Institute of Electronic Materials Technology

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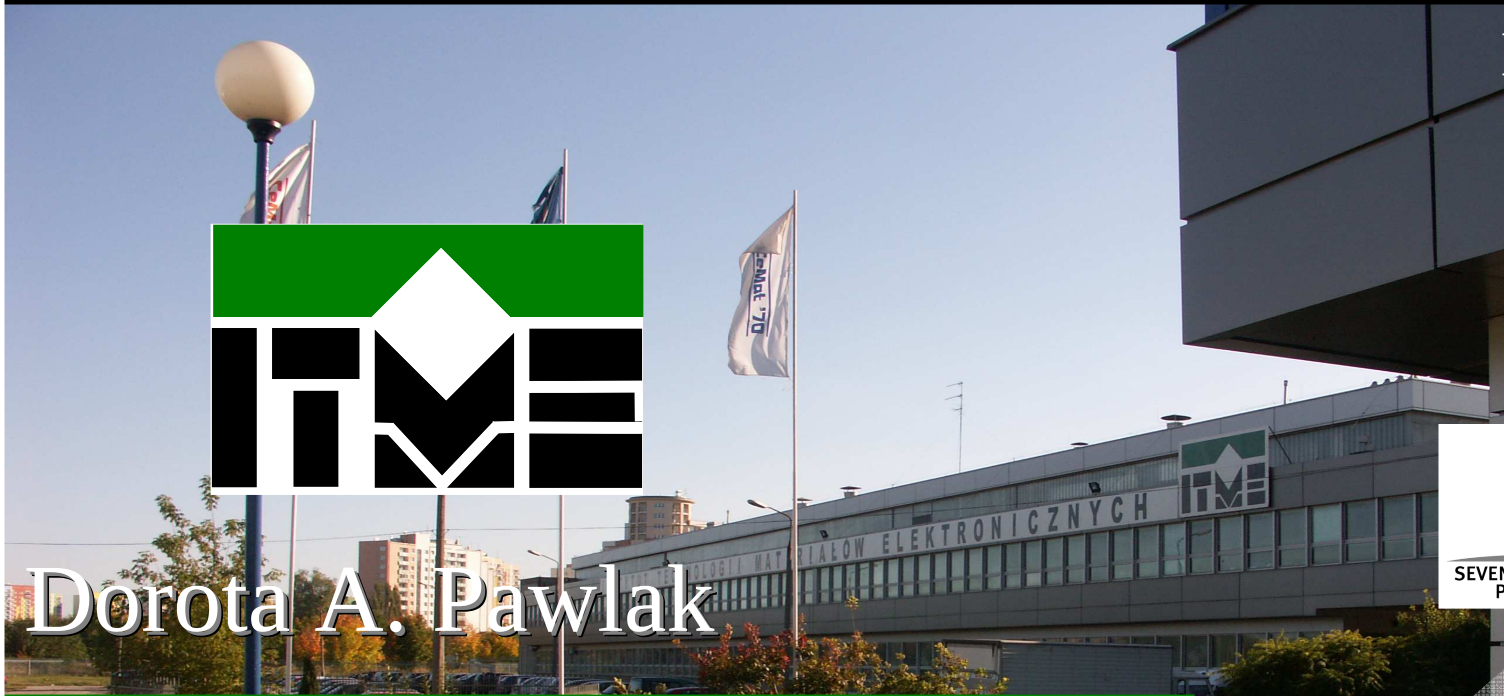

Dorota A. Pawlak

Self-organized eutectic micro- and nanostructures and other bottom-up approaches towards applications

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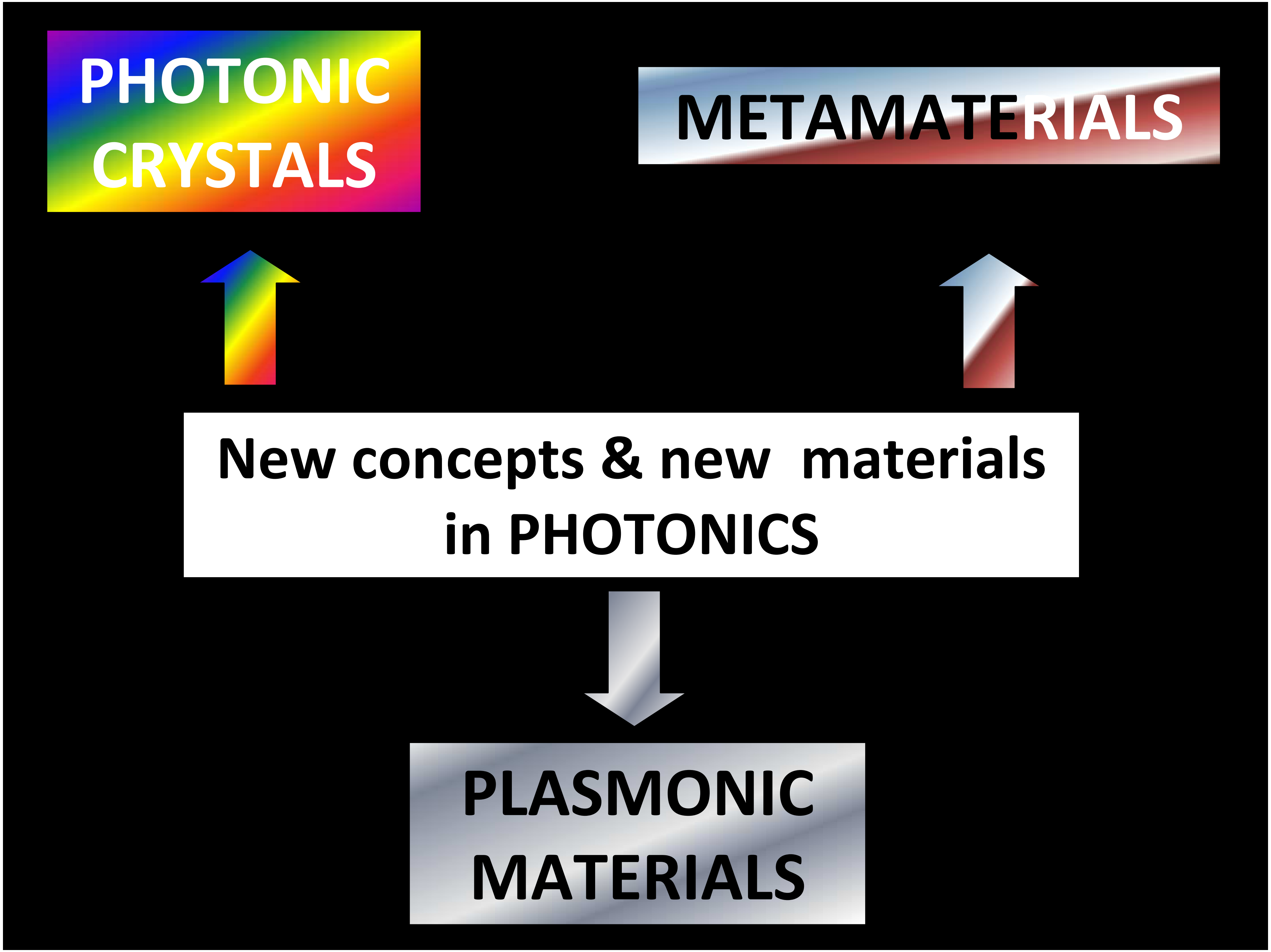
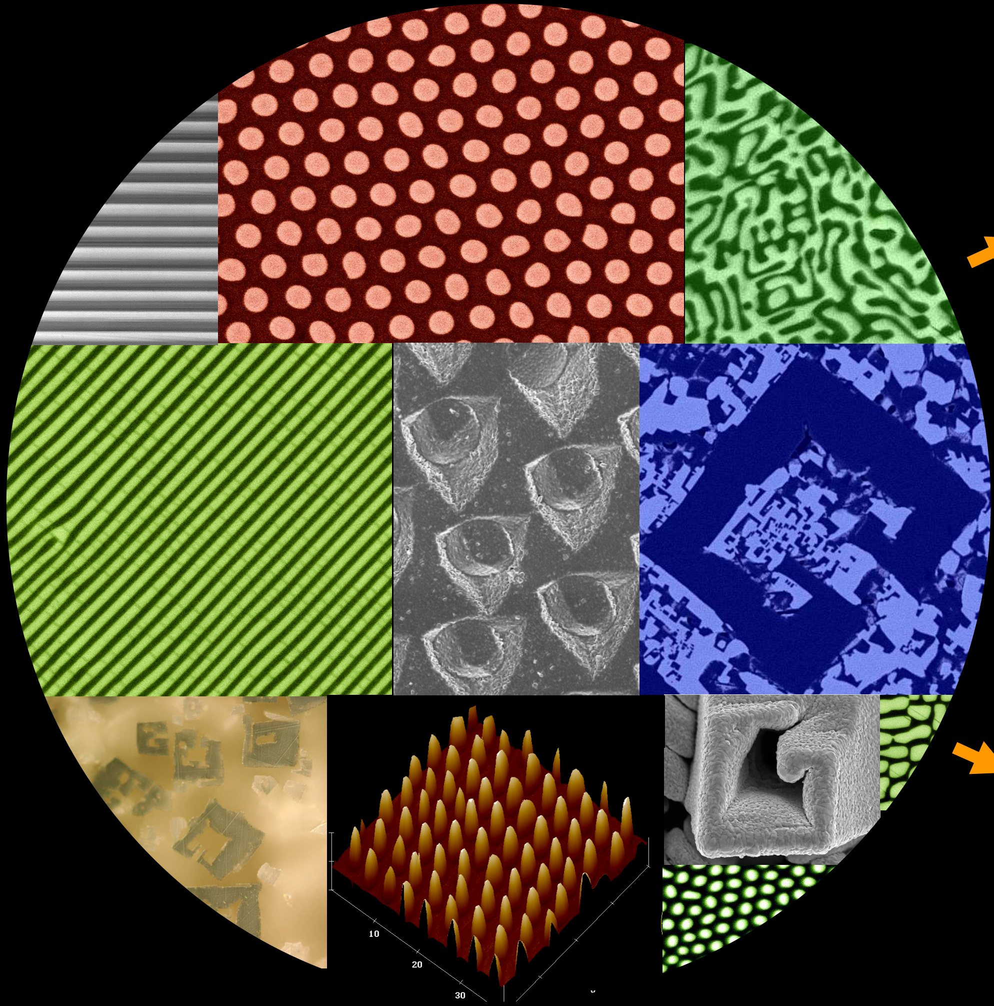
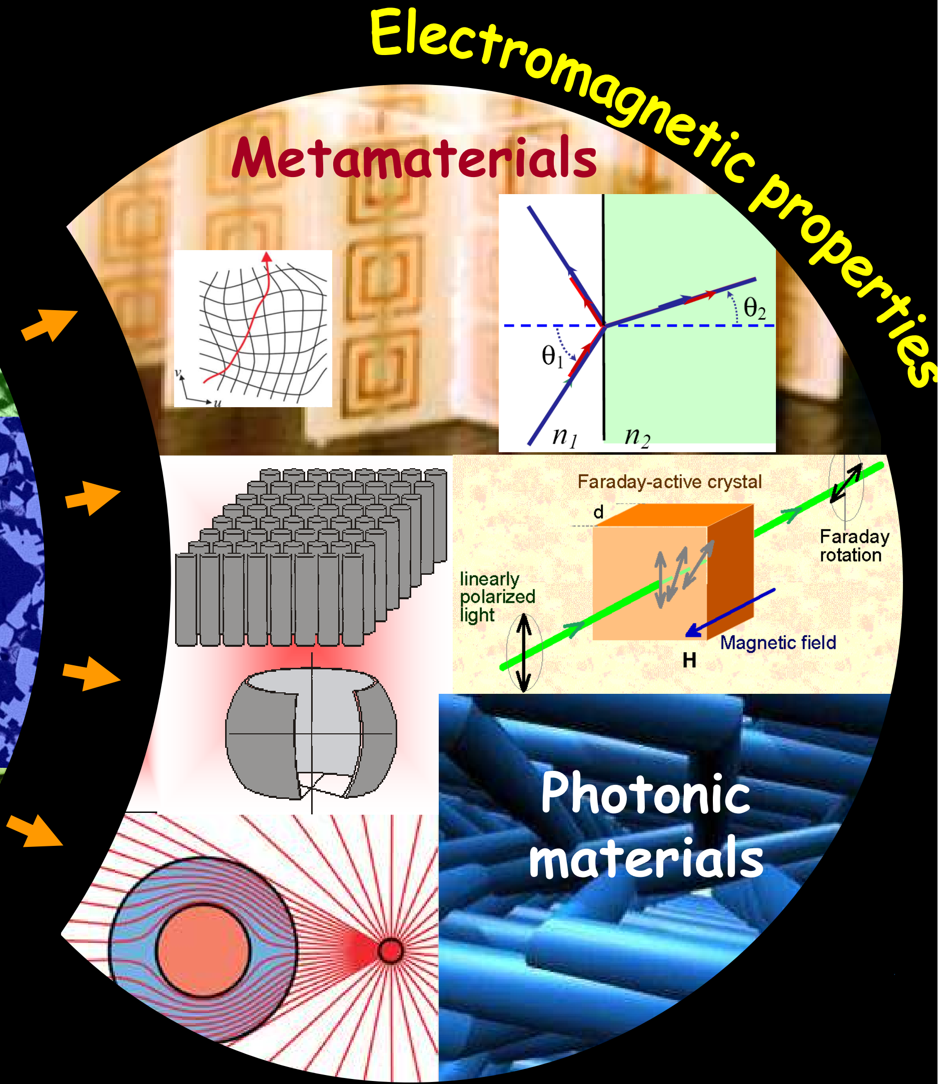

