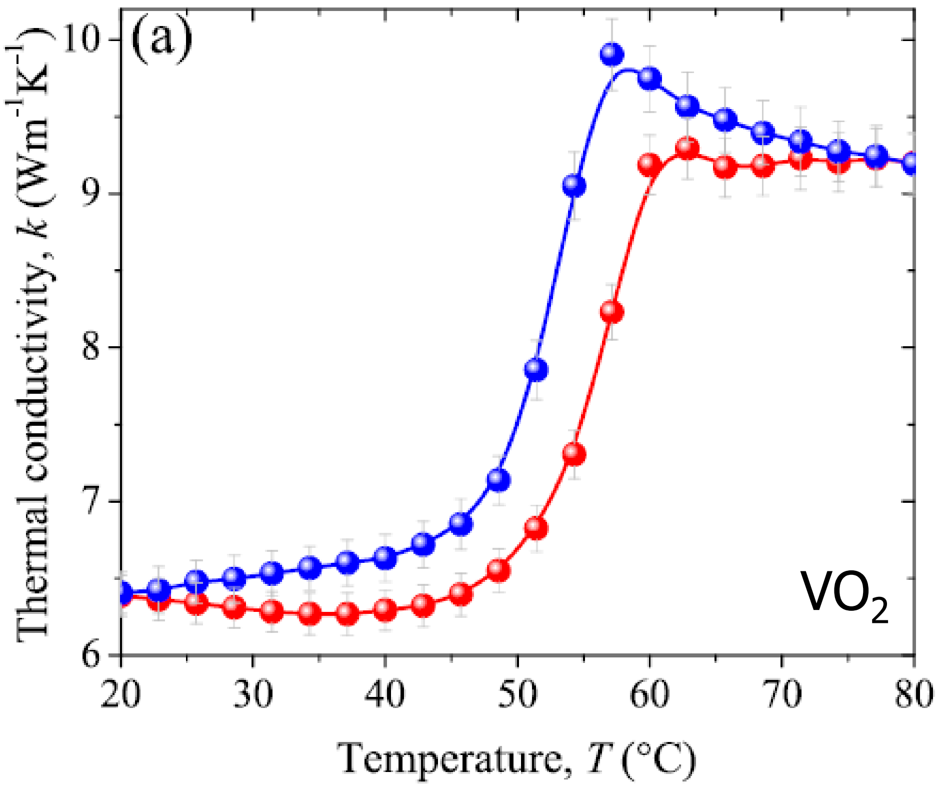
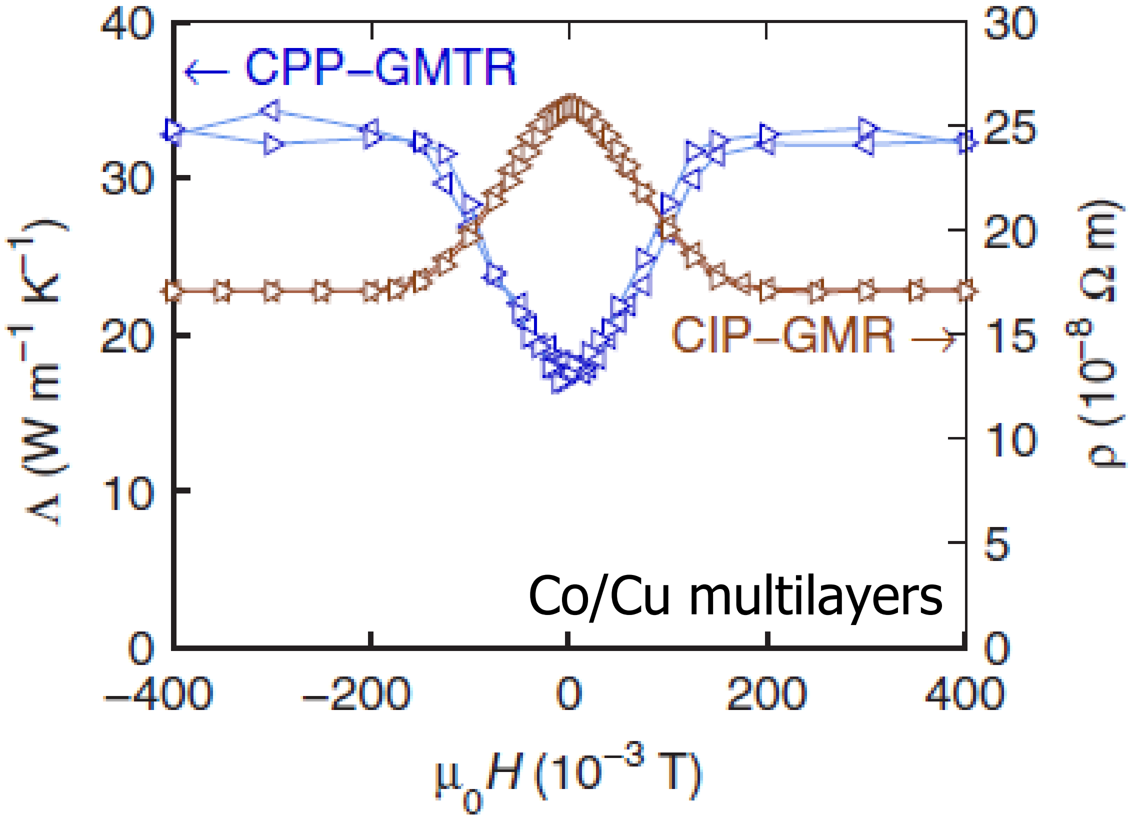
# Current strategies for thermal switches




insulator-metal transition

(phase change materials)

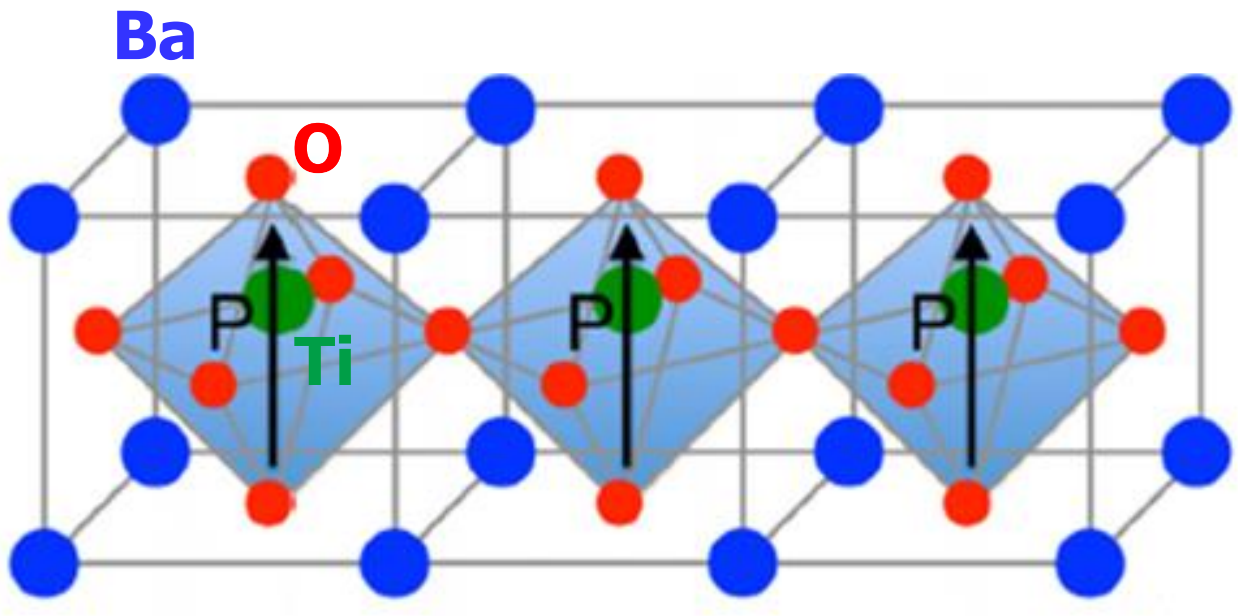



giant magnetoresistance

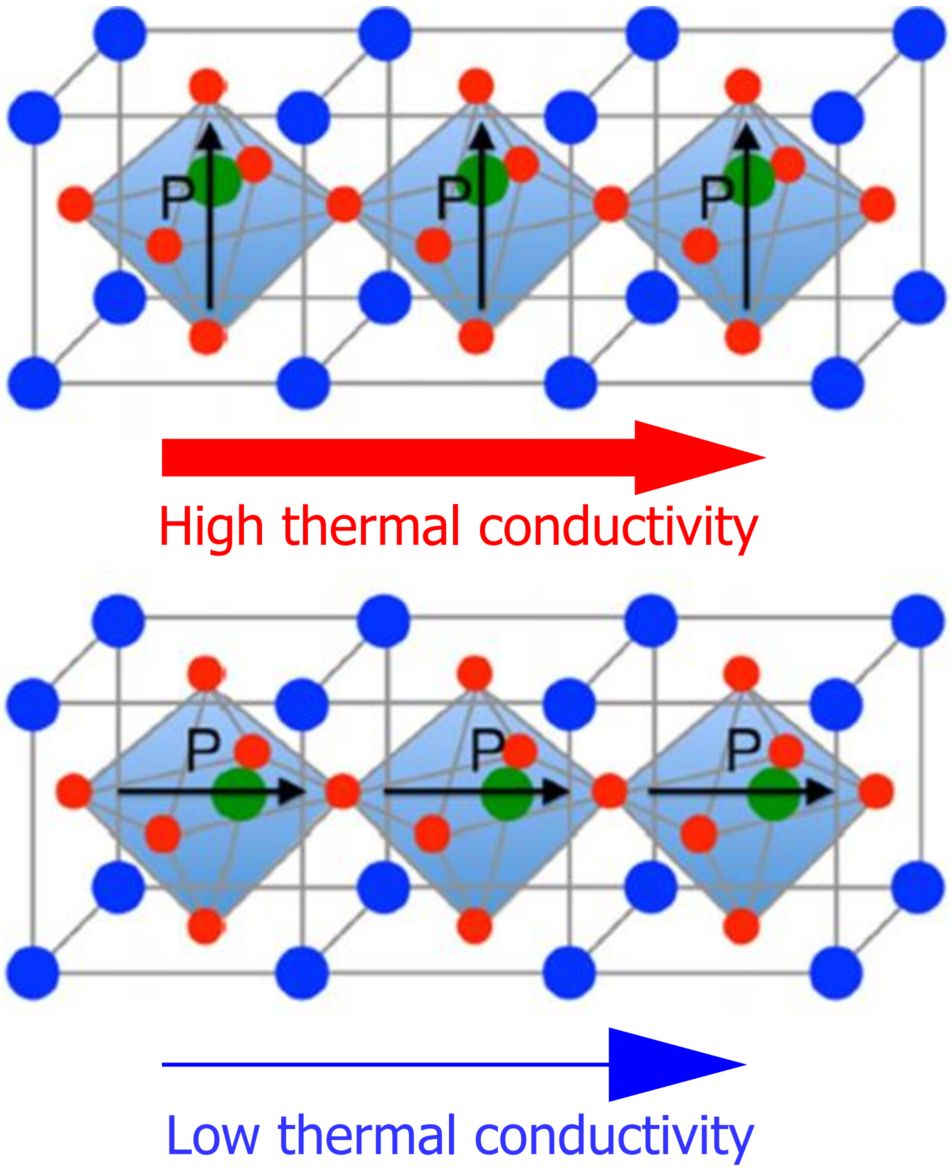


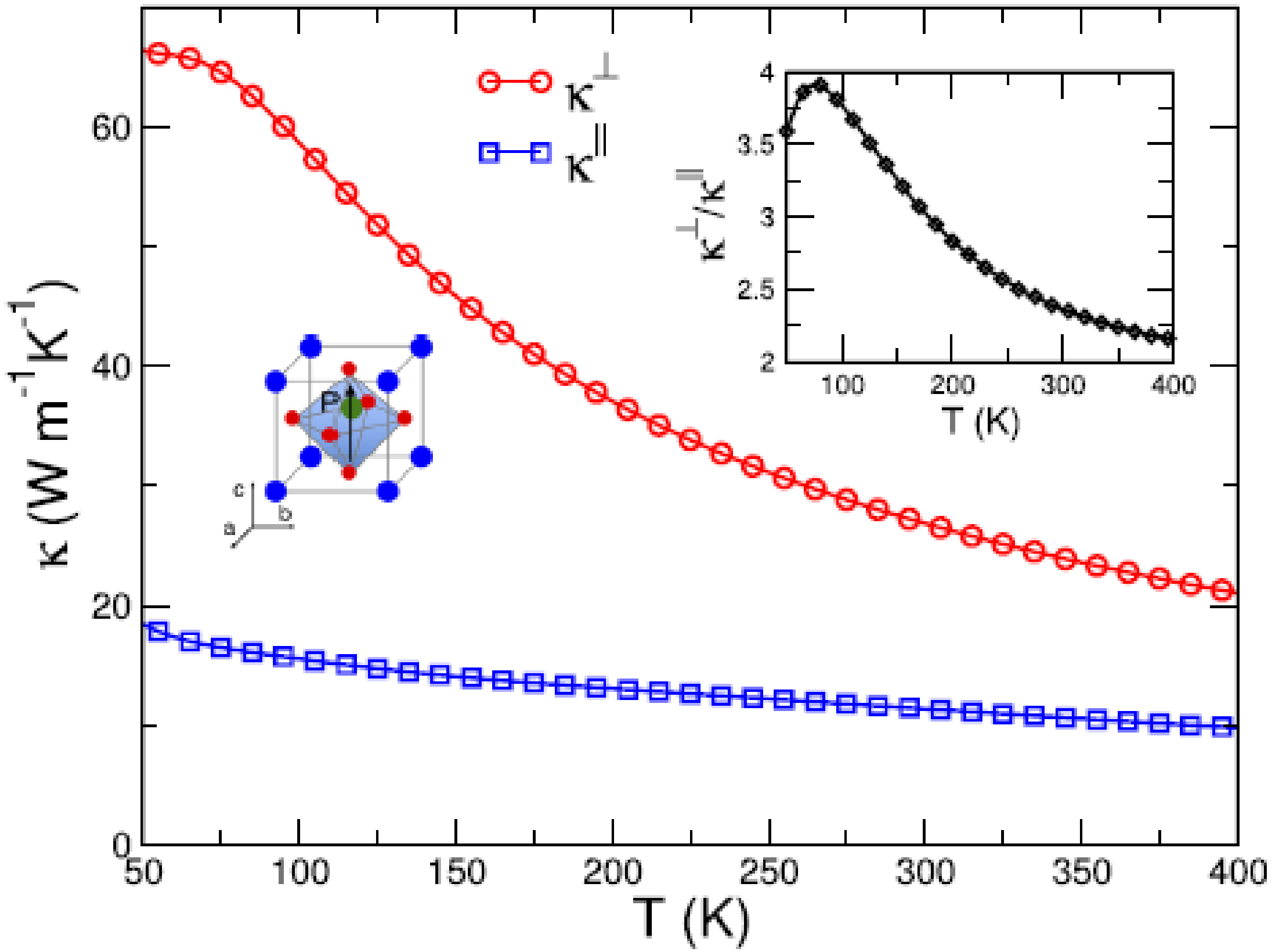
Gomez-Heredia *et al.* Sci. Rep. **9** (2019). Kimling *et al.* Phys. Rev. B, **91** (2015).