PHOTONIC CRYSTALS
METAMATERIALS
New concepts & new materials in PHOTONICS
PLASMONIC MATERIALS

Our research





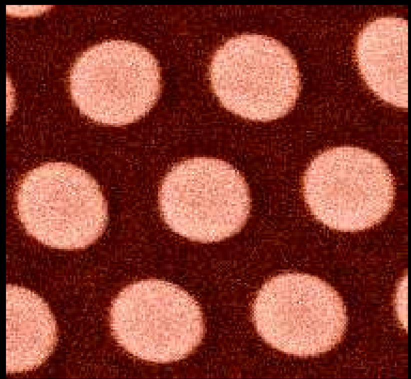
Bottom-up materials

Photonics/photovoltaics

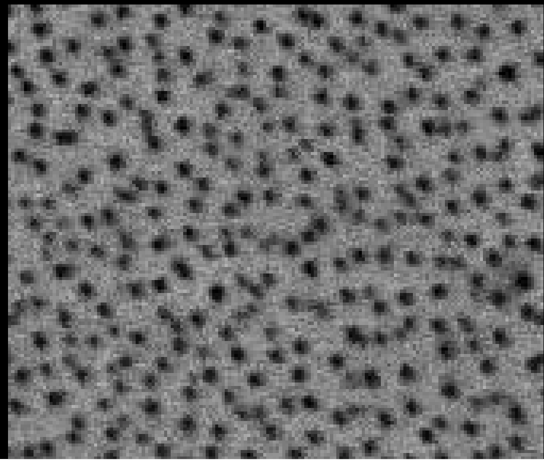
Our bottom-up approaches

based on directional solidification

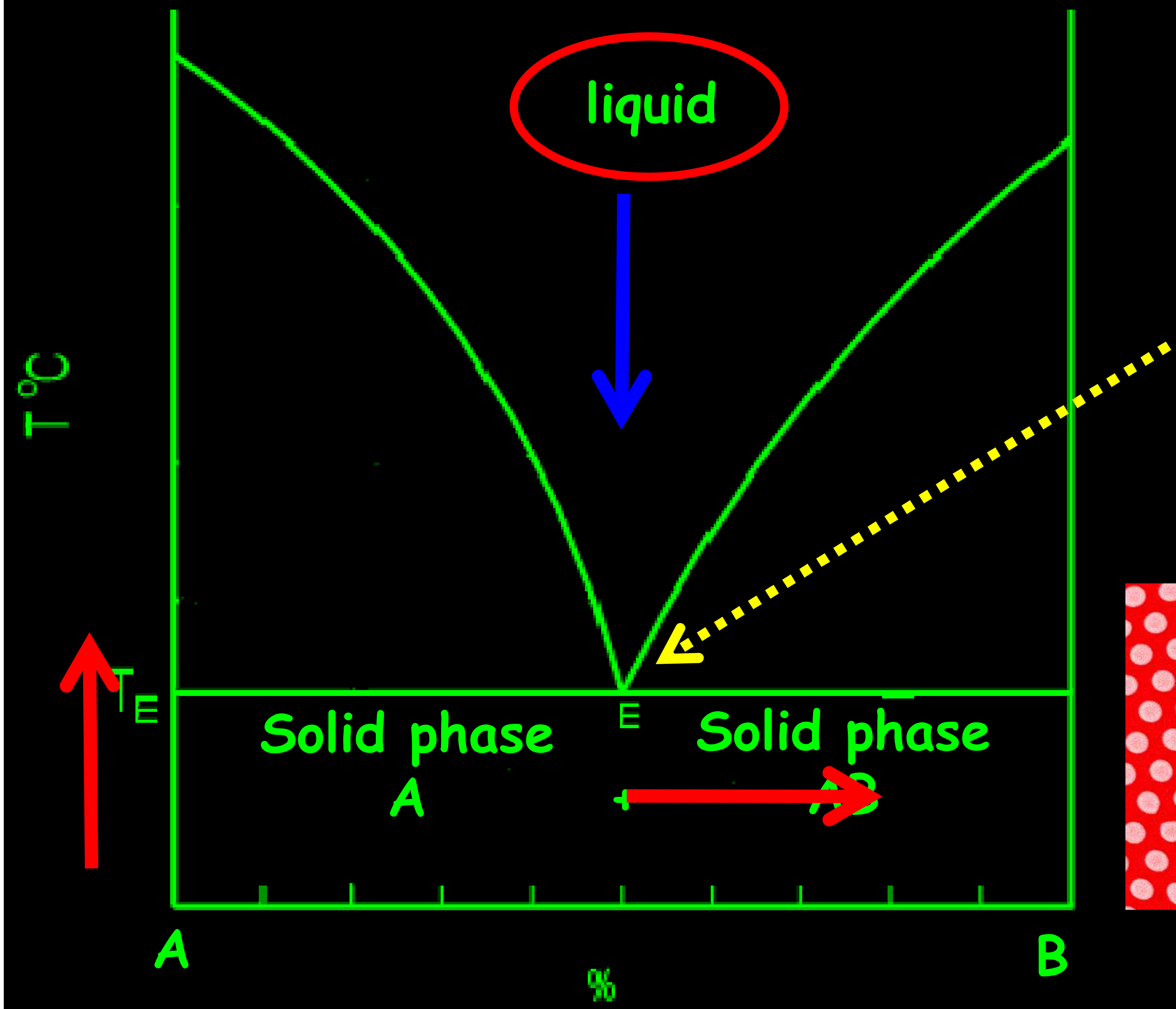
EUTECTIC solidification



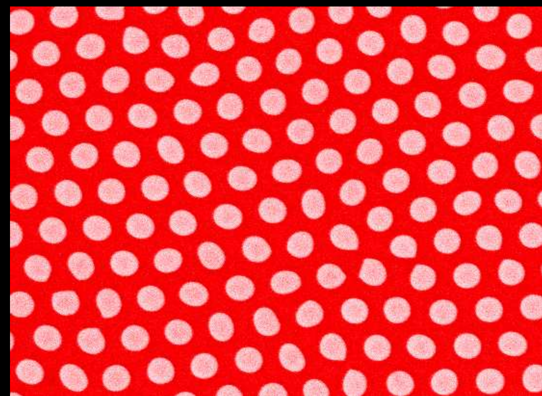
NANOPARTICLES dispersion



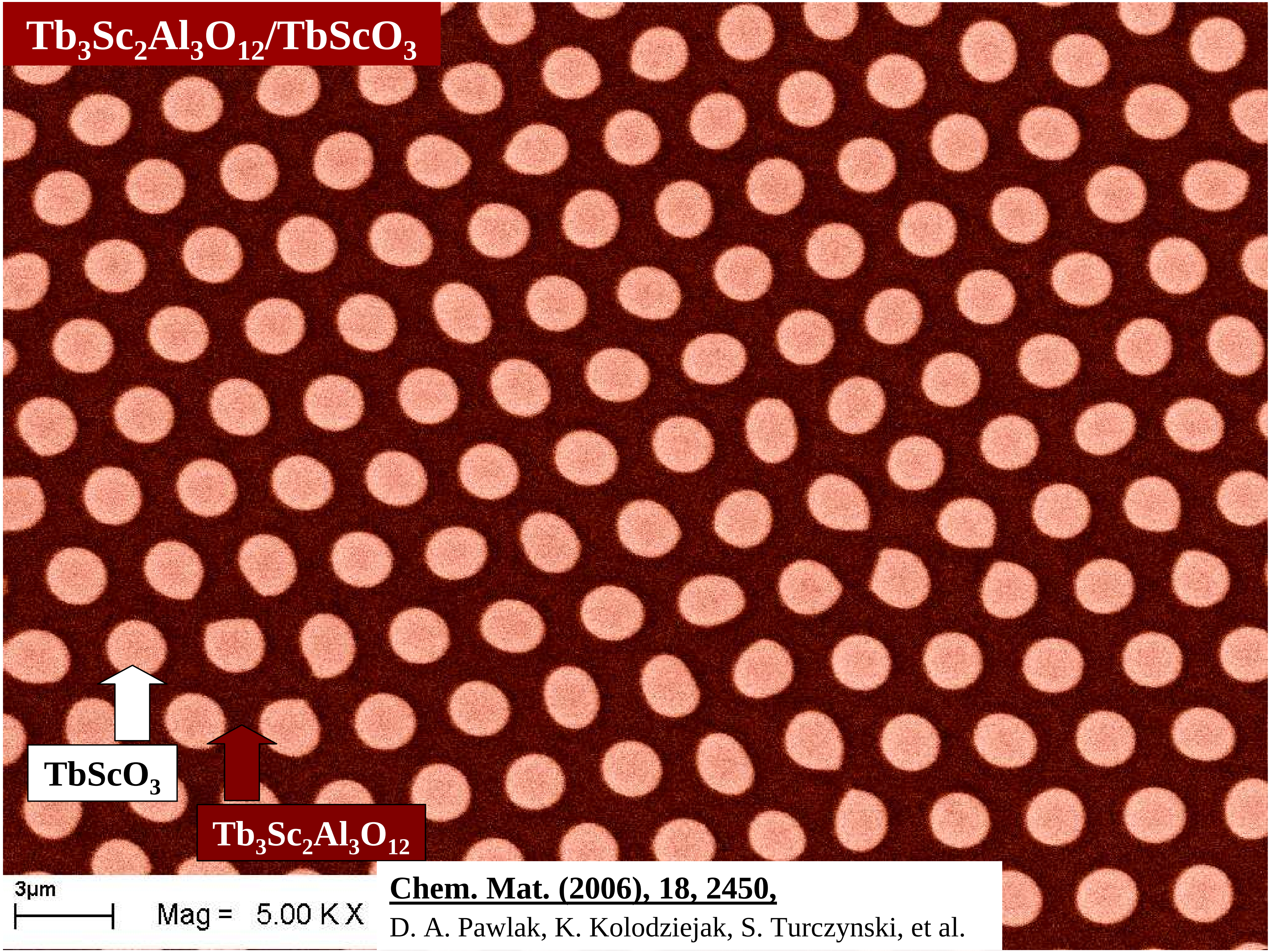
Binary eutectic phase diagram



Eutectic point



$Tb_3Sc_2Al_3O_{12}/TbScO_3$



Chem. Mat. (2006), 18, 2450,
D. A. Pawlak, K. Kolodziejak, S. Turczynski, et al.