# A ferroelectric perovskite



# Prediction: anisotropy-driven thermal conductivity

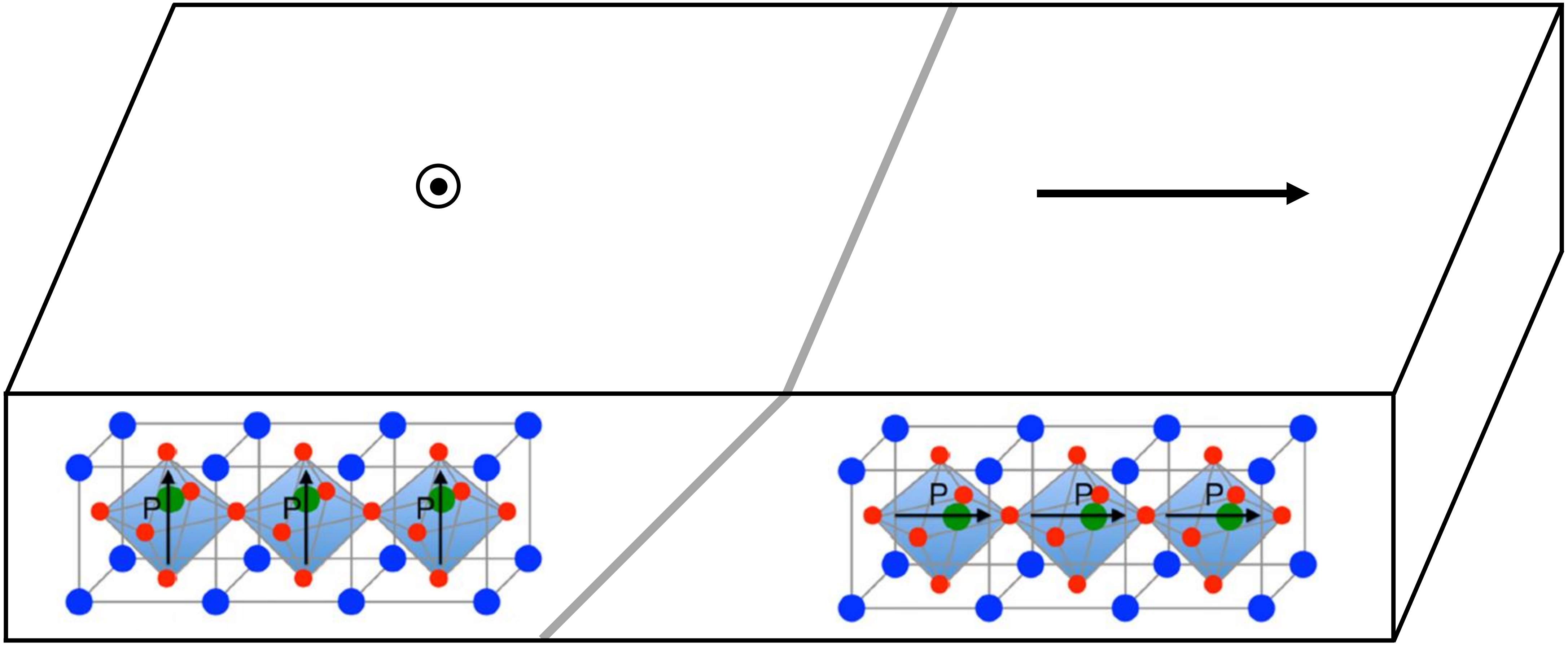



Seijas-Bellido *et al.* APL **115** (2019).

# $BaTiO_3$: an experimental model for a verification

$BaTiO_3$ single crystals at room temperature have a tetragonal symmetry and spontaneously exhibit ferroelectric domains

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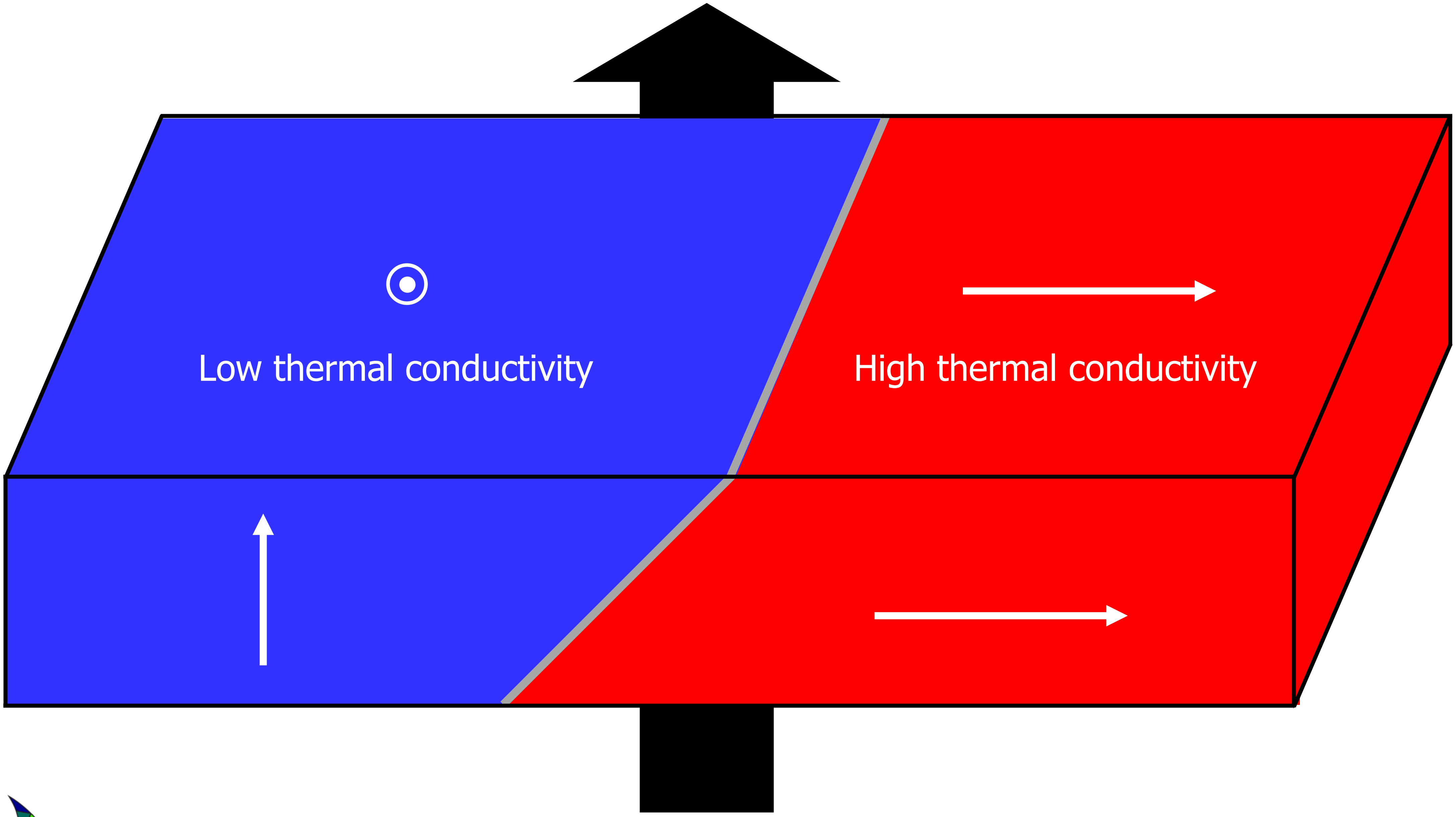
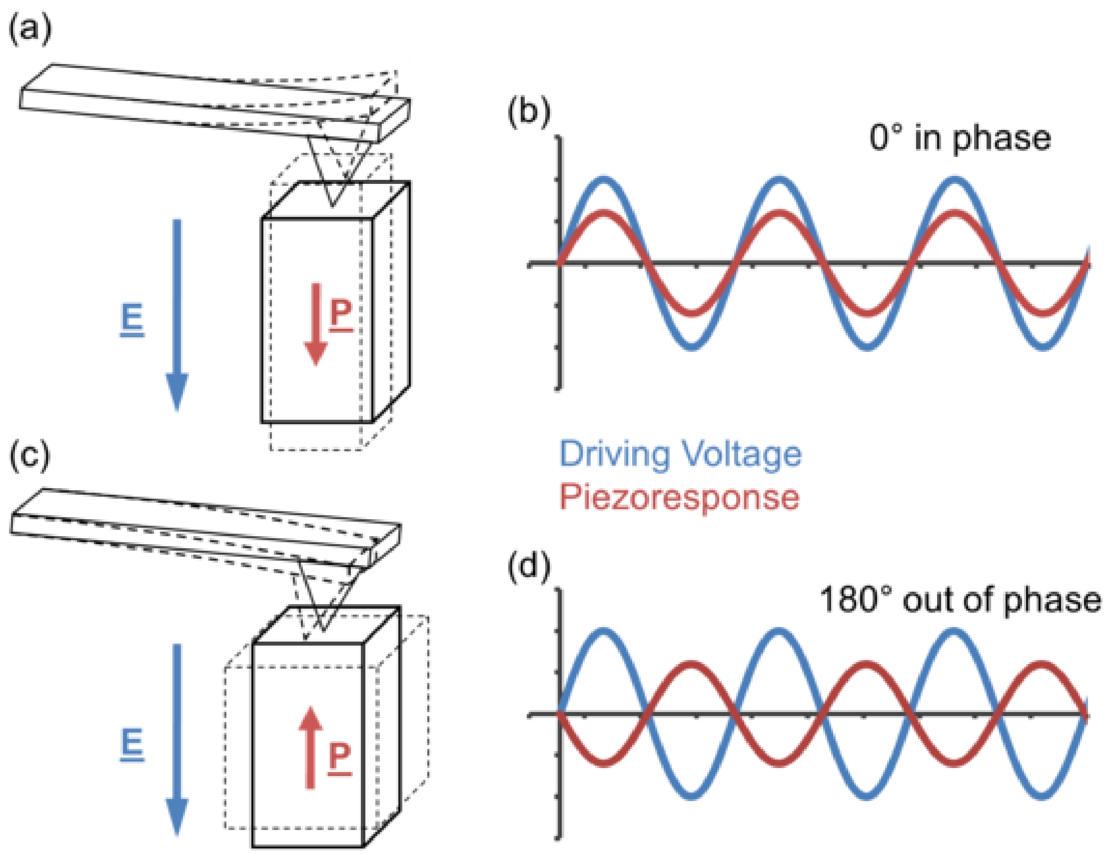
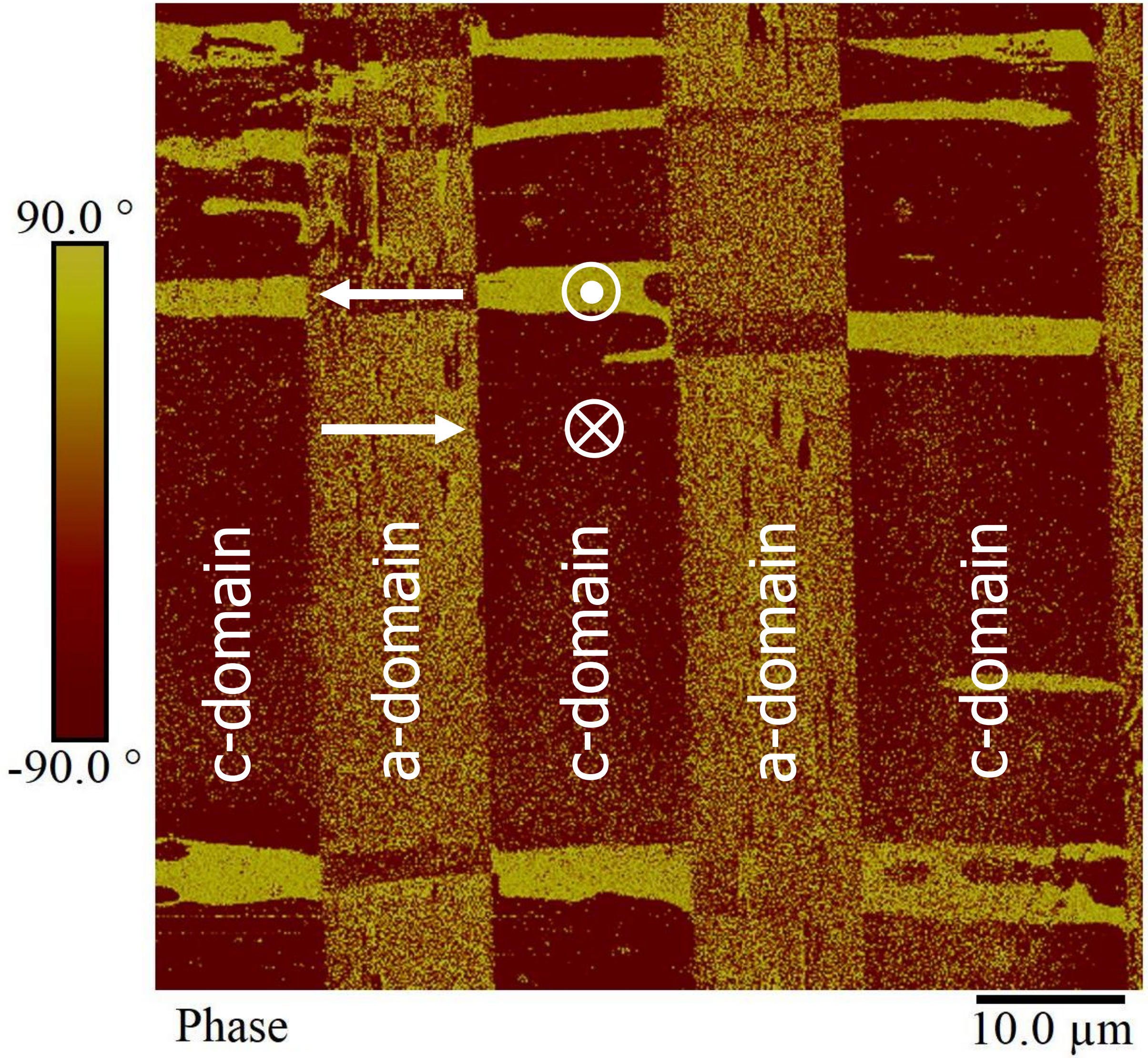


# Image of ferroelectric domains

Piezoresponse force microscopy image of the domains

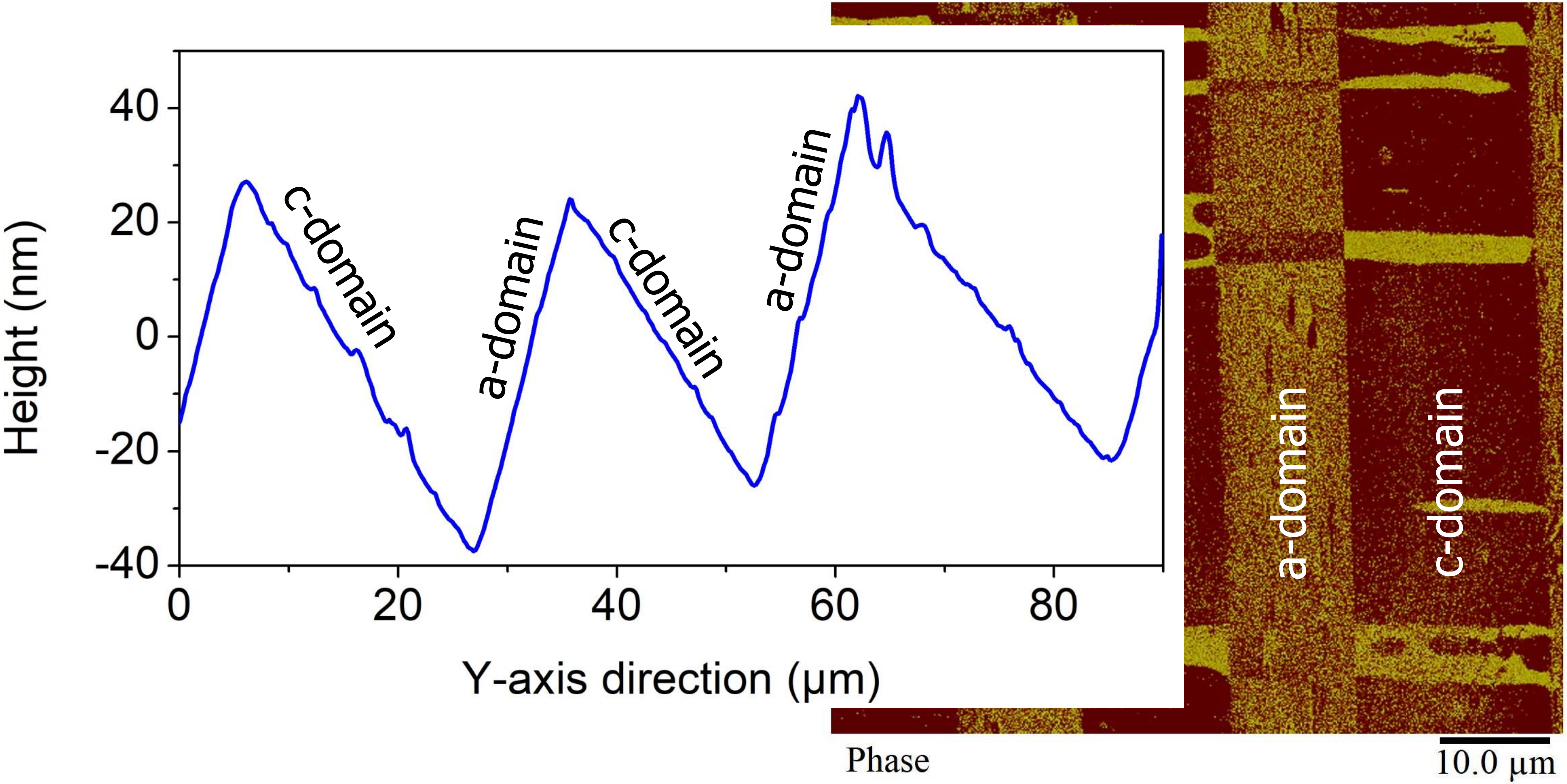


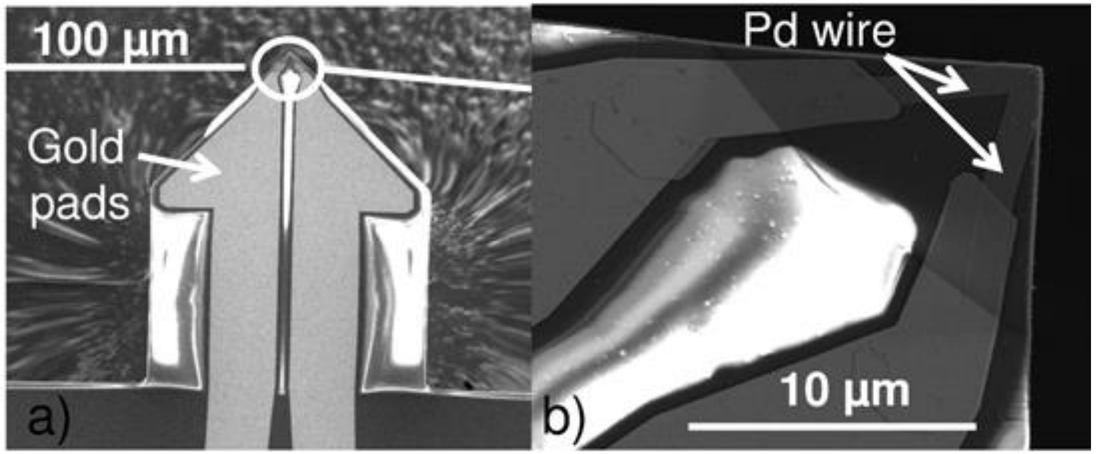

wikipedia.org/wiki/Piezoresponse_force_microscopy

# Image of ferroelectric domains

Piezoresponse force microscopy image of the domains

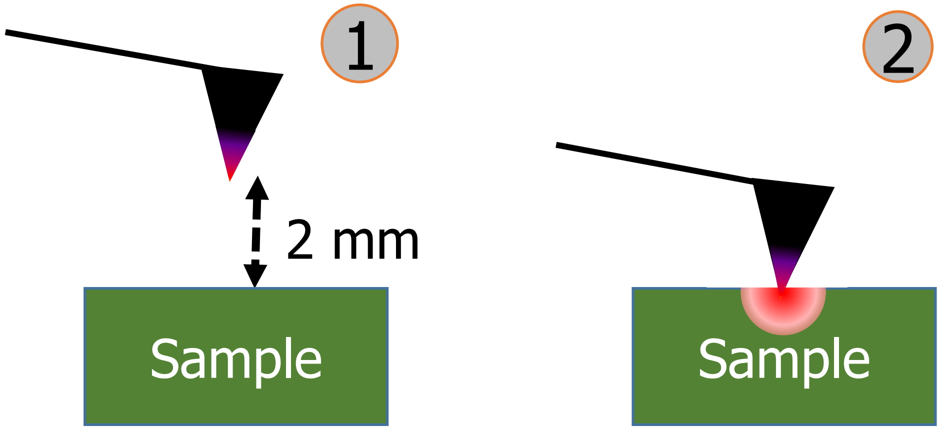


# Scanning Thermal Microscopy measurement




*KelvinNanoTechnology probe (KNT)*

Measurement in 2 steps




Out of contact (OC)

In contact (IC)

$$\Delta G_p = G_{p-IC} - G_{p-OC} = \frac{G_{contact}}{1 + \frac{G_{contact}}{G_{sample}}} - G_{env}$$

$$G_{sample} = \left( \frac{1}{4b\kappa_{BaTiO_3}} + \frac{4}{3\pi b^2} \frac{\Lambda_{ph-BaTiO_3}}{\kappa_{BaTiO_3}} \right)^{-1}$$

$\Lambda_{ph-BaTiO3} \cong$ 100 nm

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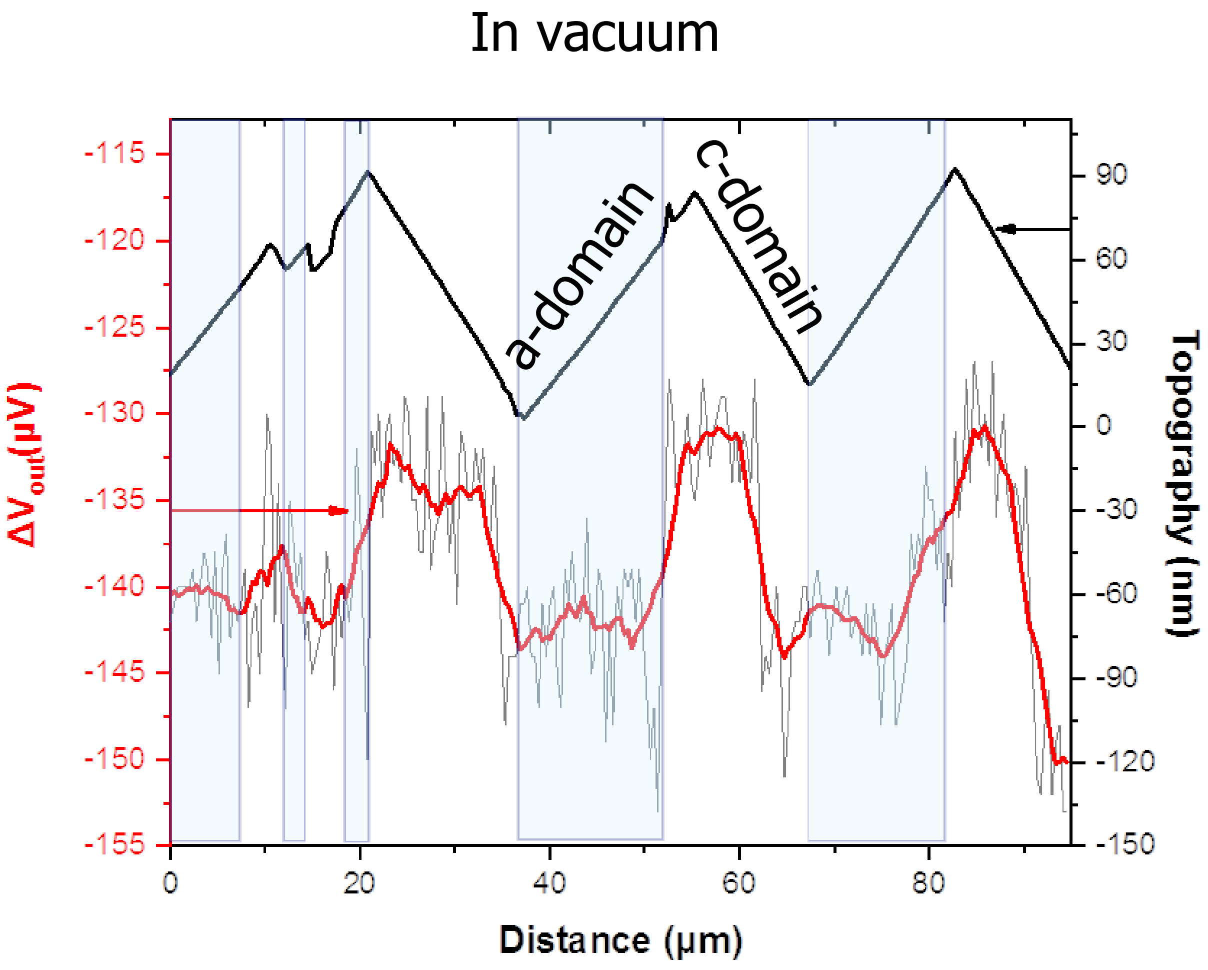
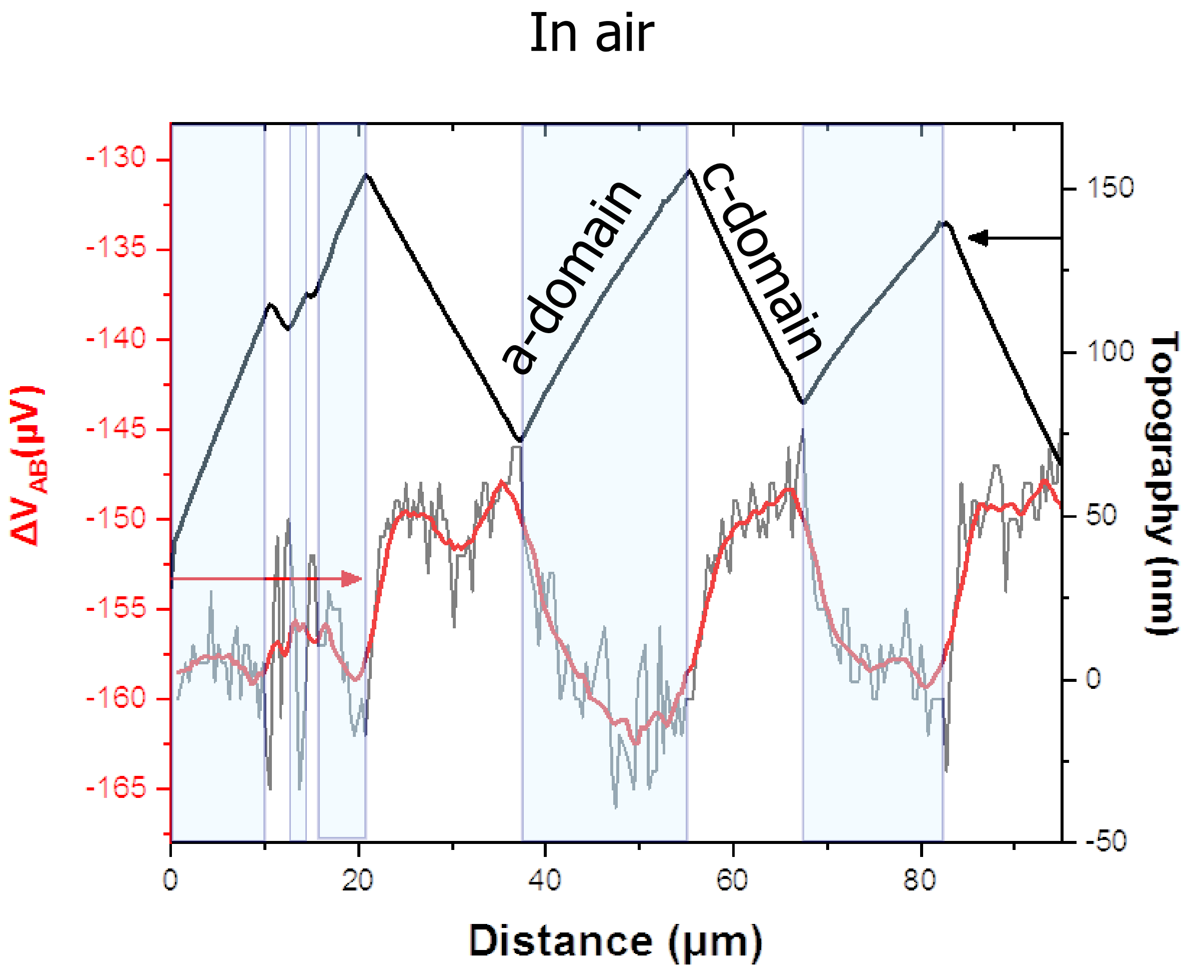
Donovan *et al.* APL **105** (2014).