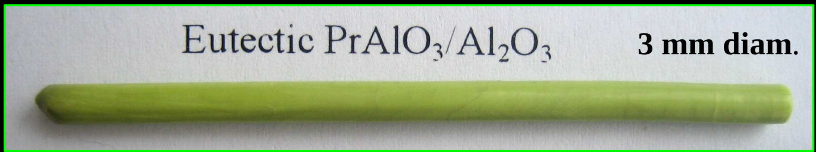
Versatility of EUTECTICS

- MONOLITH and MULTIPHASE MATERIAL
- Almost arbitrary COMPONENT materials
- Many special GEOMETRICAL MOTIFS
- Controlled structuring size

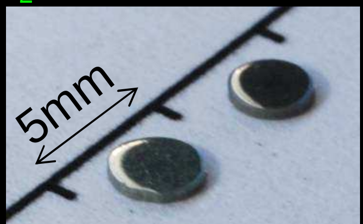
  from micro to nano regime

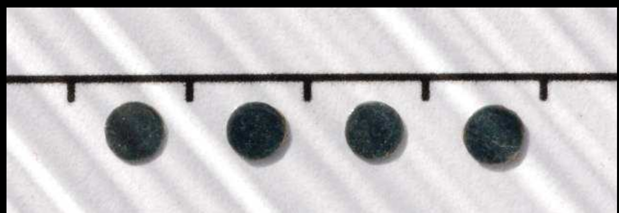
• MONOLITH and MULTIPHASE MATERIAL

BULK 3D material - Monolith

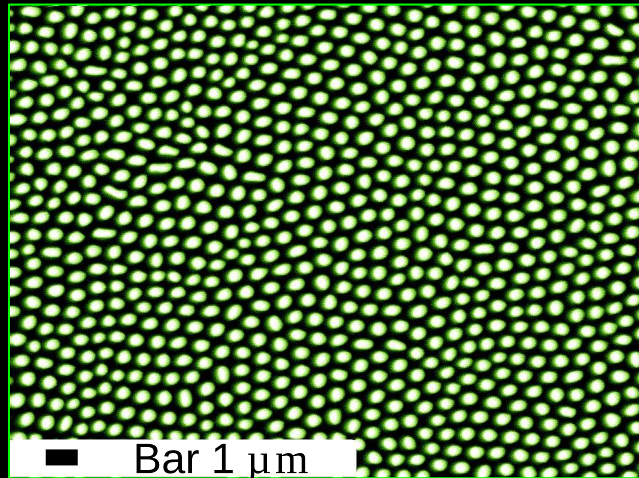


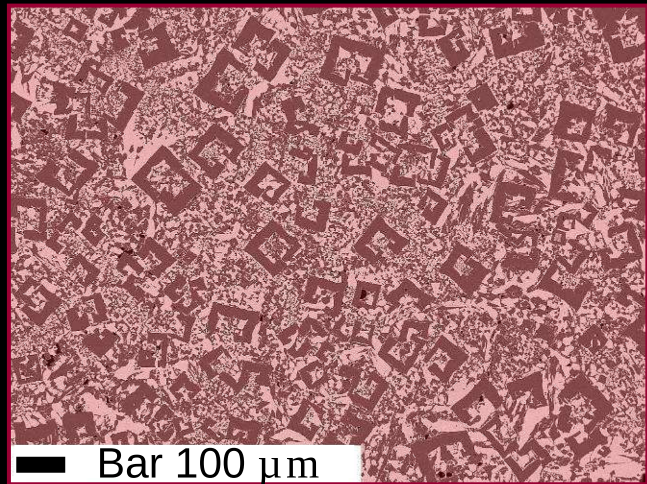
$SrTiO_3$-TiO_2





Micro/nano structured





• Almost arbitrary COMPONENT materials

METALS

SEMICONDUCTORS

ISOLATORS

OXIDES

FLUORIDES

(Anti) FERROELECTRICS

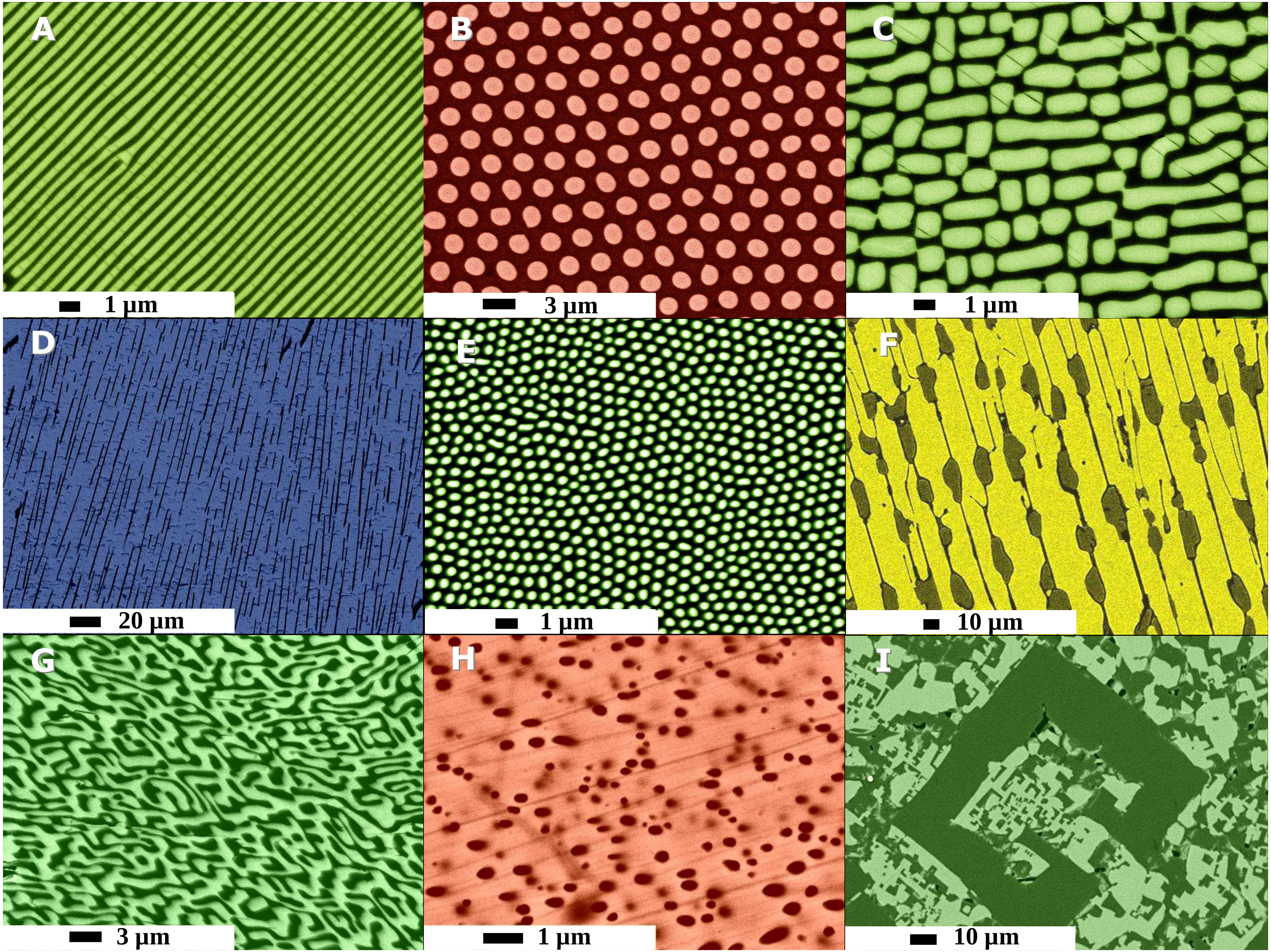
(Anti) FERROMAGNETICS

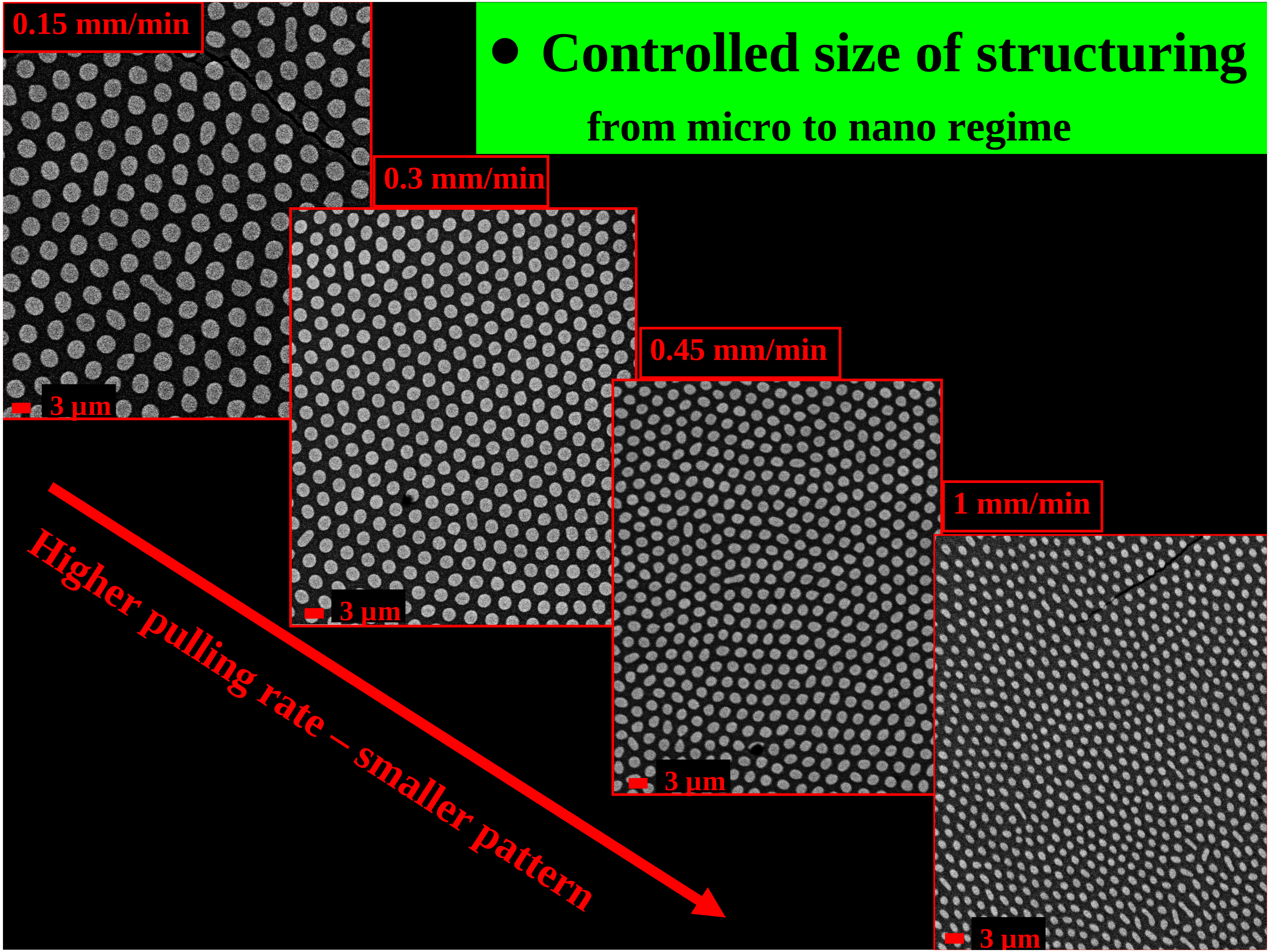
NONLINEAR

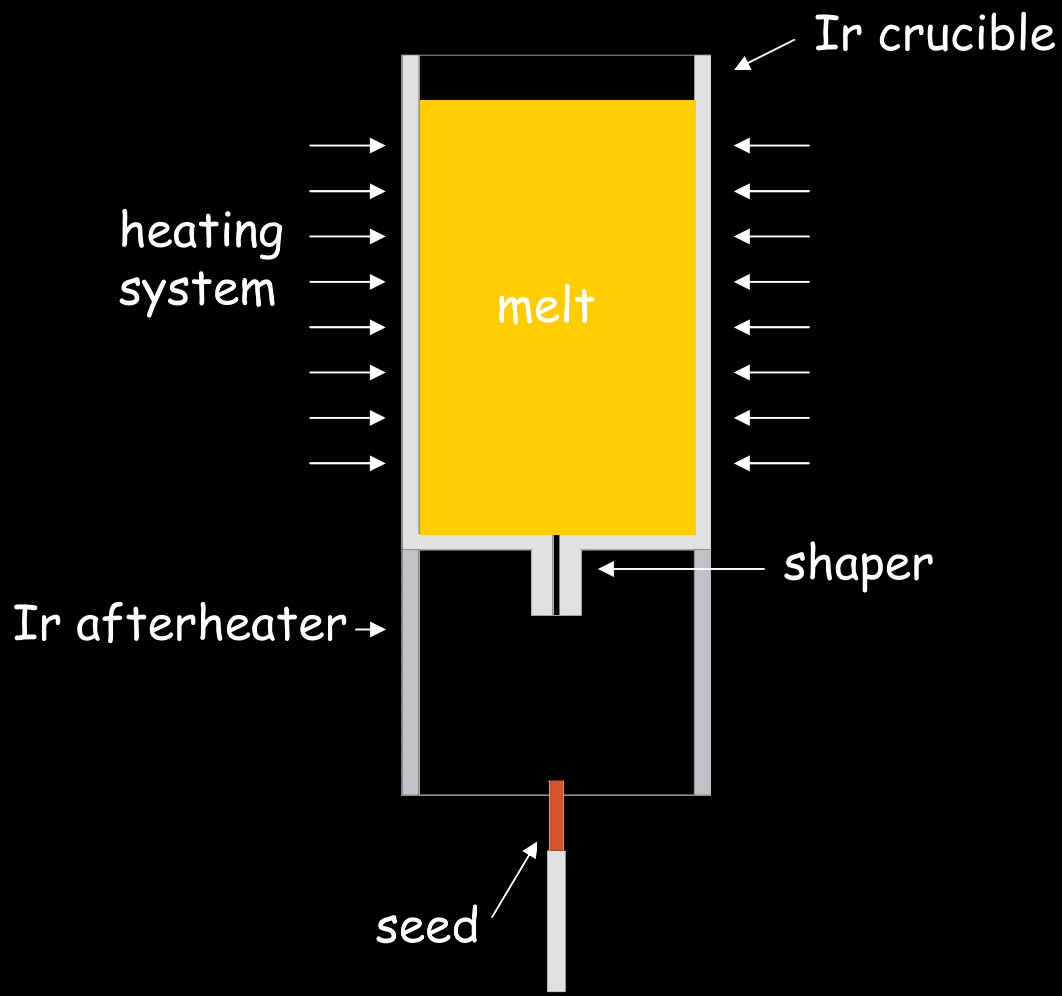
OPTICALLY ACTIVE

ORGANIC COMPOUNDS

etc.

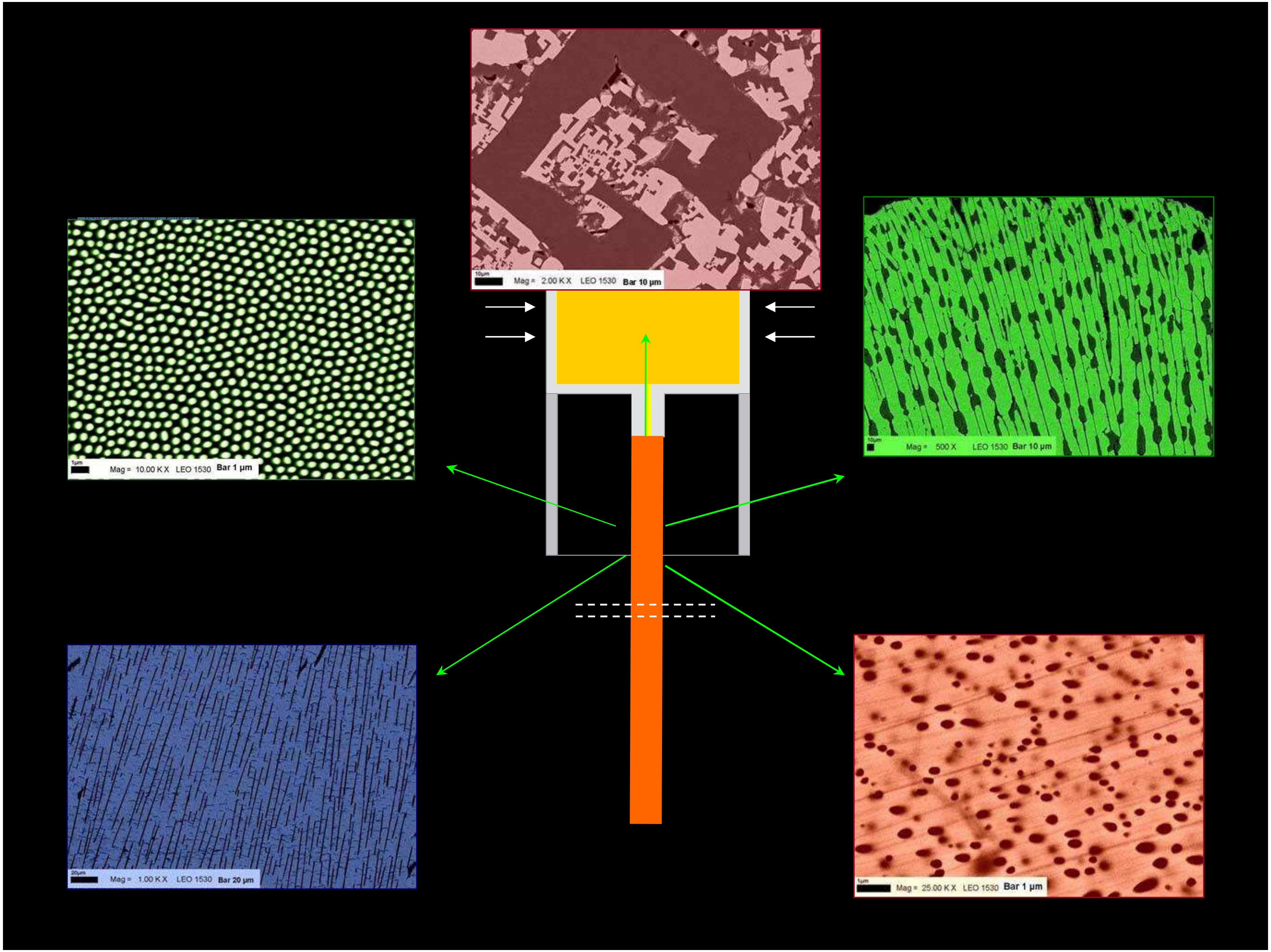

A
1 µm
B
3 µm
C
1 µm
D
20 µm
E
1 µm
F
10 µm
G
3 µm
H
1 µm
I
10 µm


• Controlled size of structuring
from micro to nano regime
0.15 mm/min
3 µm
0.3 mm/min
3 µm
0.45 mm/min
3 µm
1 mm/min
3 µm
Higher pulling rate – smaller pattern



Micro-pulling down method

Fukuda, T. et al. *J. Cryst. Growth* **1994**, 142, 339-343



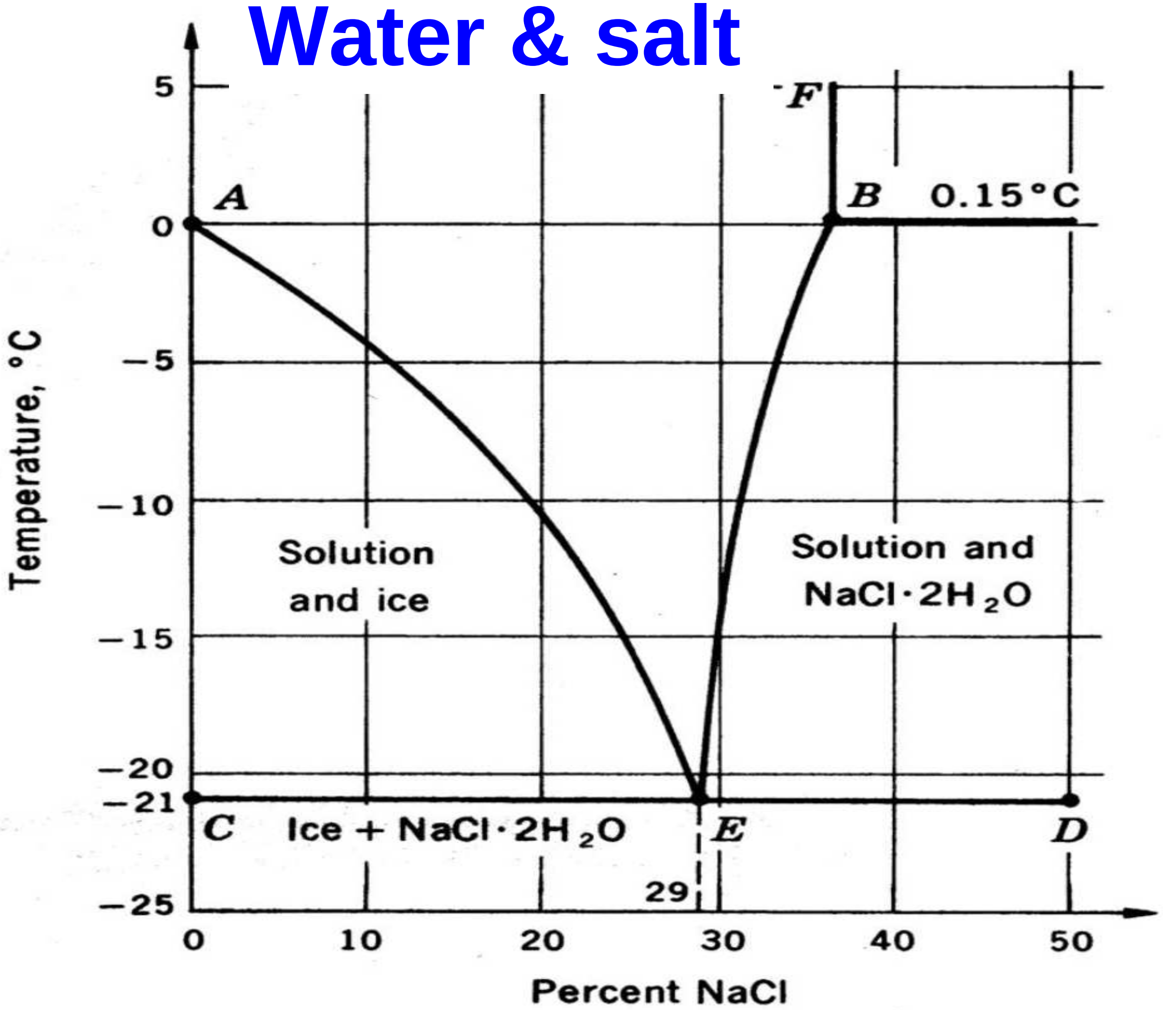
10µm
Mag = 2.00 K X LEO 1530 Bar 10 µm
1µm
Mag = 10.00 K X LEO 1530 Bar 1 µm
10µm
Mag = 500 X LEO 1530 Bar 10 µm
20µm
Mag = 1.00 K X LEO 1530 Bar 20 µm
1µm
Mag = 25.00 K X LEO 1530 Bar 1 µm