# Scanning Thermal Microscopy measurement




$\kappa_{a\text{-domain}} - \kappa_{c\text{-domain}} = +\ 0.3\ W\ m^{-1}\ K^{-1}$

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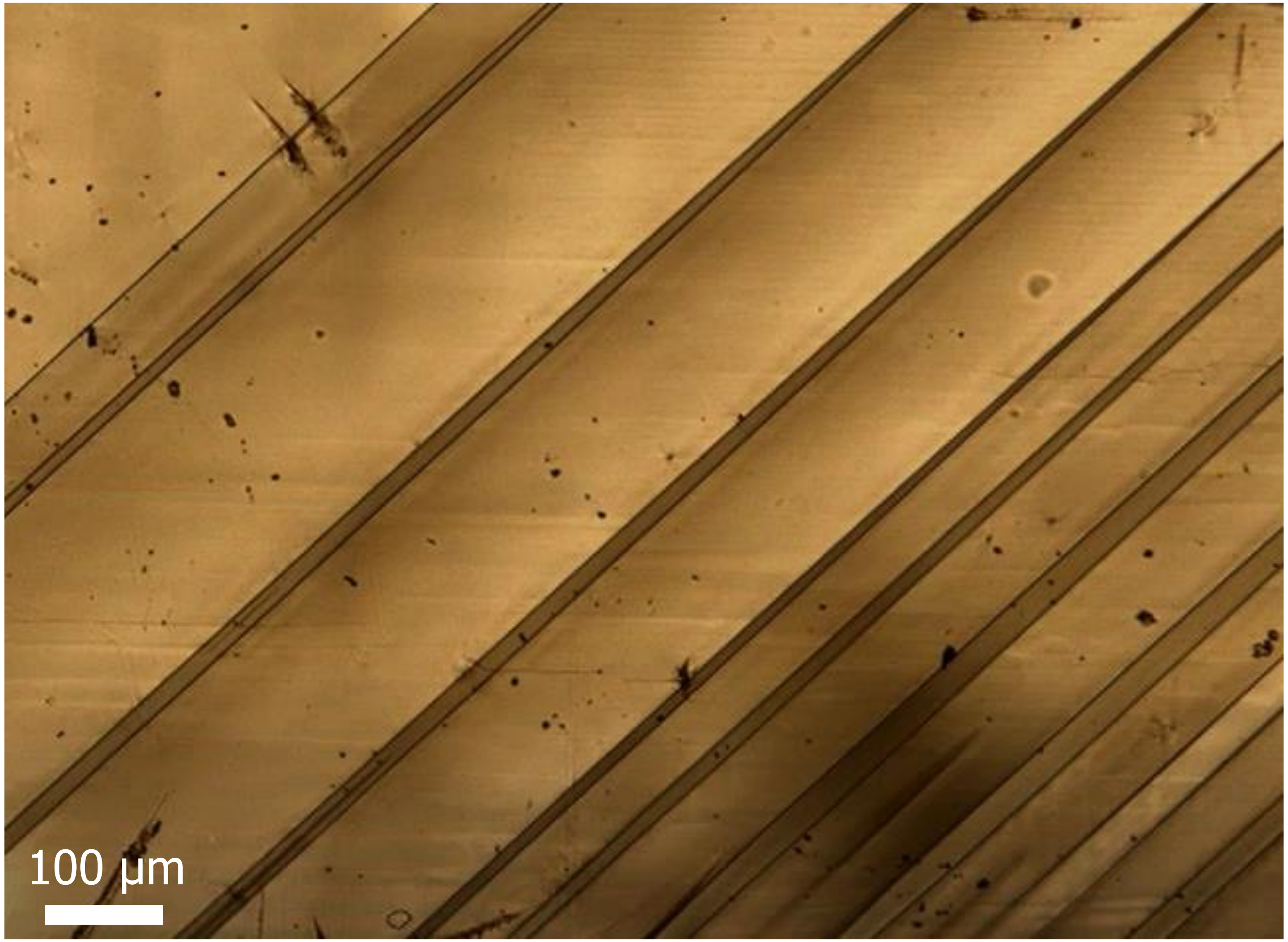
# Ferroelectric domains move under an electric-field

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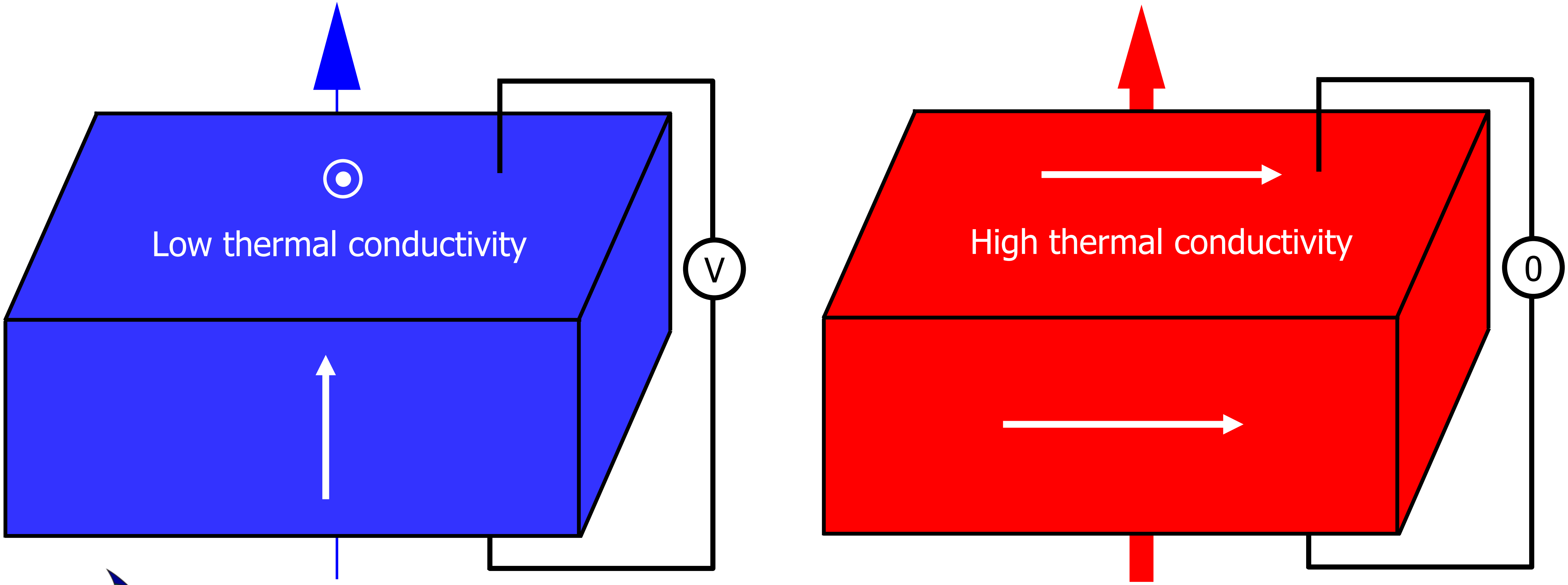
# Take home message: a ferroelectric thermal switch

Ferroelectric domains exhibit different thermal conductivities
Ferroelectric domains move under an electric field
→ it's a thermal switch!

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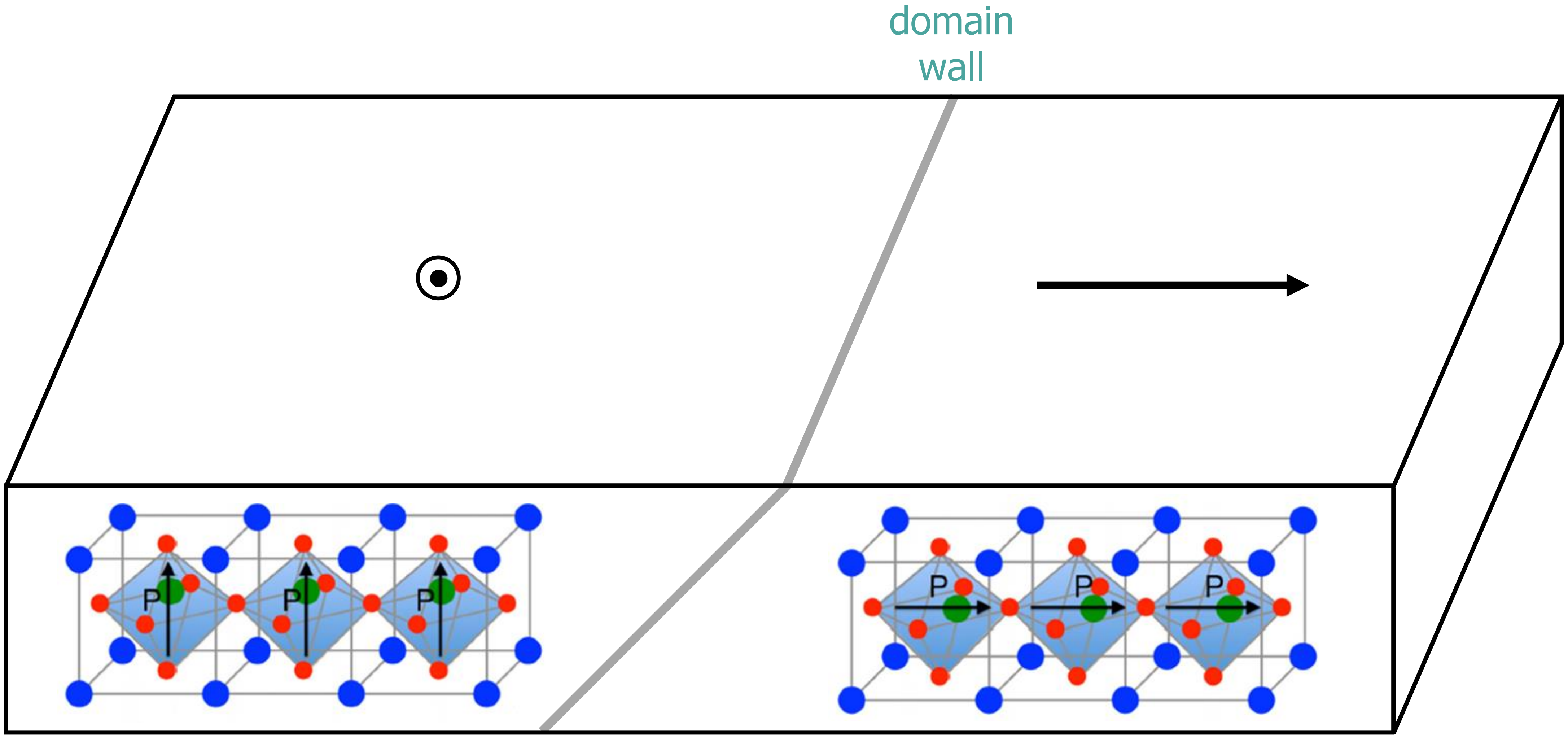
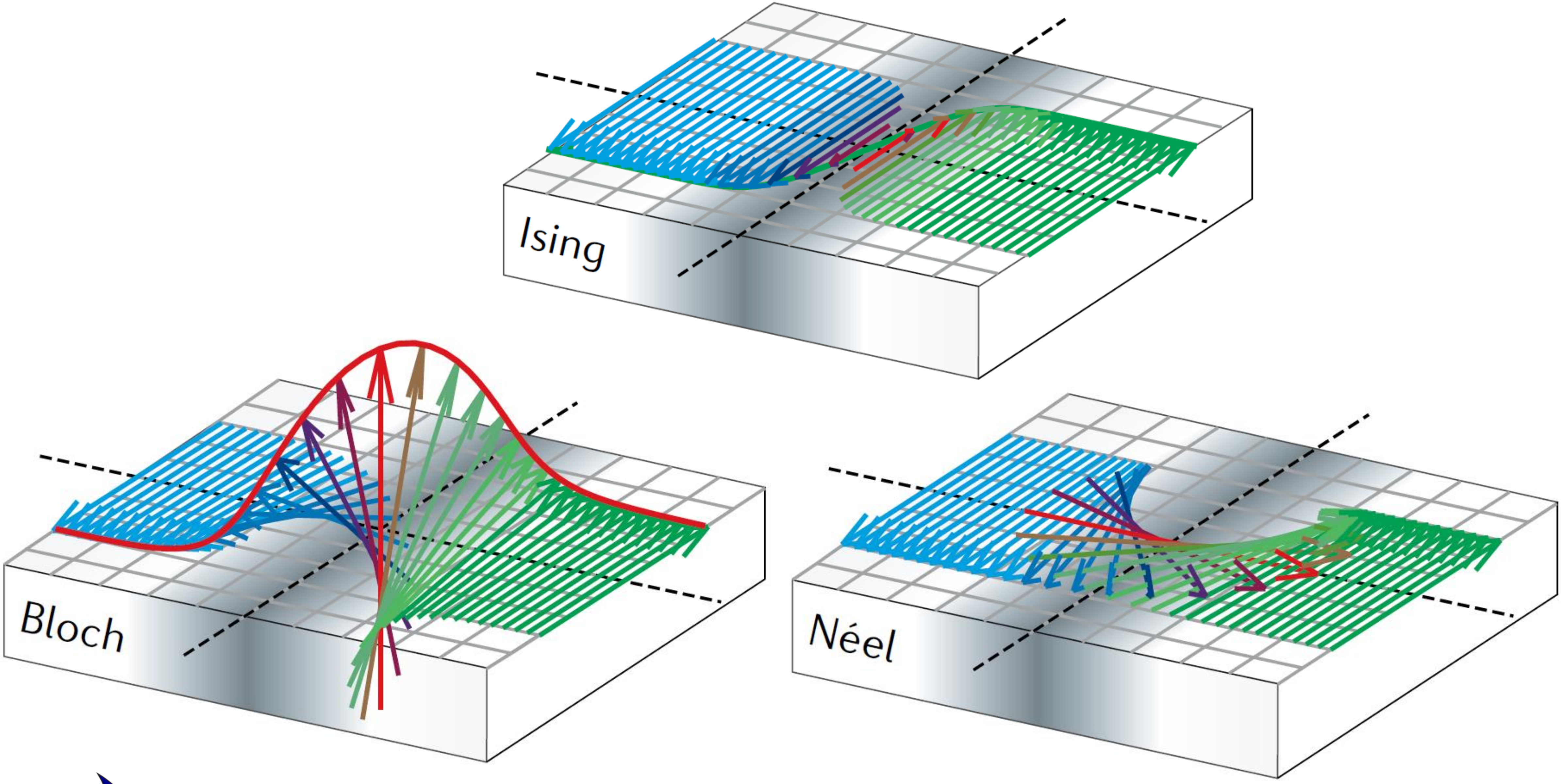
# What about domain walls?



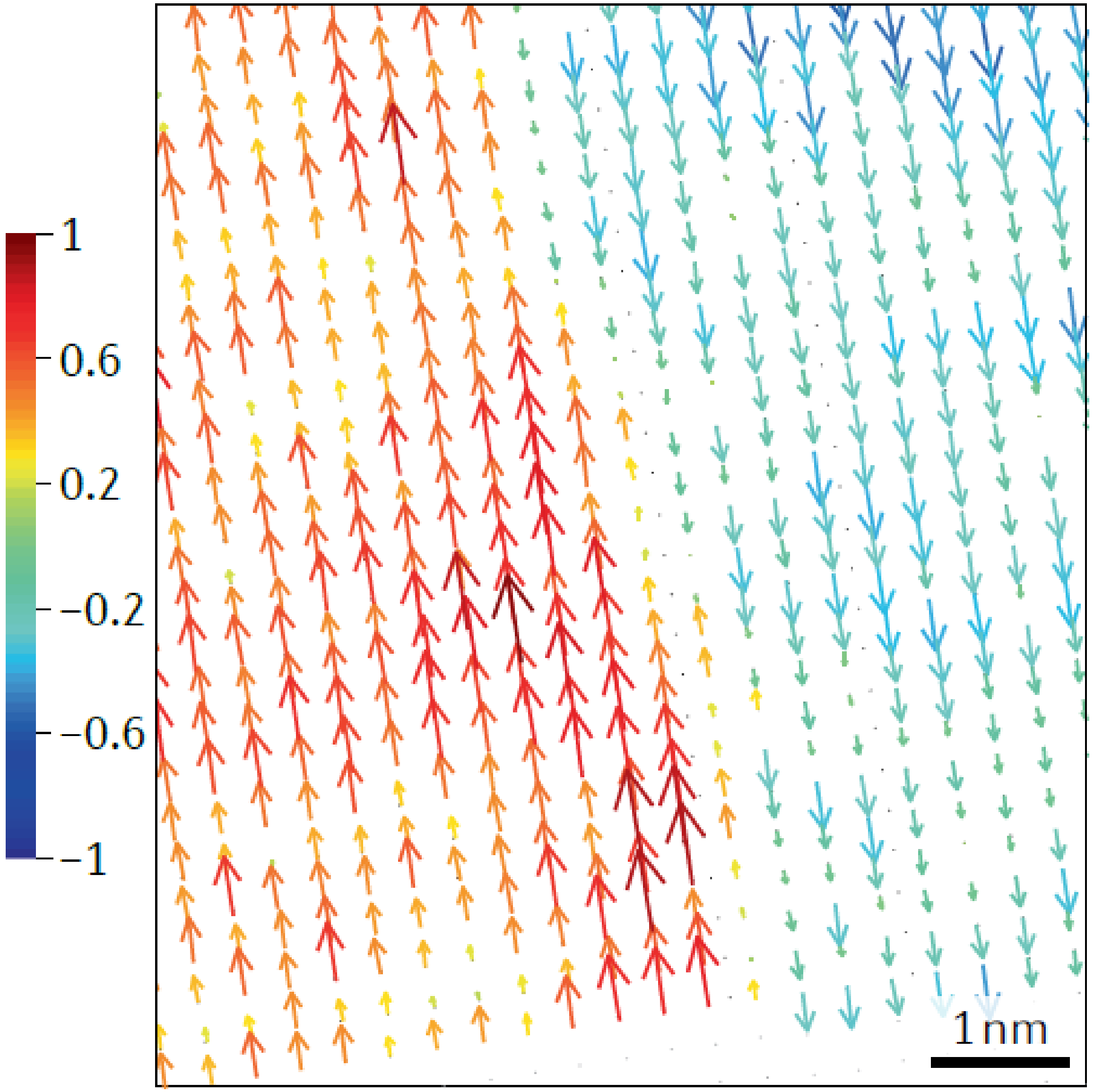
# A zoo of ferroelectric domain walls




Nataf *et al.* Nat. Rev. Phys. **2** (2020).

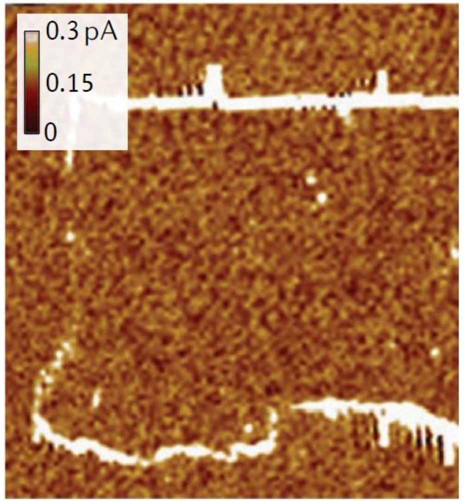
# Image of a real ferroelectric domain wall

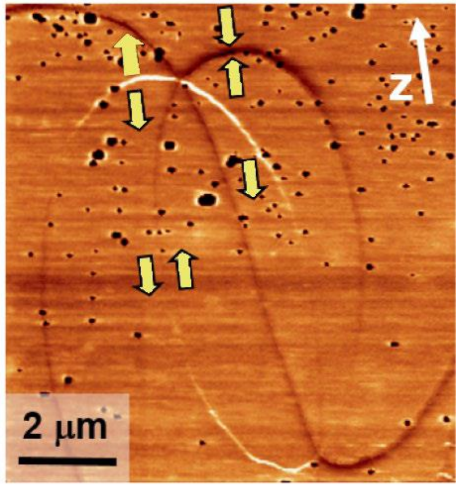
Scanning transmission electron microscopy on a 180° Ising domain wall in $LiNbO_3$




Gonnissen, Batuk, Nataf *et al.* Adv. Funct. Mater. **26** (2016).

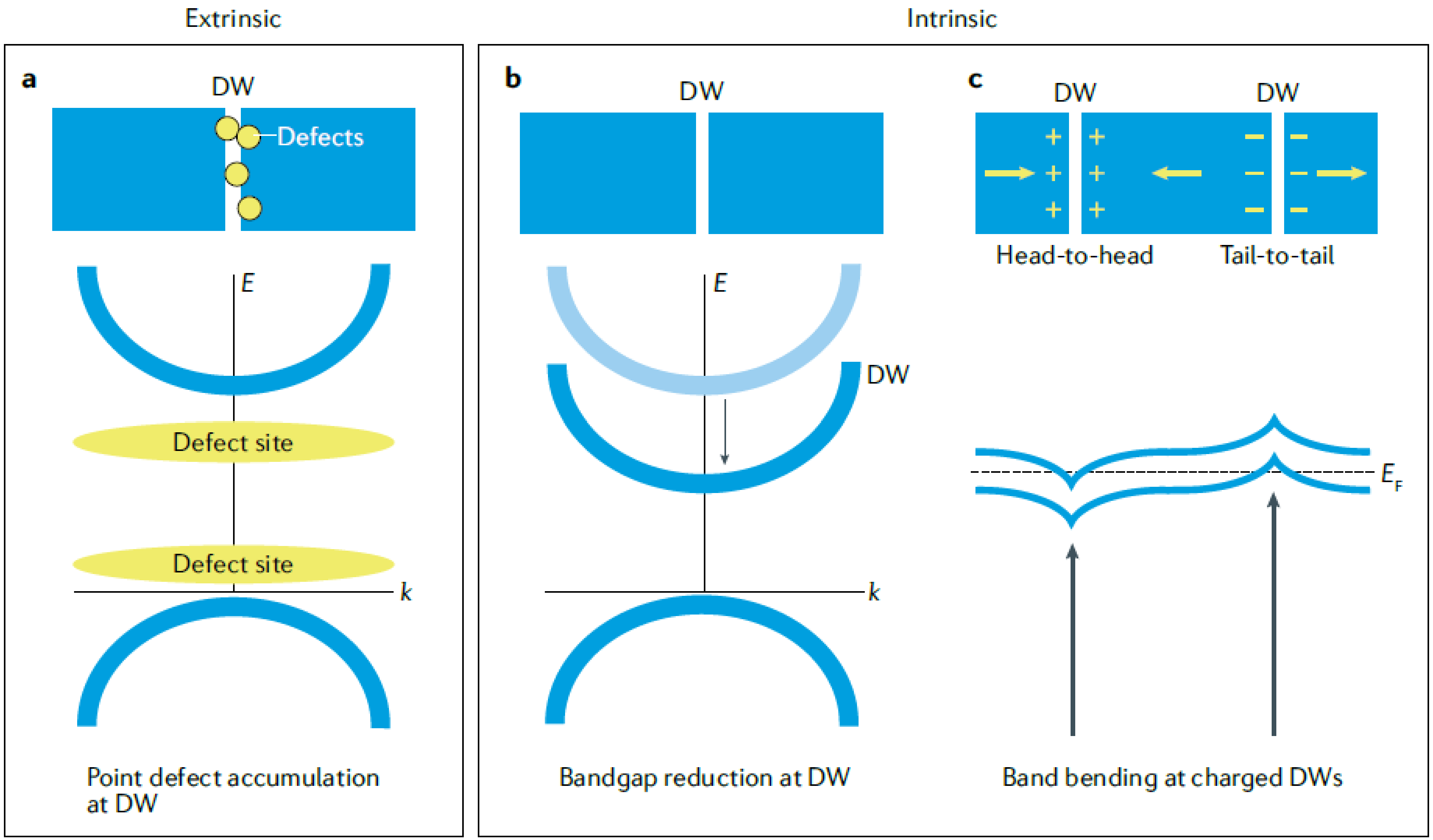
# Domain-wall engineering: electric conduction in ferroelectrics

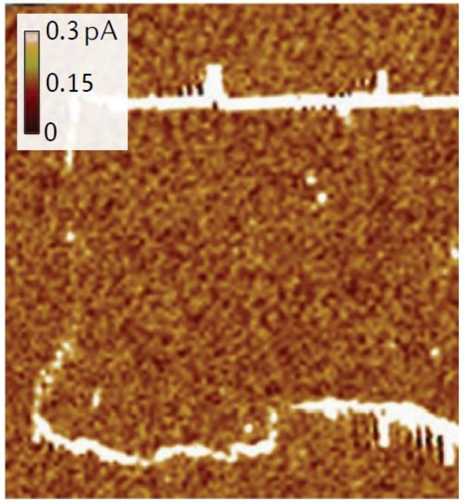


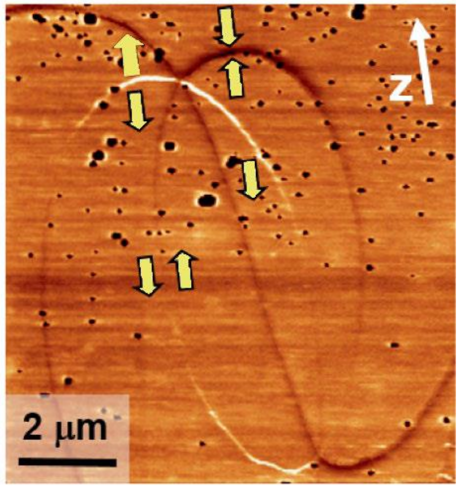




Nataf *et al.* Nat. Rev. Phys. **2** (2020). Meier, Selbach, Nat. Rev. Mater. **7** (2021). Sharma *et al.*, Materials **12**, 2927 (2019).

# Domain-wall engineering: electric conduction in ferroelectrics

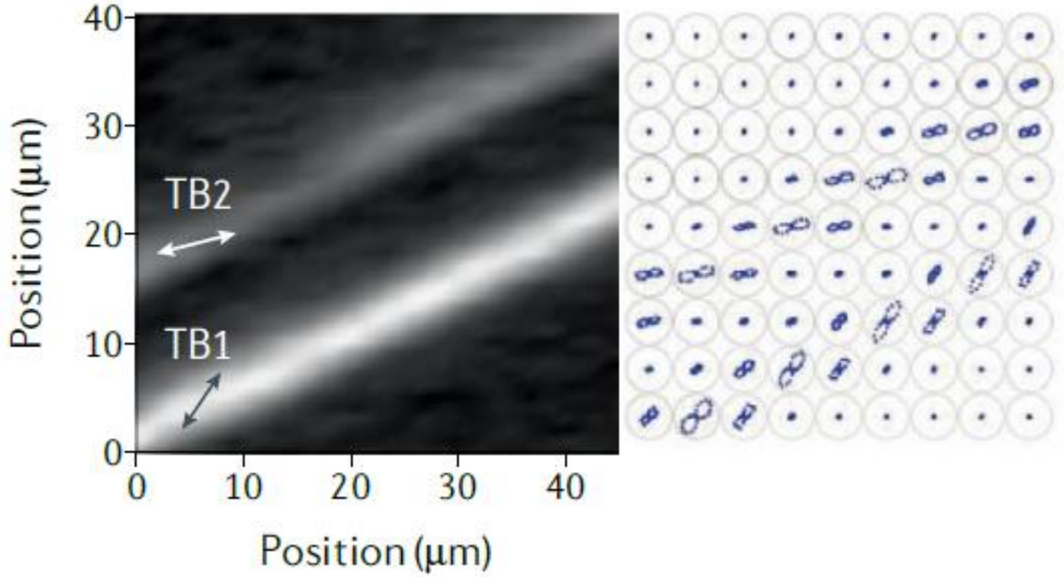


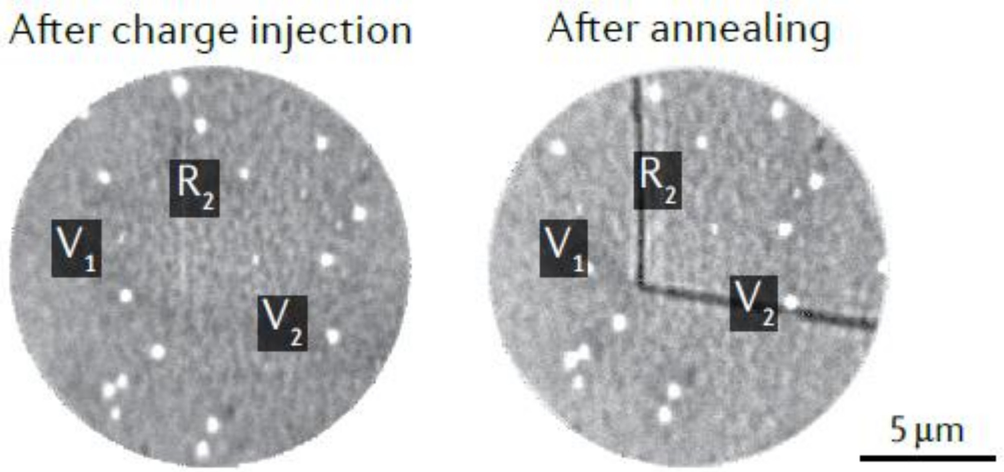




Nataf *et al.* Nat. Rev. Phys. **2** (2020). Meier, Selbach, Nat. Rev. Mater. **7** (2021). Sharma *et al.*, Materials **12**, 2927 (2019).

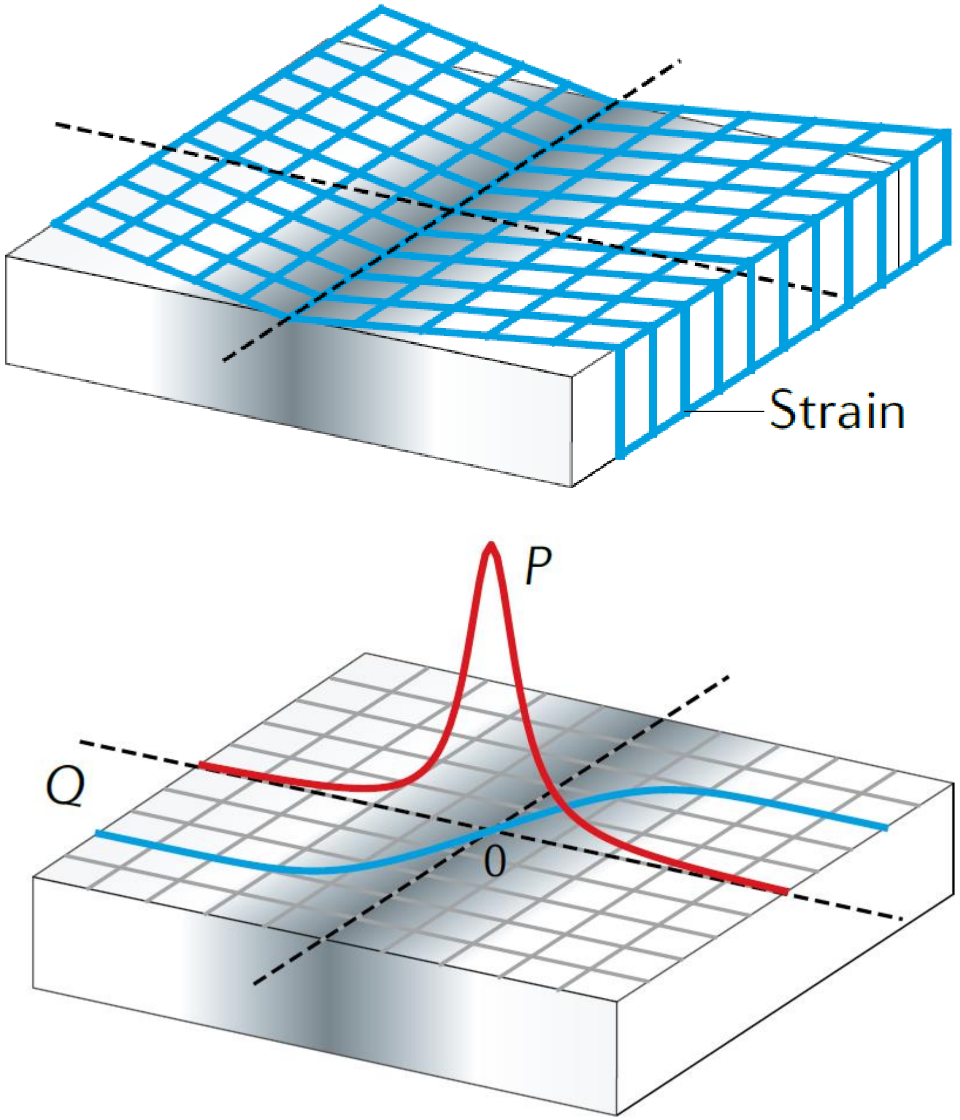
# Domain-wall engineering: polarization in non-polar materials