Eutectic for Polish winter

Eutectic point at:

-21°C, 29% NaCl

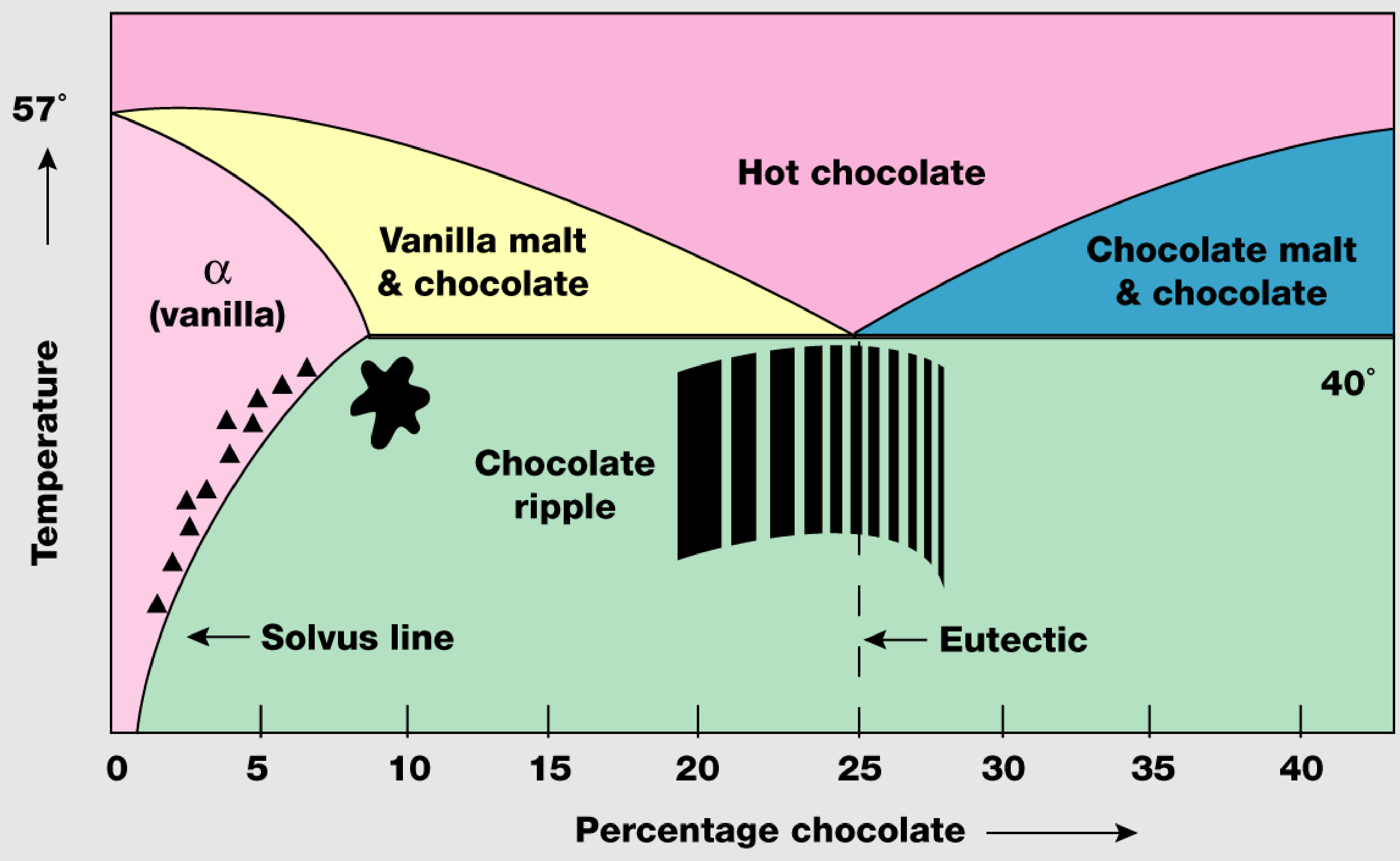
Water & salt



Other applications

- alloys - steals (better mechanical properties)
- Some inks for printers (eutectic mixtures)
- Liquid crystals eutectics – the stable liquid crystalline phase in a broader temperature range – LCD – liquid crystal display

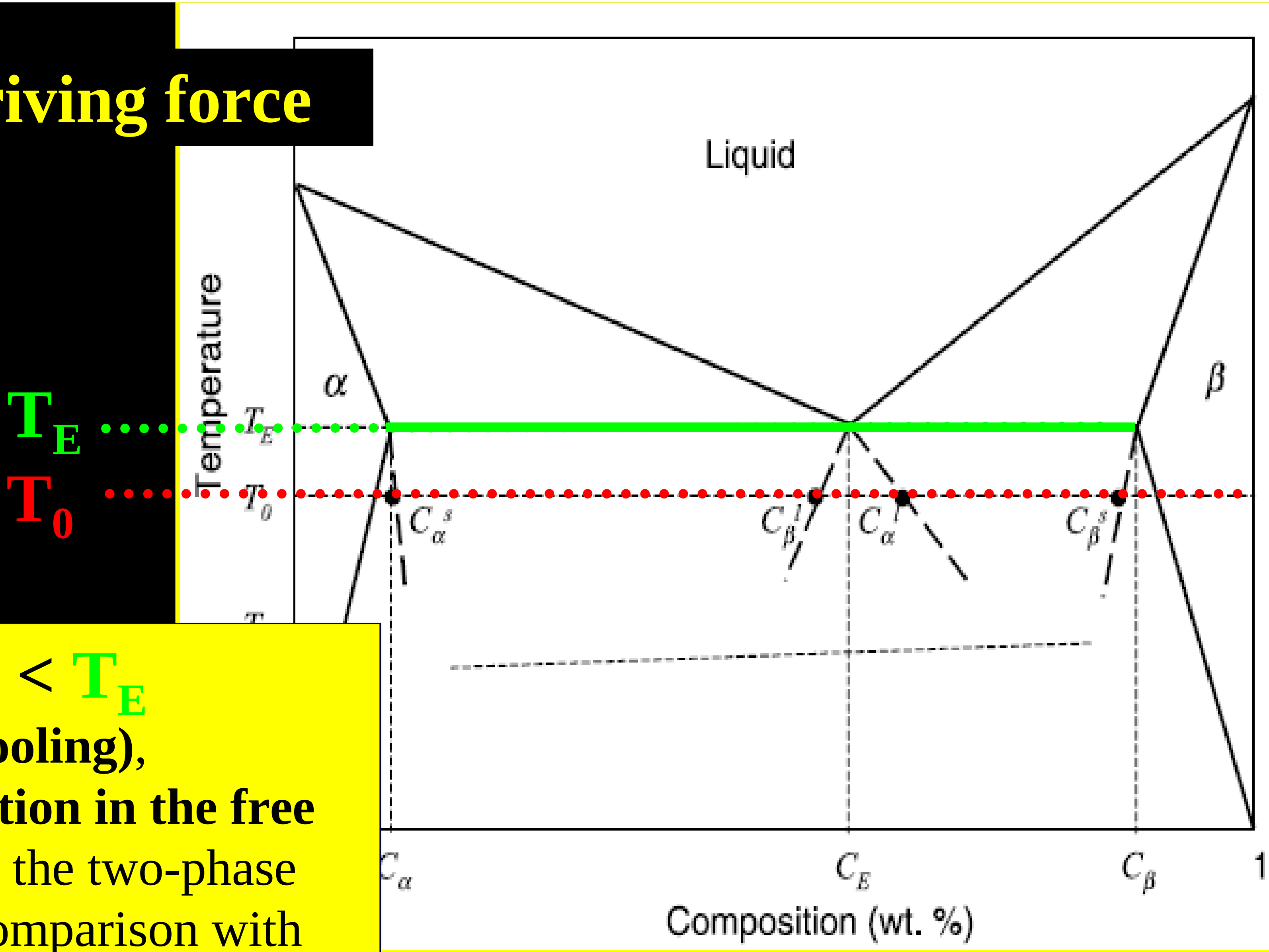
Eutectic especially for people loving chocolate!



Source: Kenneth A. Jackson at the University of Arizona.

http://science.nasa.gov/newhome/headlines/msad15sep99_1.htm

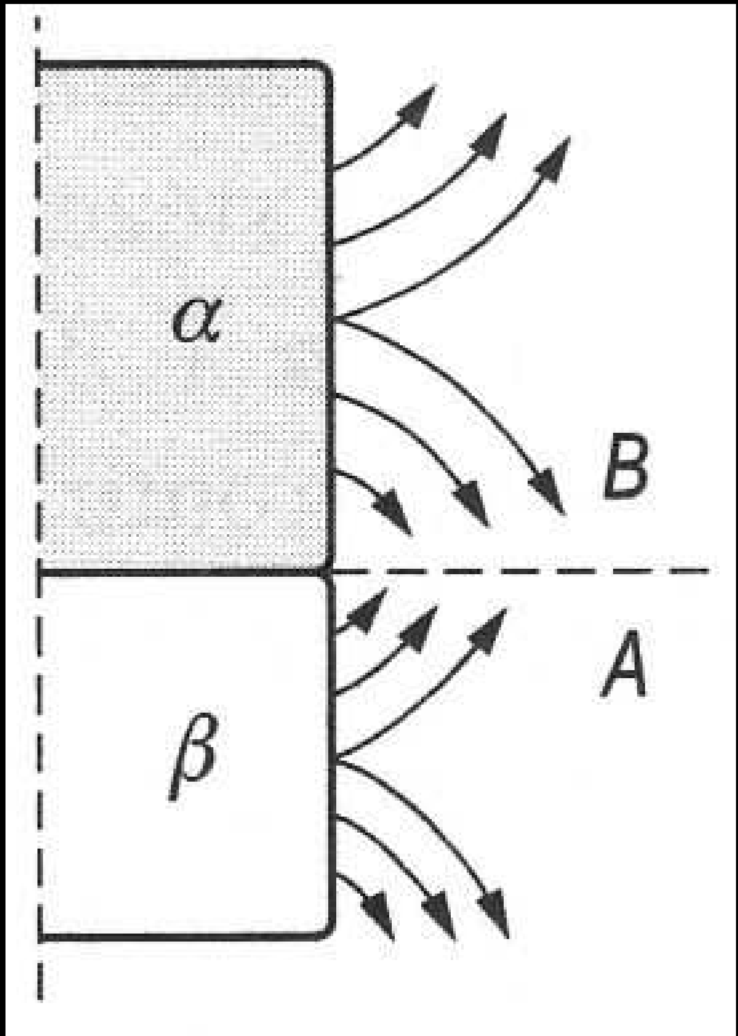
The driving force



When $T_0 < T_E$ **(under-cooling)**, the **reduction in the free energy** of the two-phase solid in comparison with the liquid is the **driving force** behind the growth of both α and β phases