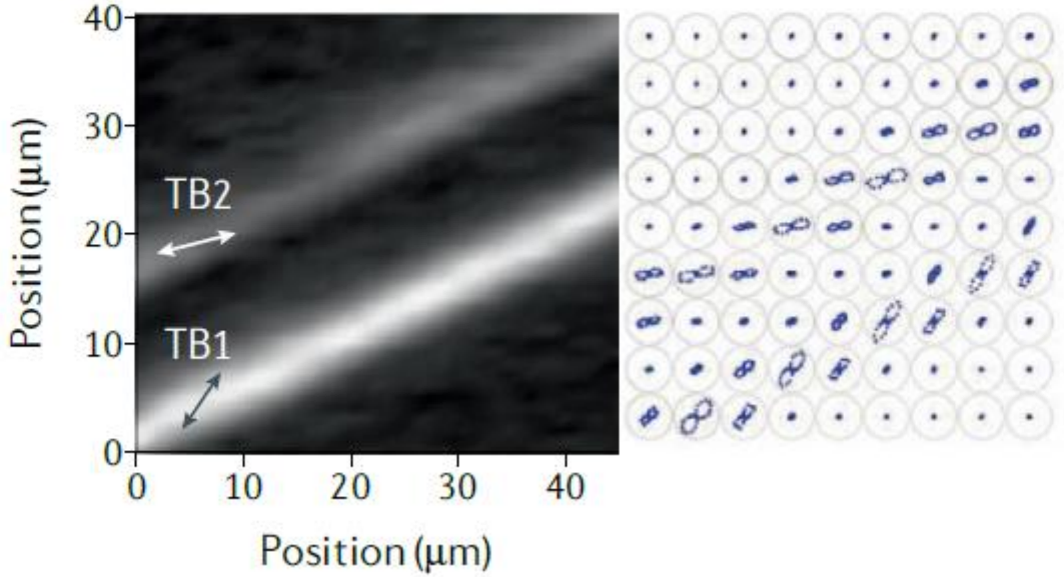


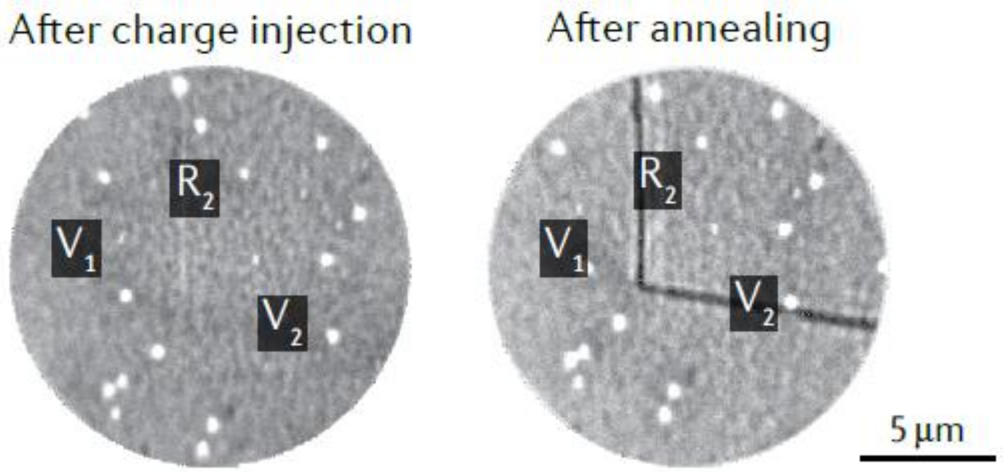




Yokota *et al.* Phys. Rev. B **89** (2014). Nataf *et al.* Phys. Rev. Mater. **1** (2017).

# Domain-wall engineering: polarization in non-polar materials




Nataf *et al.* Nat. Rev. Phys. **2** (2020). Cherifi-Hertel *et al.* J. Appl. Phys. **129** (2021).

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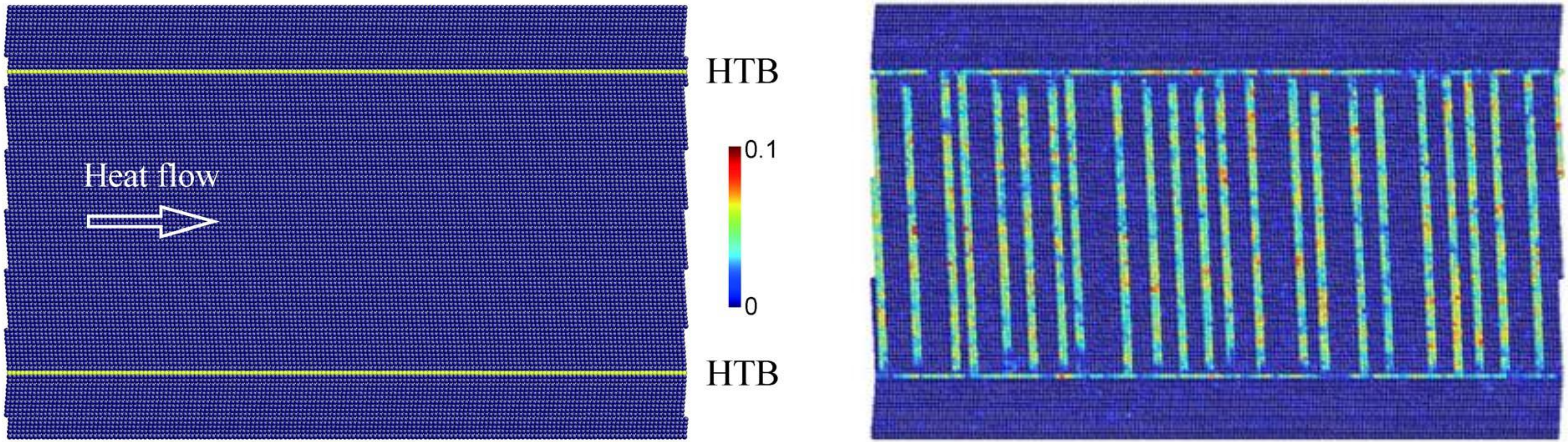
**Domain-wall engineering in ferroelectric and ferroelastic materials**

Domain walls are 2D topological defects that can move in response to an electric-field or an applied pressure. When this spatial confinement is combined with observations of emergent functional properties, it becomes clear that domain walls represent new and exciting objects in matter.

# Prediction: domain walls reduce the thermal conductivity




High thermal conductivity

$\kappa_{High}/\kappa_{Low} = 4$

Low thermal conductivity

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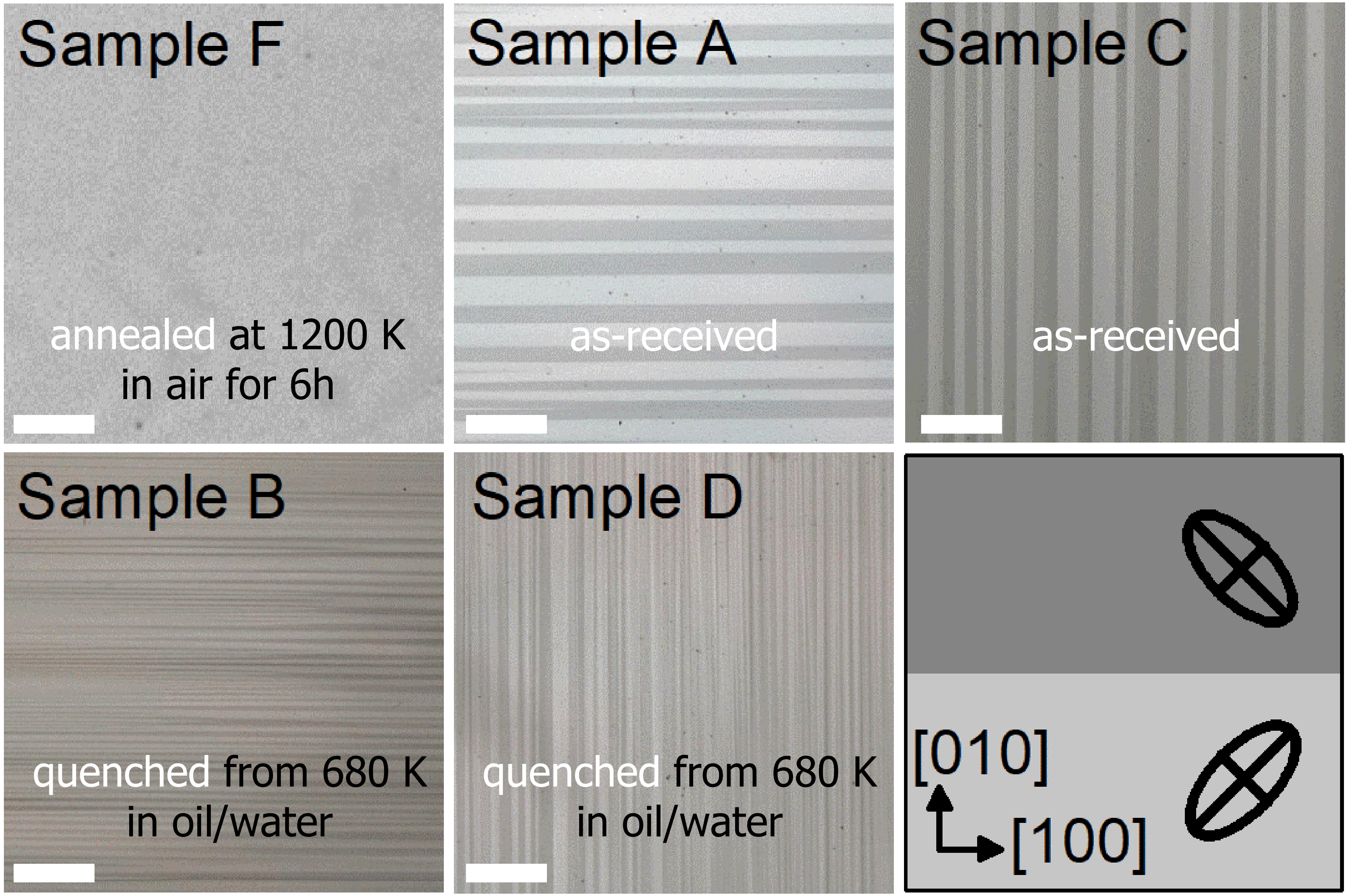
Li *et al.* Sci. Rep. **4** (2014). Royo *et al.* Phys. Rev. Mater. **1** (2017).

# A set of suitable samples: $LaAlO_3$ single crystals

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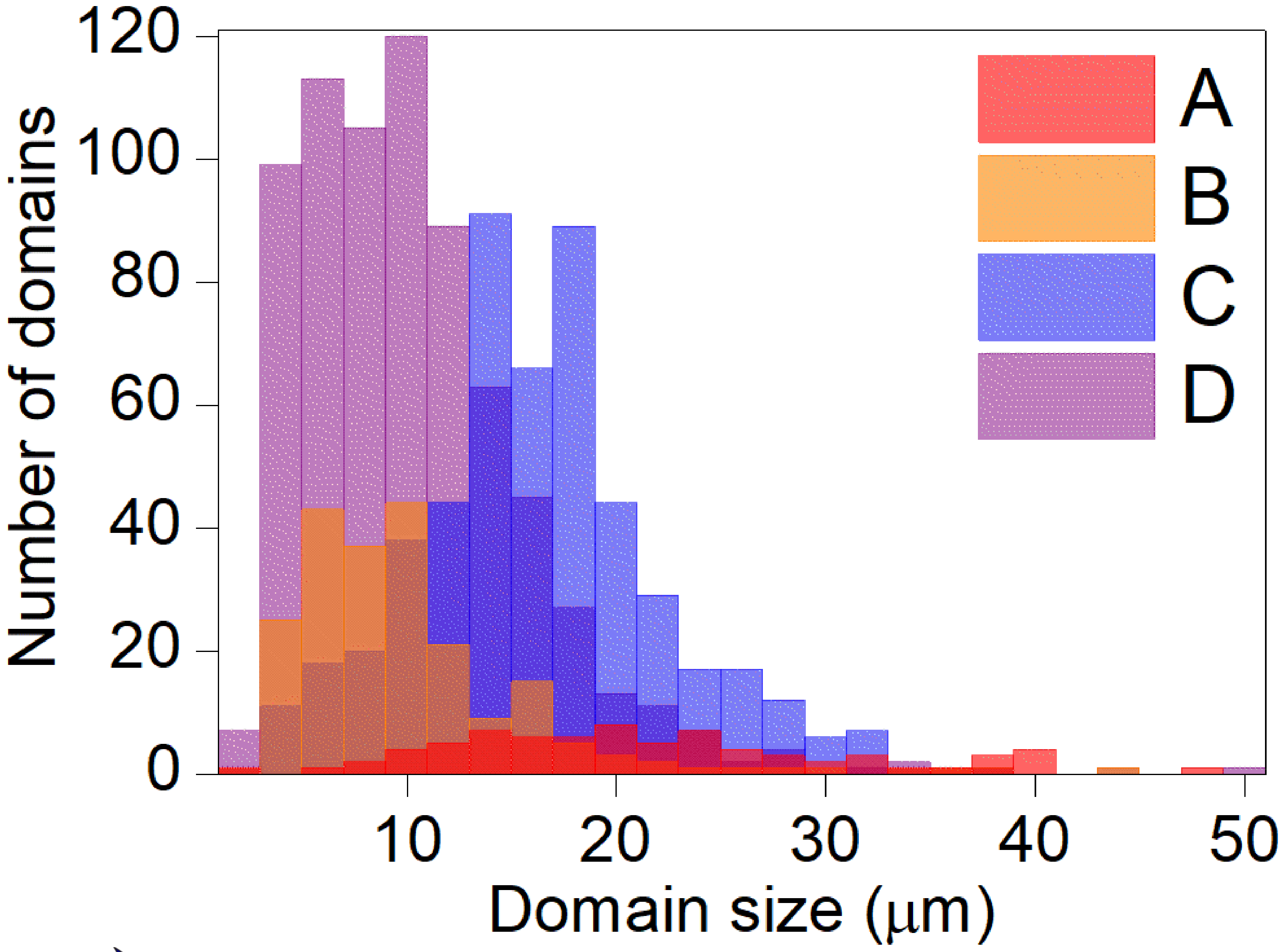
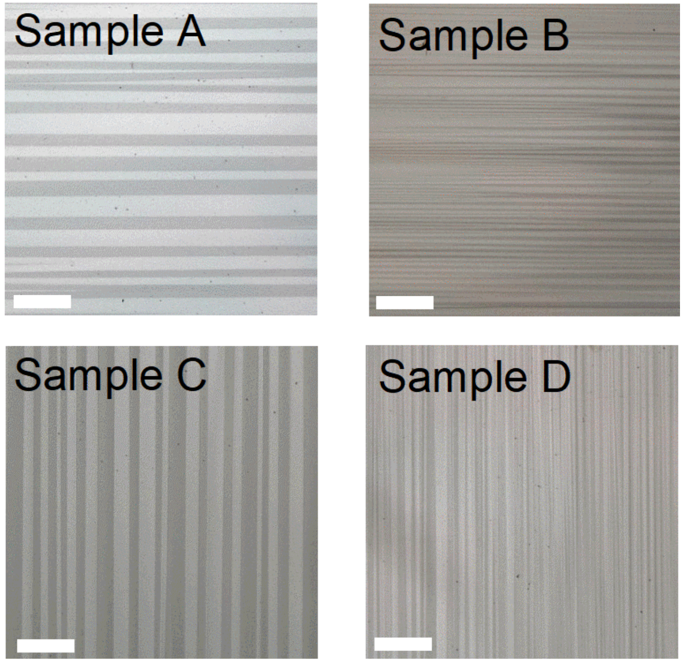
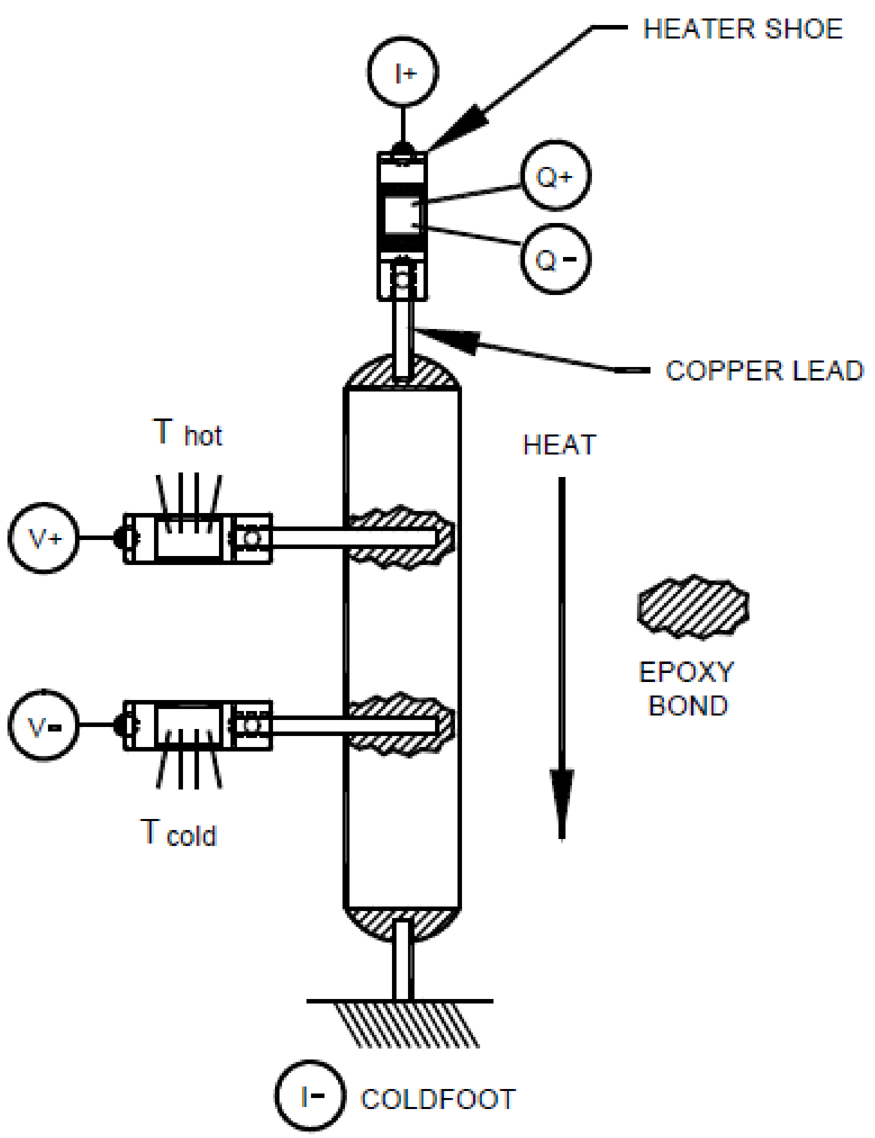
# Different densities of domain walls