T_E – the eutectic temperature
T_0 – the growth temperature
C_E – the eutectic composition

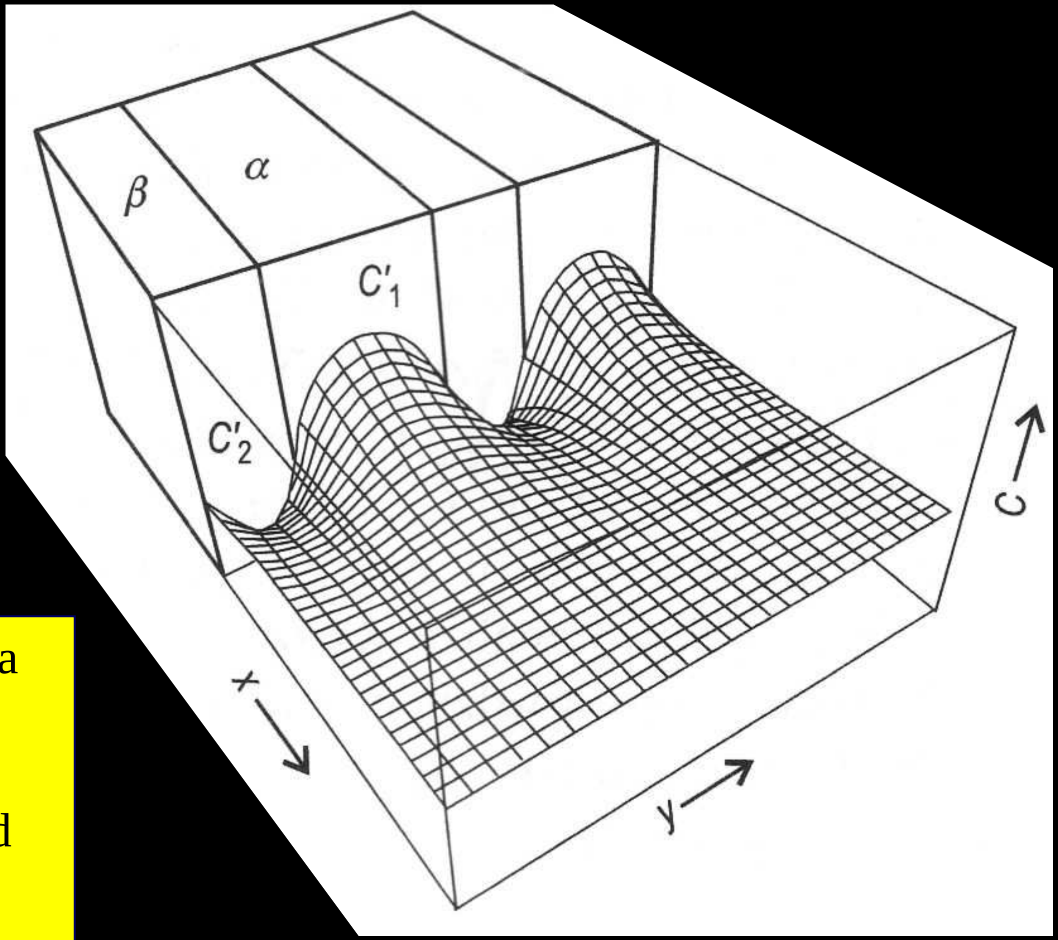
COUPLED GROWTH



A **solute redistribution** takes place because **each solid phase rejects** the **other solute** component and…

COUPLED GROWTH

…and
the concentration profile in the liquid ahead of the lamella tips is **no** longer **a flat surface**



Extensive lateral mixing takes place as a consequence of this concentration gradient at the α - β interface, and a diffusion flux parallel to the solid-liquid interface reduces the concentration oscillation

Metallodielectric materials

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METALLO-DIELECTRIC STRUCTURES

from eutectics

1. Removing one of the phases in the eutectic and filling it with metallic phase

D. A. Pawlak et al., Chem. Mat. 18, 2450, (2006).

D. A. Pawlak et al., Adv. Funct. Mat. (2010) .

2. Direct growth of eutectic including metallic phase

M. D Watson, et al., J. Amer. Ceram. Soc., 53, 112-113, (1970).

R. P. Nelson, J. Amer. Ceram. Soc., 53, 527, (1970).

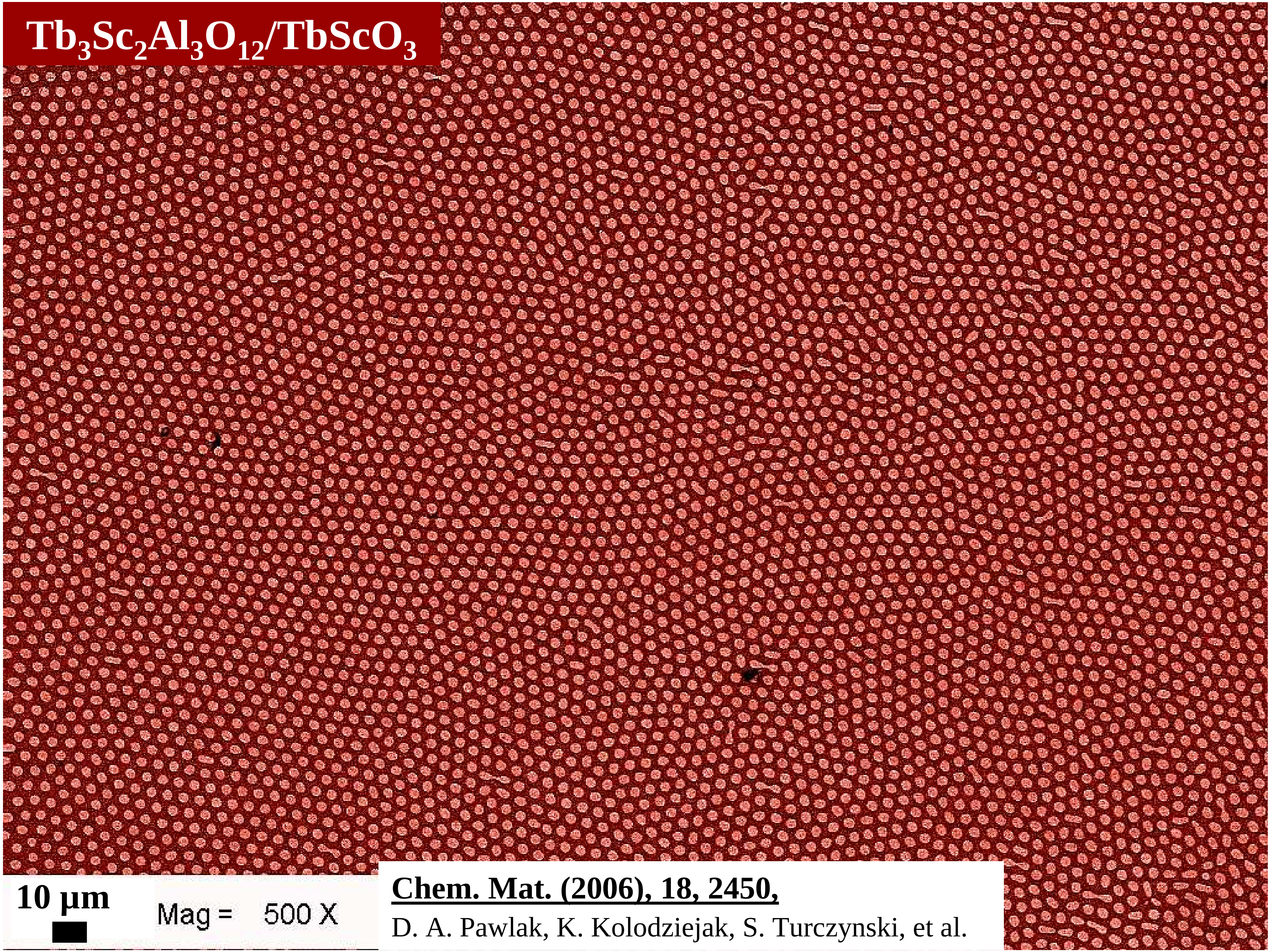
3. Growing an eutectic with an oxide which can be easily reduced to metal + ionic conductor phase

A. Revcolevschi, et al., Nature, 316, 335, (1985).

R. I. Merino, et al. Recent Res. Devel. Mat. Sci 4, 1, (2003).

M. A. Laguna-Bercero, et al. J. Eur. Ceram Soc. 25, 1455, (2005).

$Tb_3Sc_2Al_3O_{12}/TbScO_3$



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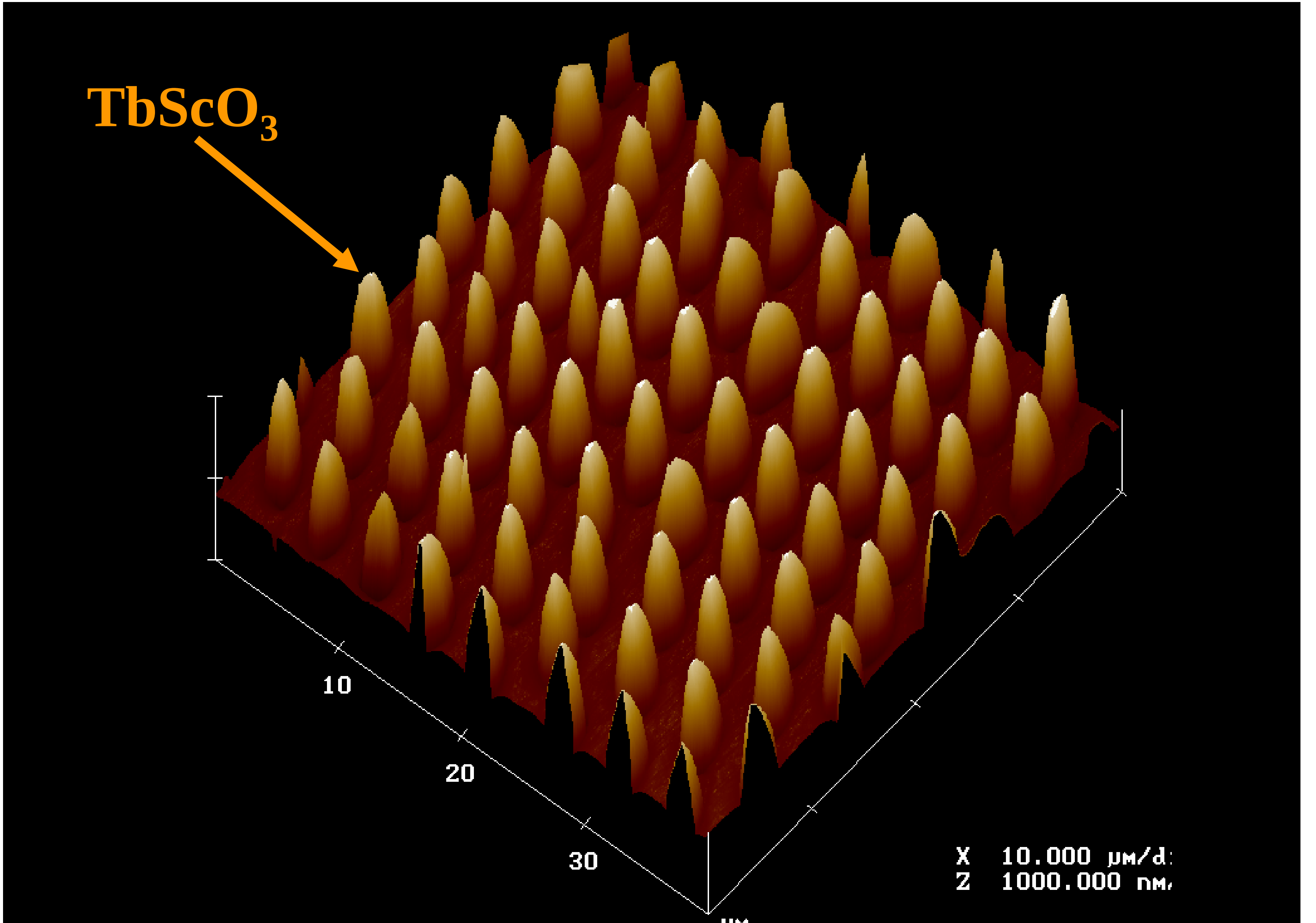
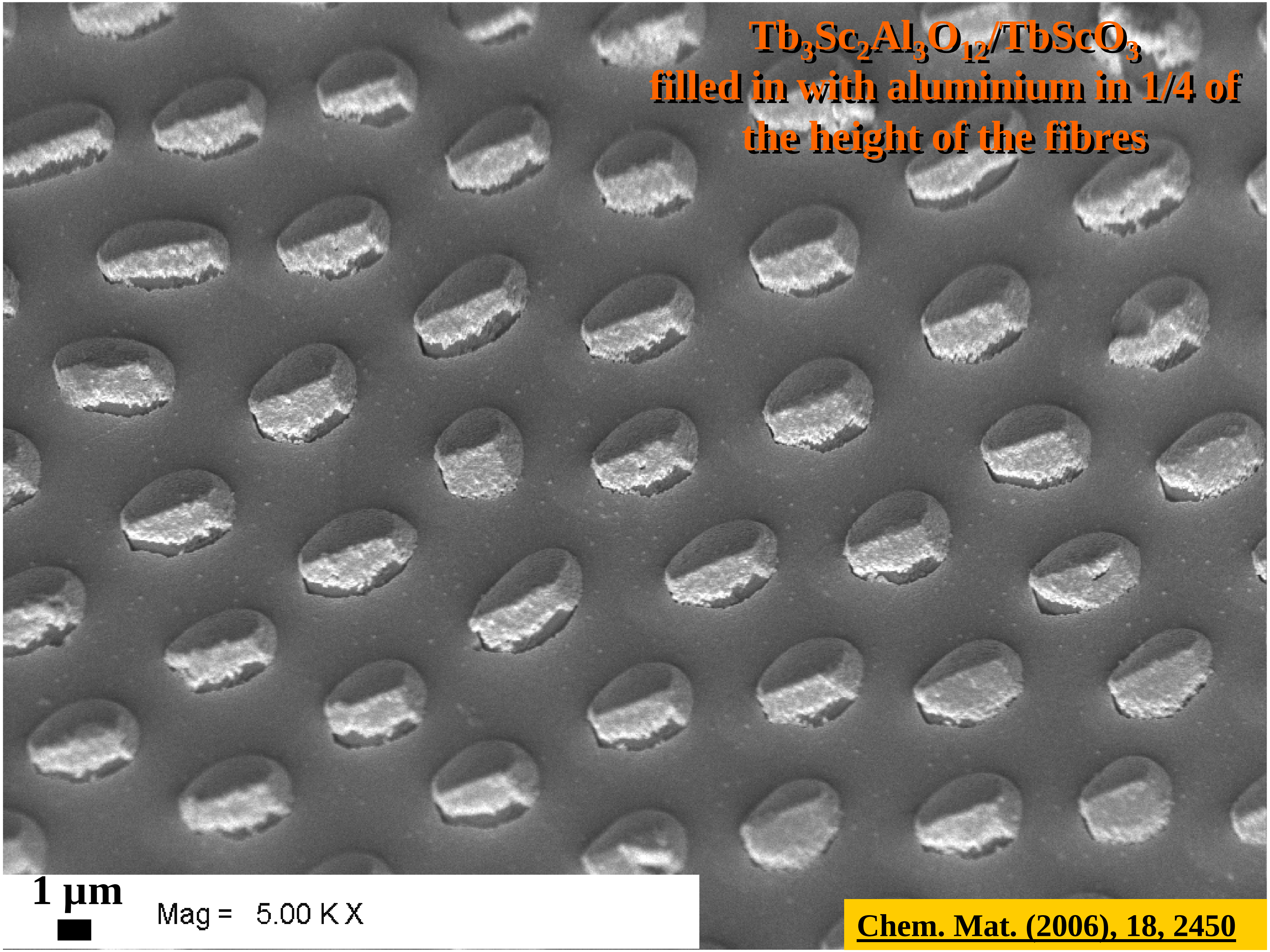


Chem. Mat. (2006), 18, 2450, D. A. Pawlak, K. Kolodziejak, S. Turczynski, et al.


$Tb_3Sc_2Al_3O_{12}/TbScO_3$
filled in with aluminium in 1/4 of
the height of the fibres
1 µm
Mag = 5.00 K X
Chem. Mat. (2006), 18, 2450

Split-ring resonator-like geometry by self-organization

D. R. Smith, et al. Science 2006, 314, 977; C. M. Soukoulis et al., Science 2007, 315, 47.

D. A. Pawlak et al., Adv. Funct. Mat. 2010


ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

FULL PAPER

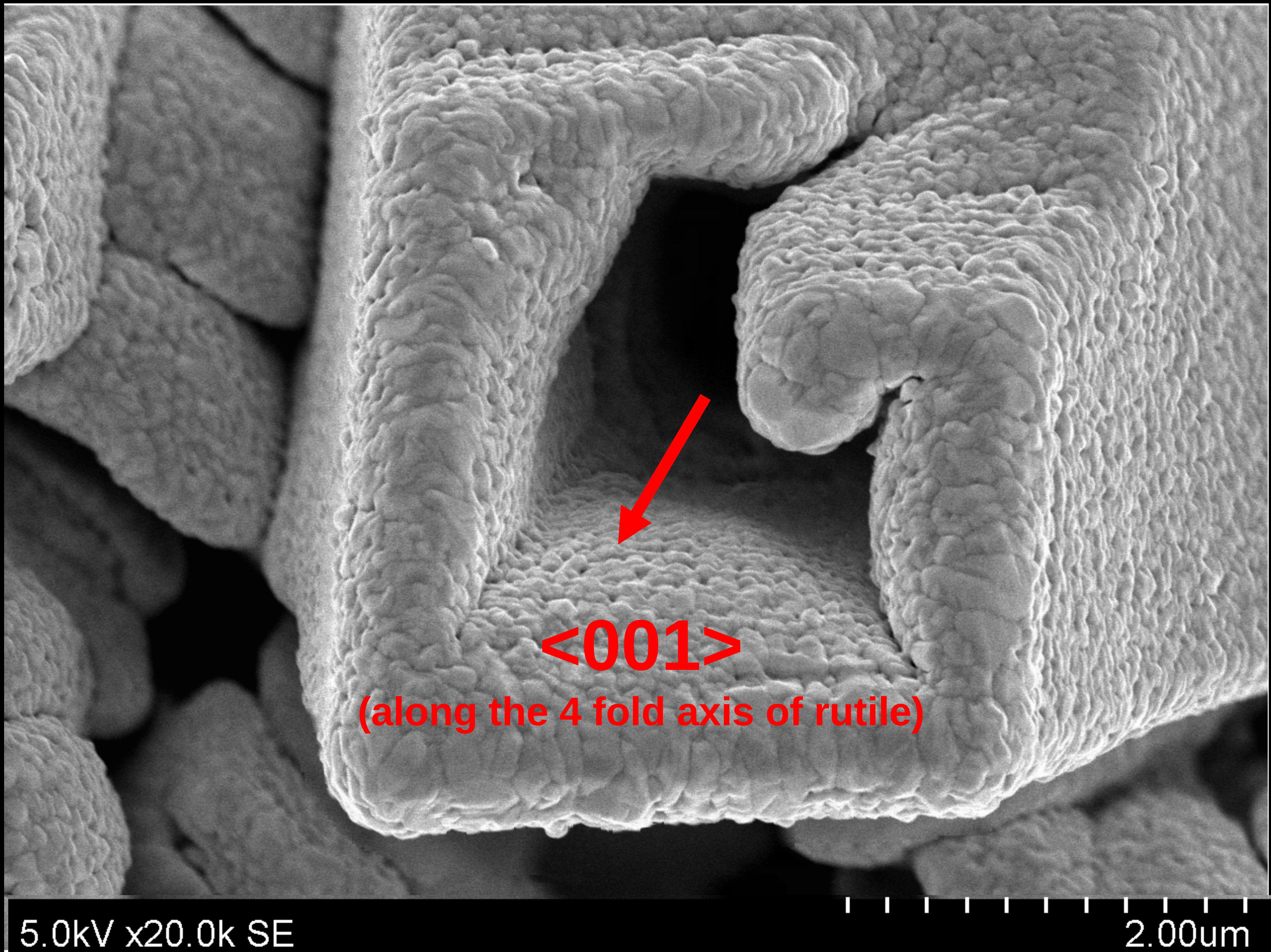
How Far Are We from Making Metamaterials by Self-Organization? The Microstructure of Highly Anisotropic Particles with an SRR-Like Geometry

By *Dorota A. Pawlak,* Sebastian Turczynski, Marcin Gajc, Katarzyna Kolodziejak, Ryszard Diduszko, Krzysztof Rozniatowski, Julita Smalc,* and *Irina Vendik*

D. A. Pawlak, et al.
Adv. Funct. Mat, (2010), 20, 1116.

HRSEM

$SrTiO_3$-TiO_2 etched and covered with silver (250 nm)



Adv. Funct. Mat. 2010, 20, 1116, Pawlak et al.

How do we get such a shape ?

Geometry of an eutectic depends on:

- Entropy of melting of phases
- Volume fraction of phases
- Growth rate
- Temperature gradient

Classification of Eutectic Microstructures
(Hunt & Jackson*) based on metals

(based on topography of the crystallization front)

Entropy of melting $$\Delta S_e = \frac{\Delta H}{T_e} = \frac{H_L - H_S}{T_e} \left[\frac{J}{Kmol}\right]$$

Dimensionless entropy of melting

$$\chi = \frac{\Delta S_e}{R_g}$$

where

$$R_g = 8{,}314472\left[\frac{J}{molK}\right]$$

- **Nonfacet-nonfacet**

  $\chi_\alpha < 2$ and $\chi_\beta < 2$ — **REGULAR**

- **Facet-nonfacet**

  $\chi_\alpha < 2$ and $\chi_\beta > 2$ — **Irregular or complex**

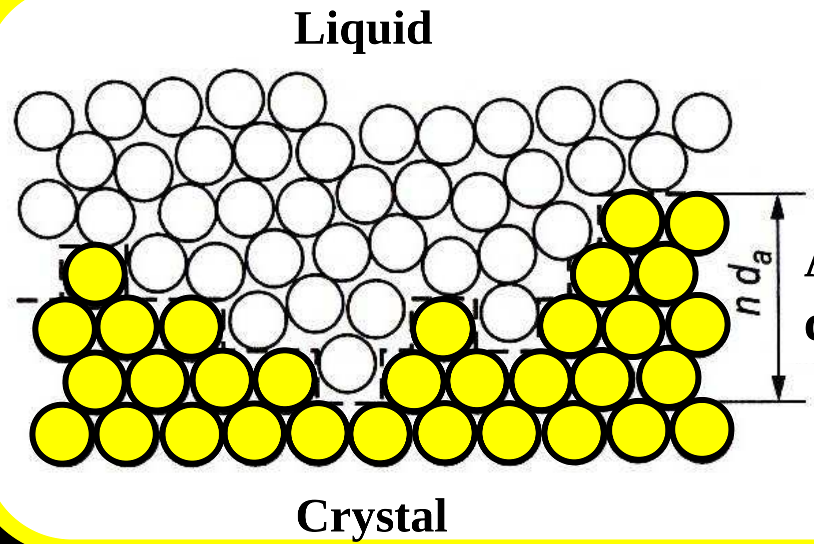
- **Facet-facet**

  $\chi_\alpha > 2$ and $\chi_\beta > 2$ — **Independent crystals**

Mag = 5.00 K X LEO 1530 CBW PAN

*J. D. Hunt, K. A. Jackson, Trans. Metal. Soc. AIME, 236 (1966) 843-852

Influence of **crystallization front (entropy of melting)** on the geometrical motifs appearing in eutectics