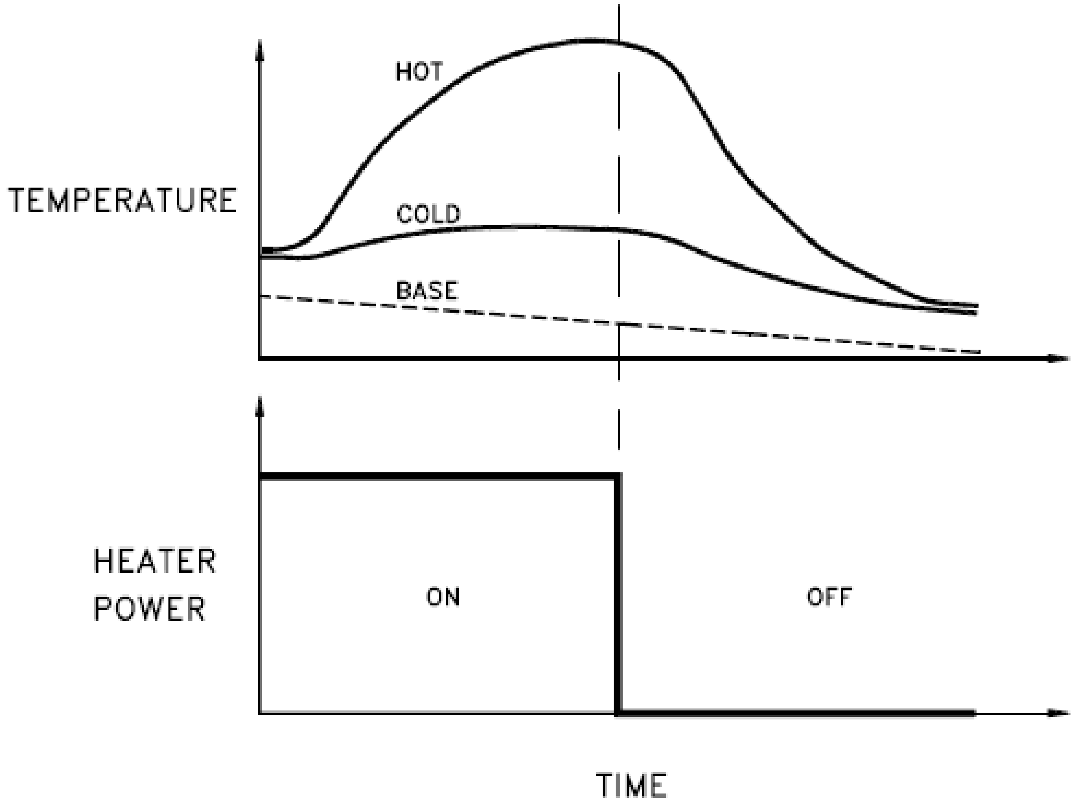



# Physical Property Measurement System (PPMS)




0.2 K $min^{-1}$

data on cooling and heating

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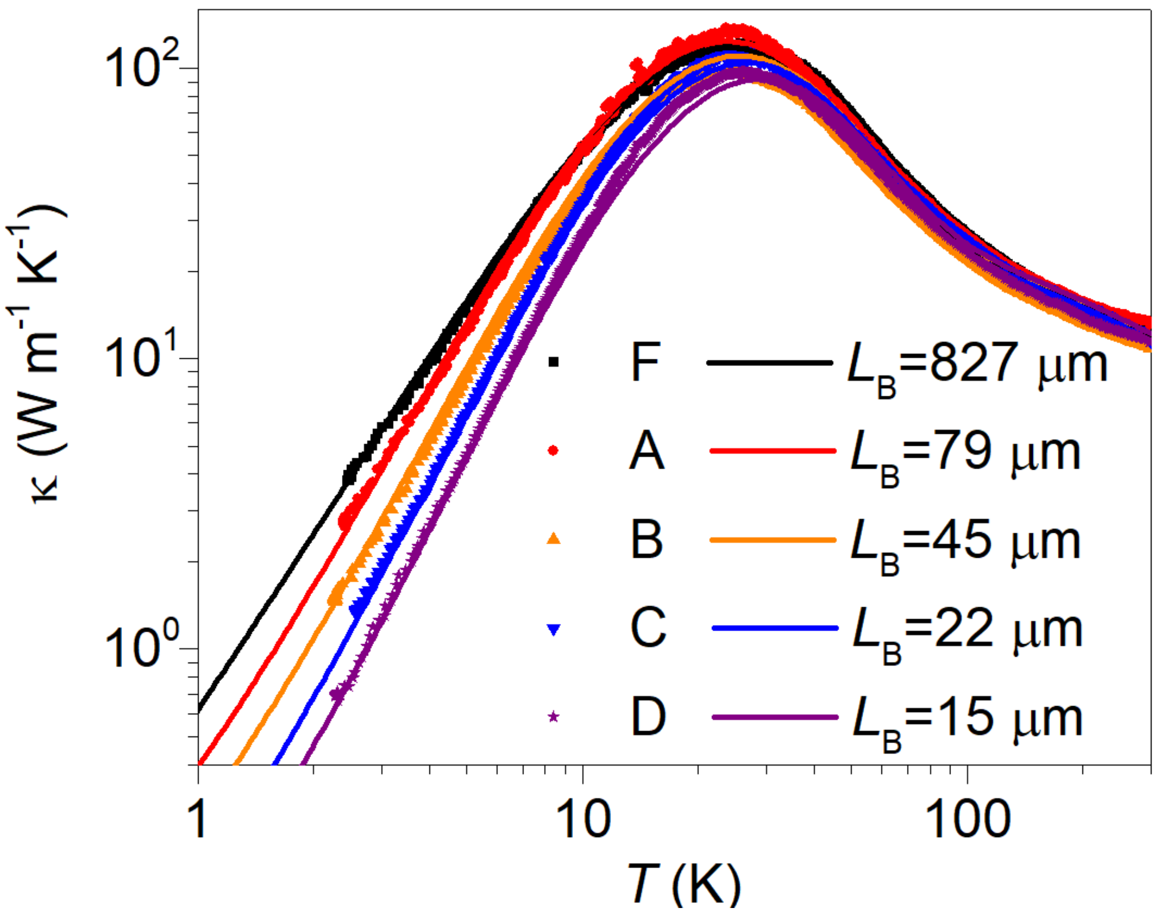
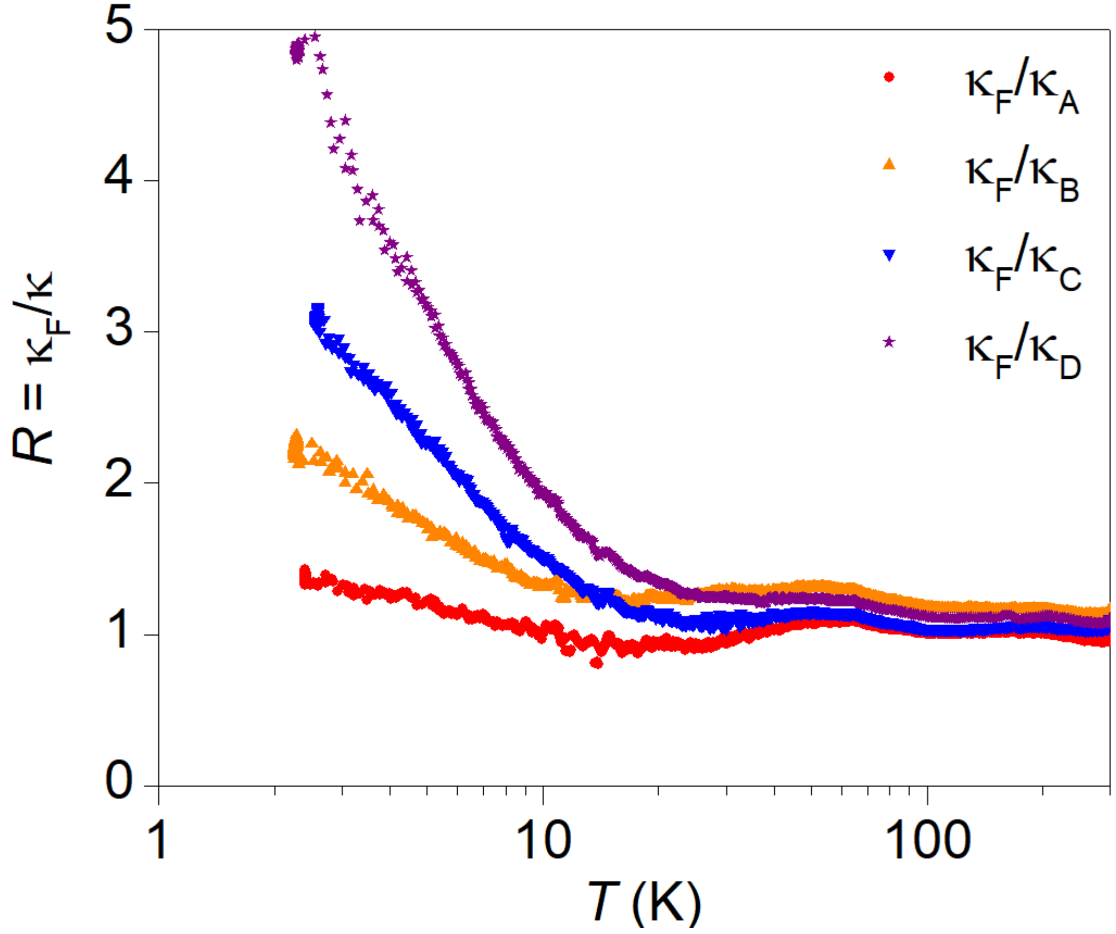
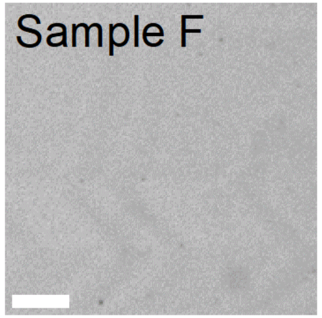
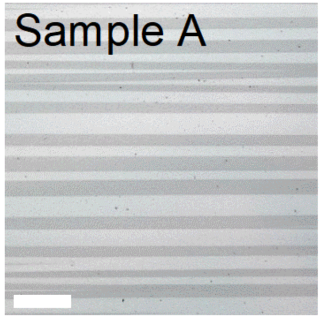
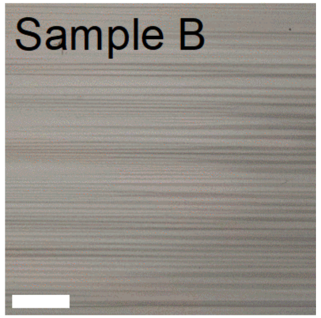
# Domain walls reduce the thermal conductivity

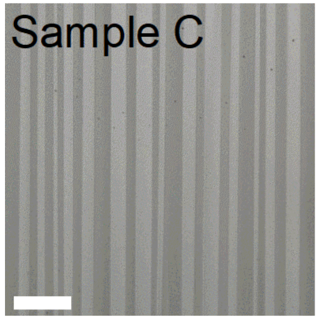


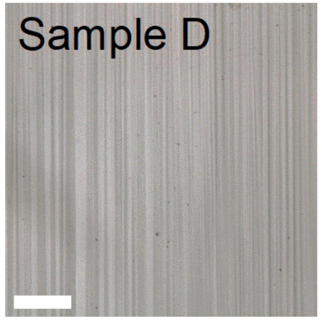

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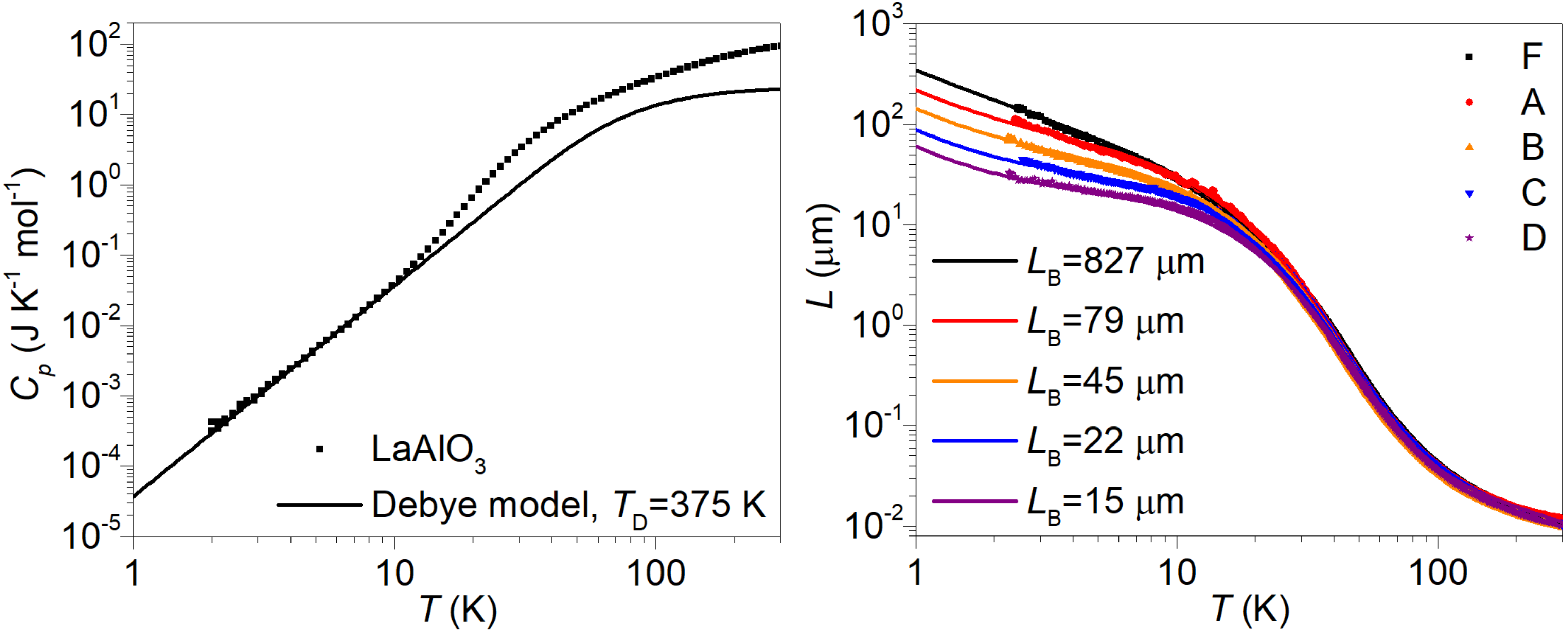
# Mean free path of the phonons