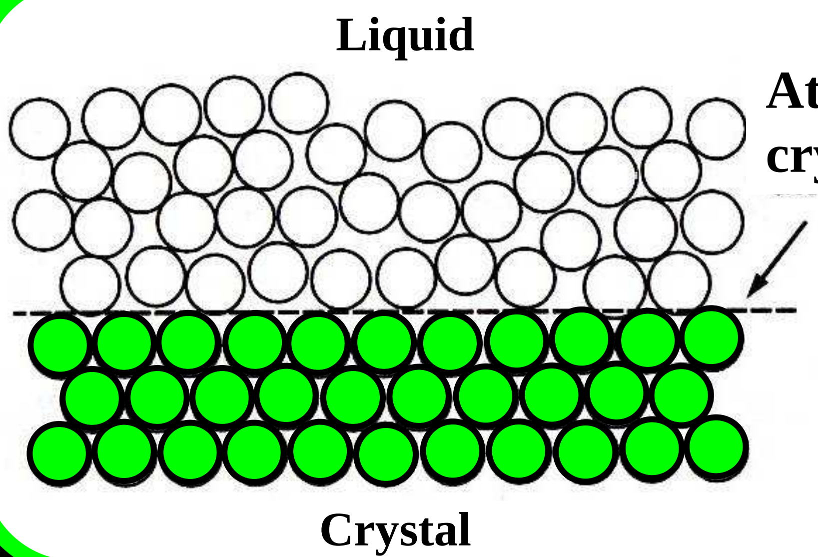


Atomically-ROUGH crystallization front

Non-faceted crystals

(curved surfaces)

$$\chi = \frac{\Delta S_e}{R_g} < 2$$



Atomically-SMOOTH crystallization front

Faceted crystals

(flat surfaces)

$$\chi = \frac{\Delta S_e}{R_g} > 2$$

Influence of **volume fraction** **(g_v)** of phases on geometry of eutectic microstructure

For regular eutectics: FIBROUS & LAMELLAR

Microstructure with minimal **energy of the phase boundaries α/β**

← Phase boundary **area**

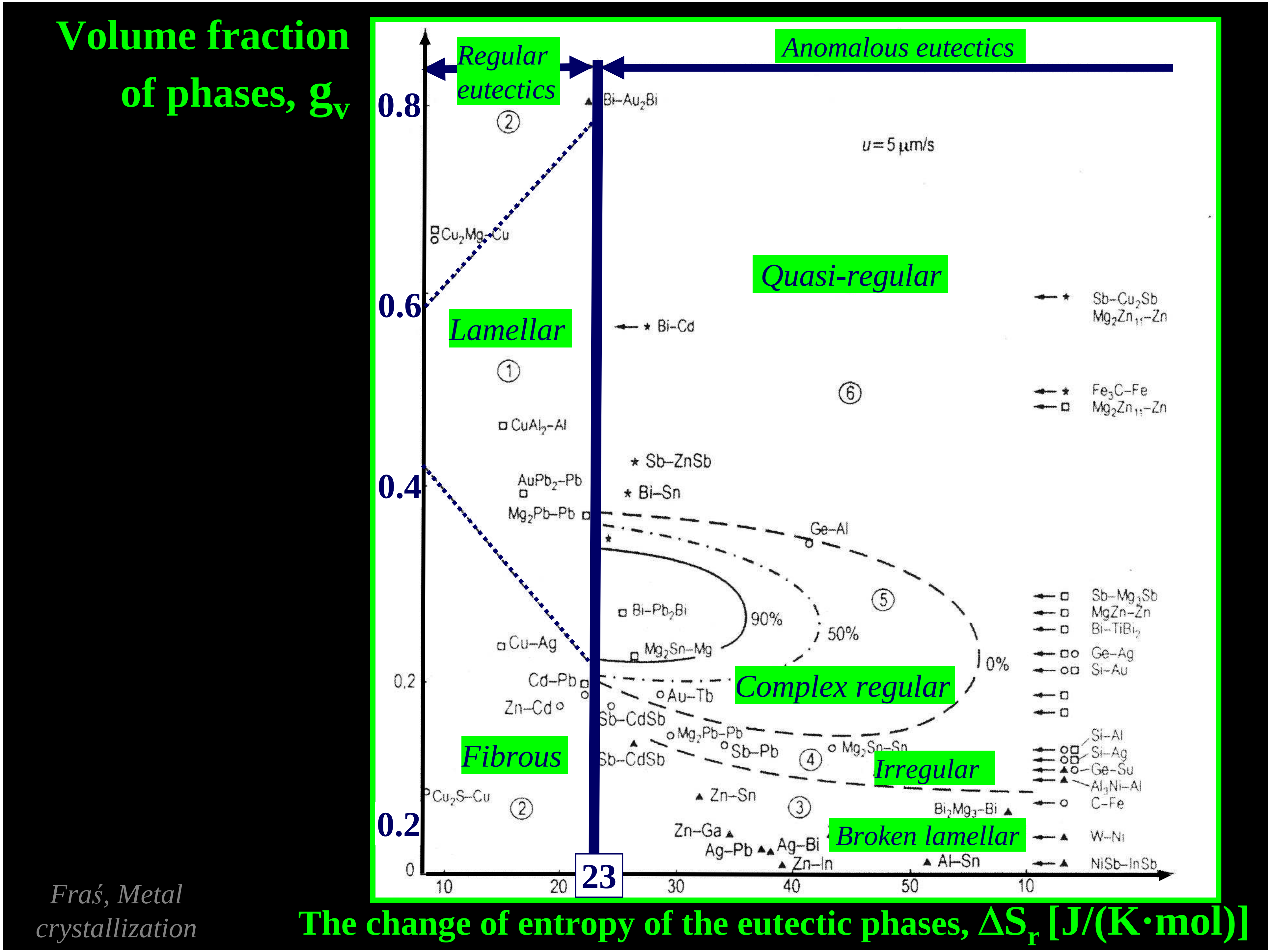
← Phase boundary **surface tension**

When

$$g_v < \frac{1}{\pi} \approx 0{,}32$$

phase boundary area is smaller for FIBROUS eutectic, thus the energy of the phase boundaries is smaller

→ **Fibrous microstructure**



Fraś, Metal crystallization

Directionally solidified materials

Photonics

-nanoplasmonic materials with:

(i) resonances at various wavelength

(ii) various geometries of particles/precipitates

(iii) various chemical composition

- solid state visible lasers
  (via enhanced PL, and up-conversion)
- nonlinear absorbers
  (via enhanced nonlinearities)
- filters
- subwavelength imaging
- directional emissivity control

Photoelectrochemistry

-photoanodes in PECs

-water purification

Photovoltaics

-Enhanced performance of Silicon Solar cells
(via enhanced up-conversion of waves above 1100 nm)

Photovoltaics Catalysis

-broadband absorption due to multi-bandgaps

-porous materials for catalysis

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SEVENTH FRAMEWORK PROGRAMME

Cooperation

NMP Theme

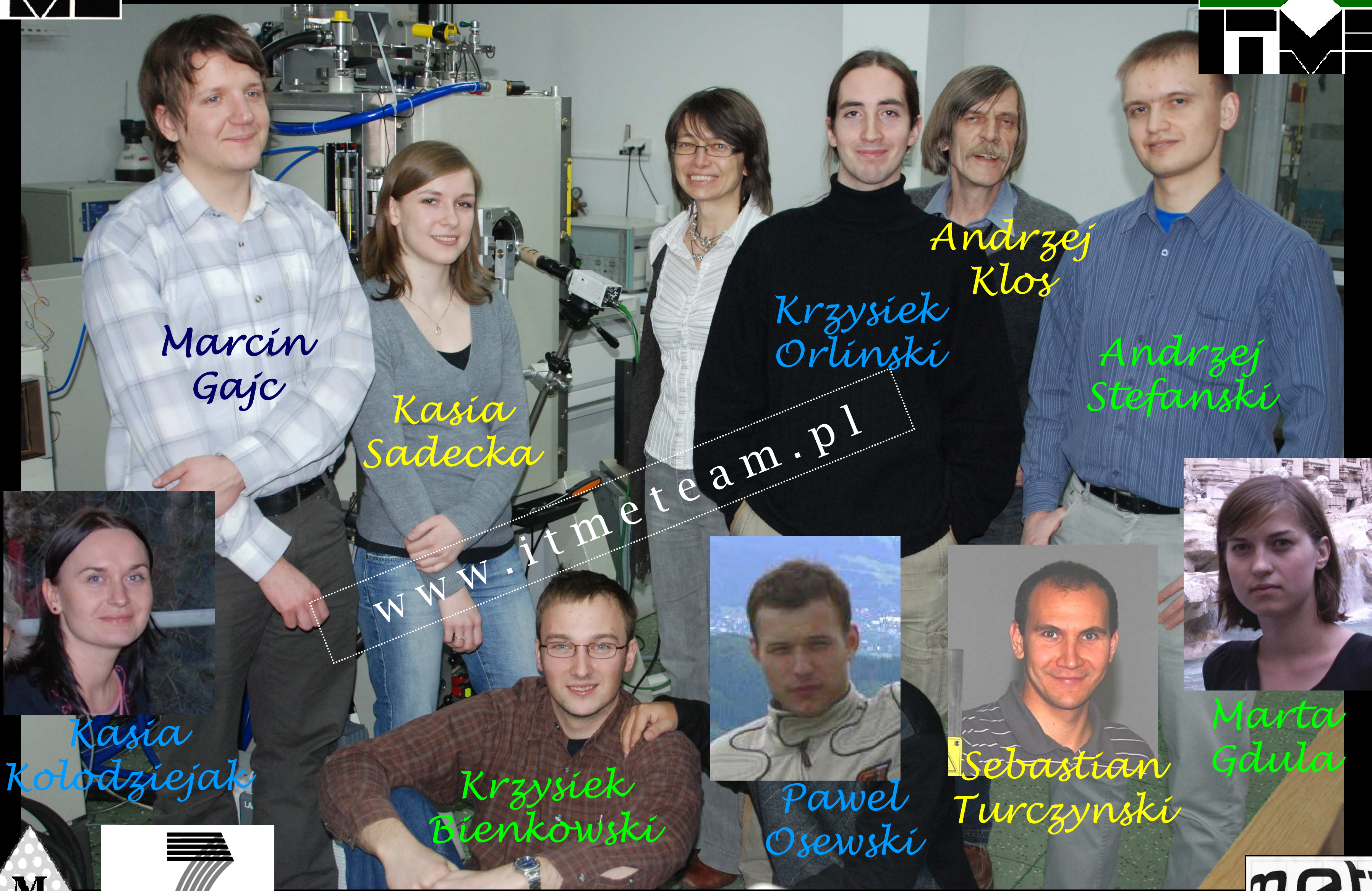
ENgineered SElf-organised Multi-component structures with novel controllaBLe Electromagnetic functionalities

ENSEMBLE

Contract NMP4-SL-2008-213669

https:/www.ensemble-fp7.eu

ITME EUTECTIC TEAM



SEVENTH FRAMEWORK PROGRAMME

INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

FNP
Foundation for Polish Science

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

meta morphose


THANK YOU!