Mean free path: $k = 1/3\ C_v\ v\ L$
Effective mean free path: $1/L = 1/L_{\text{domain wall}} + 1/L_{\text{monodomain}}$

Scattering mechanisms:
**domain walls**, dislocations, Umklapp



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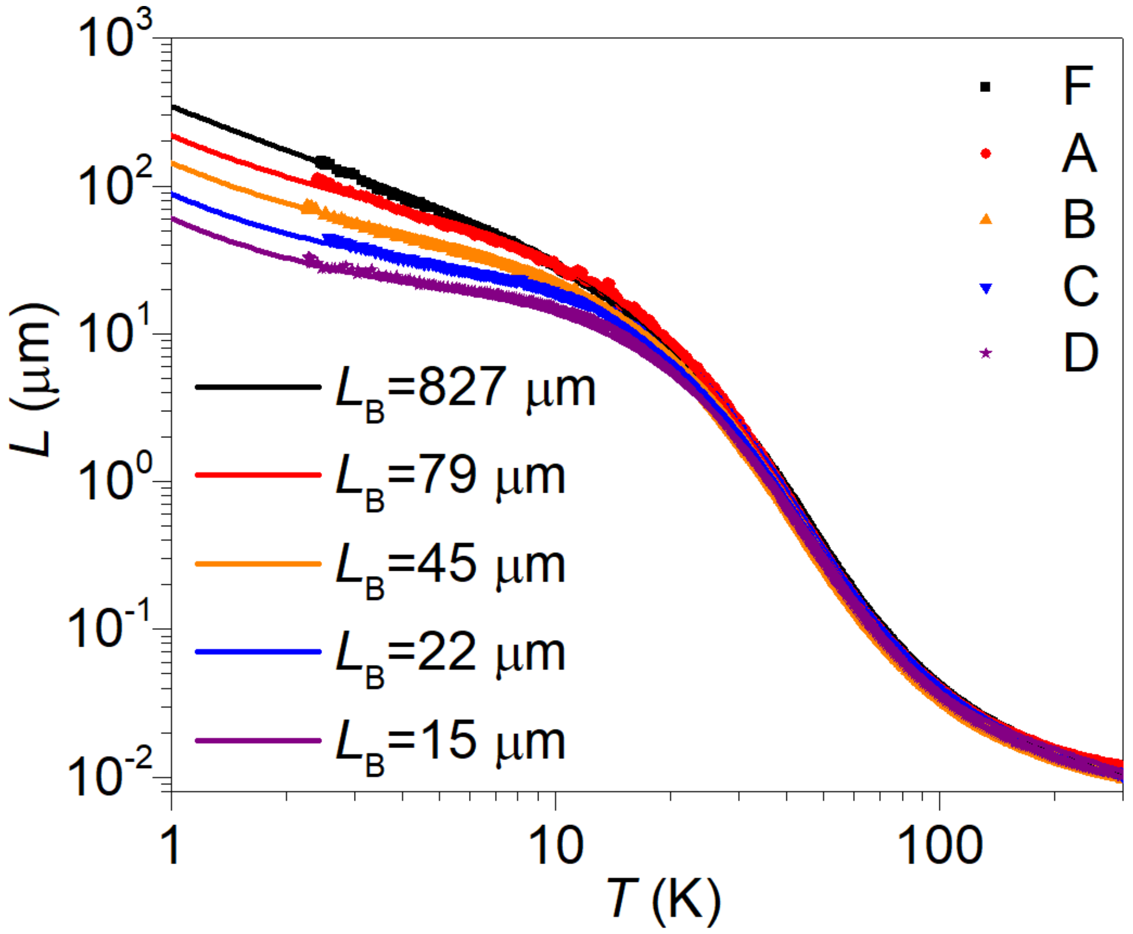


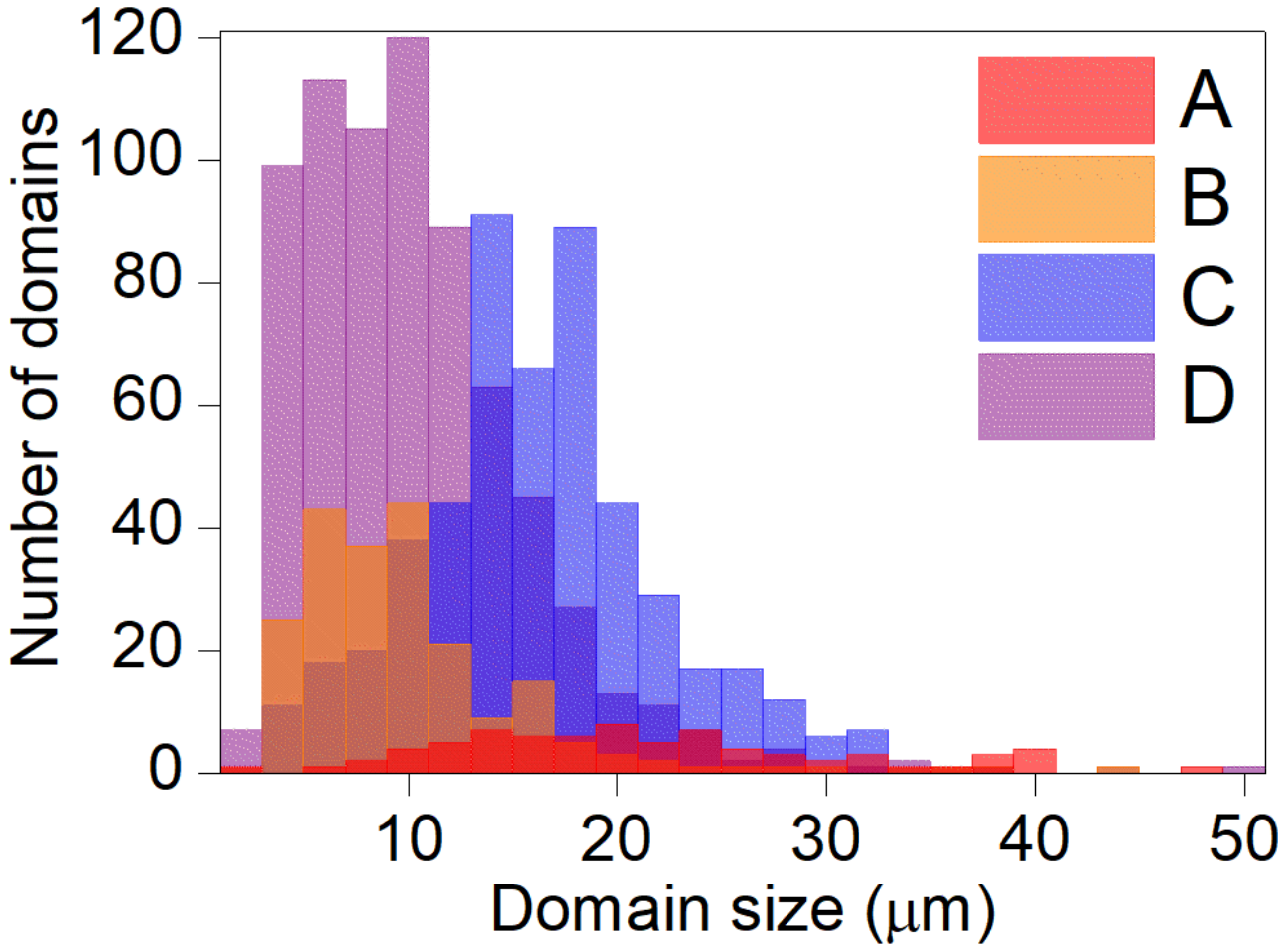


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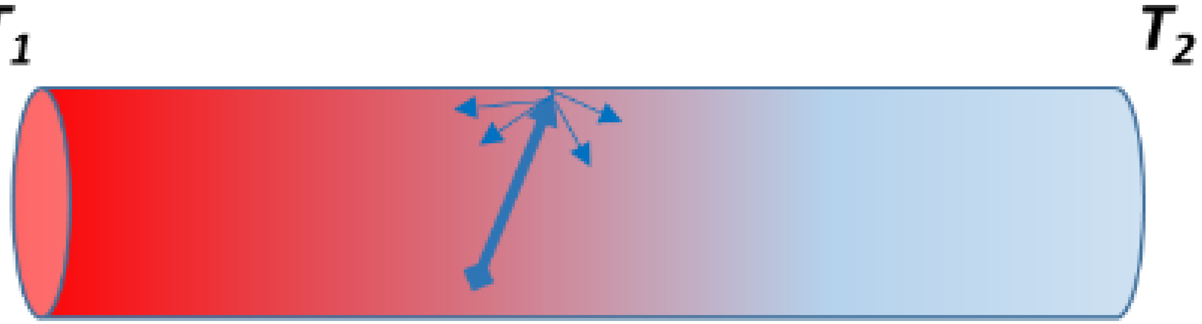



Each domain can be considered as an independent rectangular rod with its own thermal conductivity

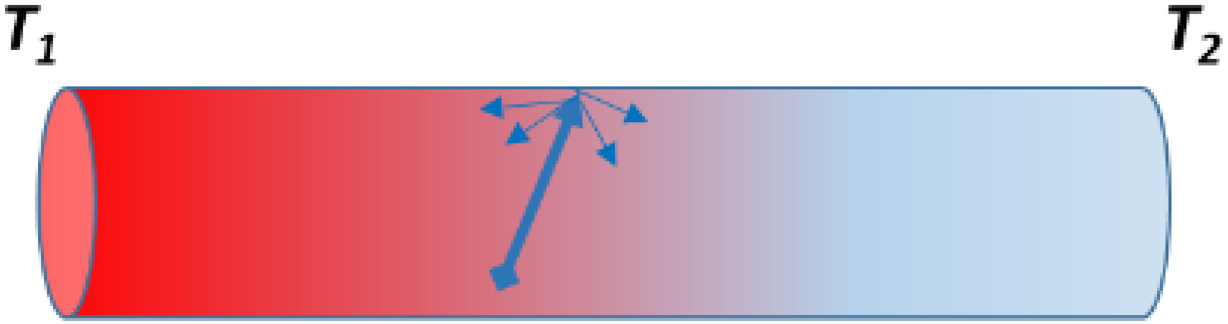
If walls are orthogonal to the flow, domains are in series, thermal resistances are additive

If walls are parallel to the flow, domains are in parallel, thermal conductances are additive



Casimir, Physica **5** (1938).

# Revisiting the Casimir model




| Samples: | F | A | B | C | D |
|---|---|---|---|---|---|
| $D$ (µm) | monodomain | 19 | 9 | 15 | 9 |
| $L_B$ (µm) | 827 | 79 | 45 | 22 | 15 |
| $L_C$ (µm) | 827 | 78 | 47 | 12 | 8 |

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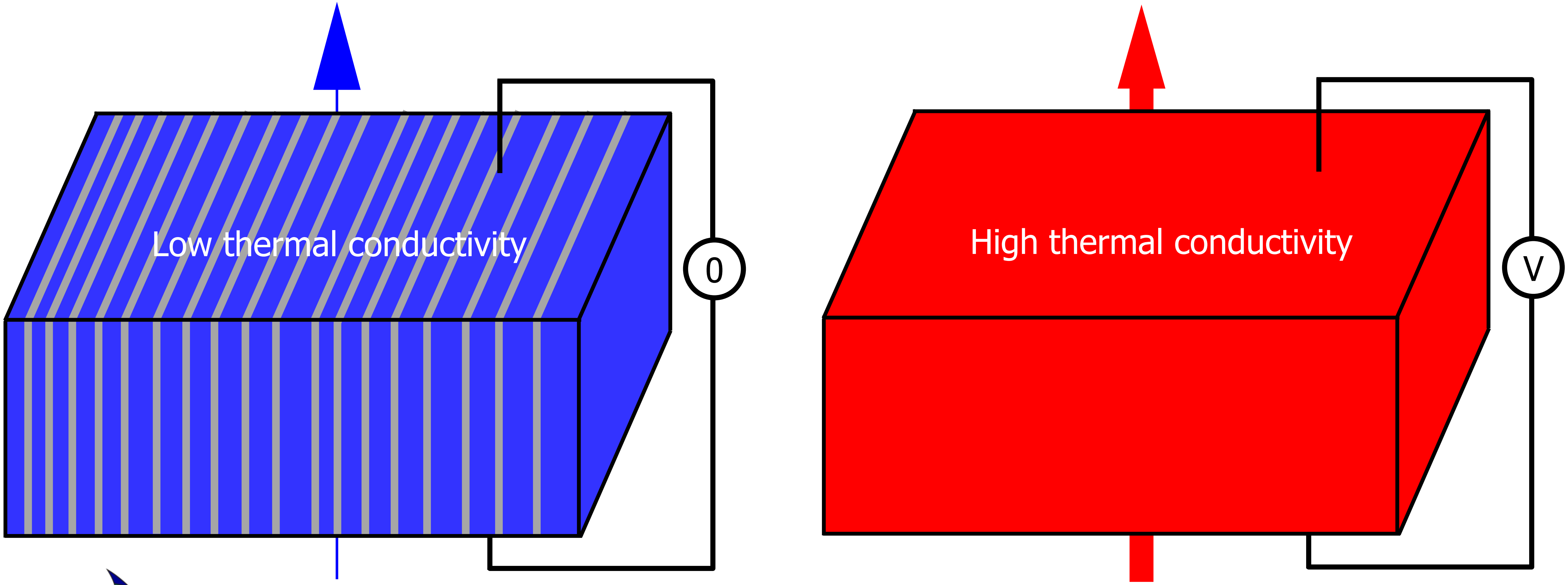
Casimir, Physica **5** (1938).

# Take home message: a "ferroelectric" thermal switch

Domain walls lead to a strong reduction of the thermal conductivity (factor 5)
Domain walls parallel to the heat flow influence the thermal conductivity
The mean free path of the phonons is larger than the size of the domains

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