Layer-by-layer design and fabrication & on-demand oxygen-engineering of novel functional oxide materials for future energy technologies


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EDUCATION

Helsinki University of Technology
MSc. 1987, Lic. Tech. 1990, D. Tech. 1993

ACADEMIC POSITIONS

FINLAND

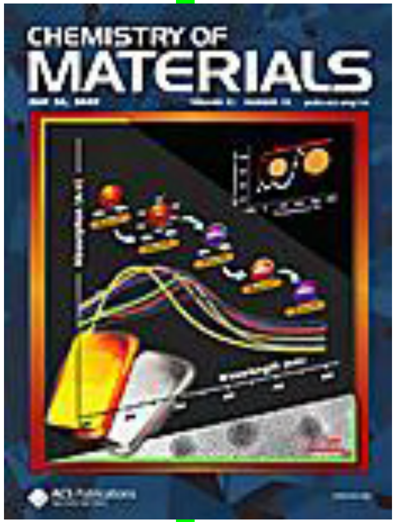
1985-1990	Assistant, TKK
1990-1999	Senior Lecturer, TKK
1999-2001	Senior Researcher, Academy of Finland
2000-2001	Professor (acting), TKK
2006 -	Professor, TKK
2008-	Director, Department of Chemistry, TKK
2009-2013	Academy Professor, Academy of Finland

JAPAN

1991-1992	Visiting Research Scientist, ISTEC
1995-1996	Visiting Ass. Professor, Tokyo Tech
2001-2005	Associate Professor, Tokyo Tech
2006-2008	Adjunct Professor, Tokyo Tech


YK Lab Study Camp 2005/07/08-09 : Tanzawa Nakagawa-Onsen
GÖTEBORG

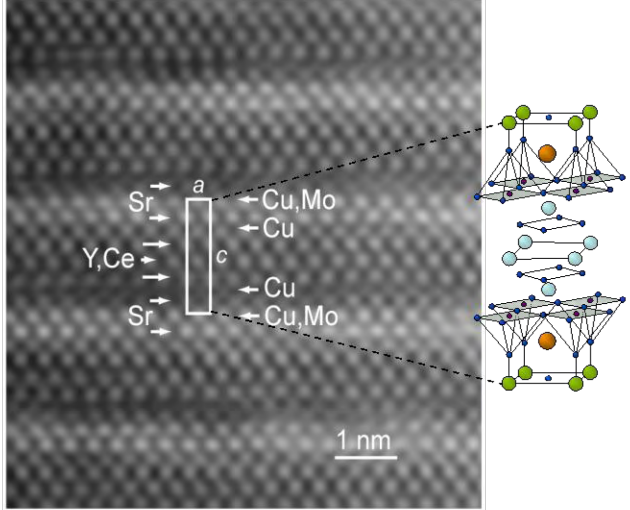
SPECIAL ISSUES of *Chemistry of Materials*

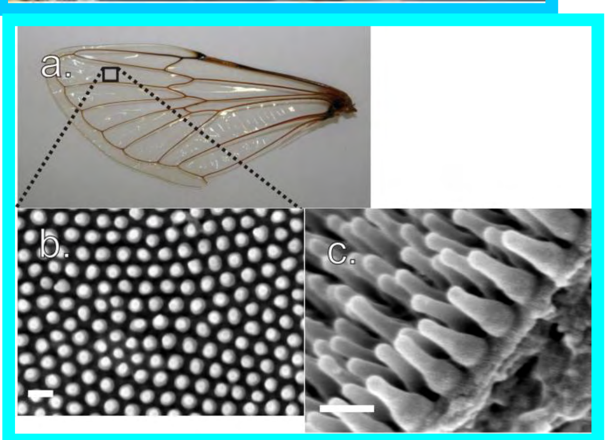


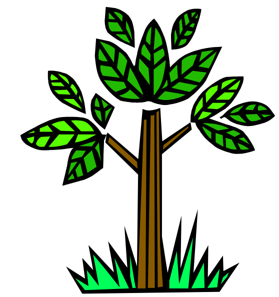
1994 **Organic Solid State Chemistry**
1996 **Nanostructured Materials**
1997 **Sol-Gel Derived Materials**
1999 **Inorganic Solid State Chemistry**
2001 **Organic-Inorganic Nanocomposite Materials**
2004 **Organic Electronics**
2008 **Templated Materials**

2010 **Materials Chemistry of Energy Conversion**

- **Thermoelectrics** (electricity from heat)
- **Fuel Cells** (electricity from fuels)
- **Photochemical Materials** (fuels from light)
- **Thermochemical Materials** (fuels from heat)
- **Batteries** (electricity storage)
- **Superconductors** (electricity transmission)







INORGANC CHEMISTRY, TKK

- **Novel Functional Oxide Materials**
  - high-T_c superconductors
  - thermoelectric materials
  - magnetoresistance materials
  - multiferroic materials
  - ion conductors
    [fuel cells, batteries, oxygen storage/separation]

- **ALD (Atomic Layer Deposition) Thin Films**
  - oxide materials for electronics
  - oxide materials for spintronics
  - oxide coatings on novel functional substrates
    (graphene, biomaterials, paper, polymers, etc.)
  - organic and polymer films
  - inorganic/organic hybrid materials

RESEARCH PROJECTS

Academy of Finland

- **2006–2009:** **Novel multi-functional misfit-layered cobalt oxides**
- **2007–2009:** **Novel multiferroic thin film materials by ALD**
- **2007–2010:** **Ultra-high-pressure synthesis and atomic-layer deposition of novel functional oxide materials**
- **2009–2013:** **Academy Professorship Grant:**
  Design of novel functional oxide materials: from bulks to thin films
- **2009-2012:** **Fin-Jpn Programme:**
  Novel tailor-made oxide thermoelectrics

Tekes

- **2008–2012:** **FiDiPro-program:**
  Novel oxide materials for energy and nanotechnologies
- **2009-2012:** **Functional Materials Programme:**
  Novel electrode materials for Li-ion battery

Ichiro TERASAKI
Waseda University

THERMO-ELECTRICS

SOFCs

Li-ION BATTERIES

Ryoji KANNO
Tokyo Institute of Technology

John B. GOODENOUGH
University of Texas at Austin

SUPER-CONDUCTORS

ELECTRON MICROSCOPY

Yoshio MATSUI
National Institute for Materials Science
NIMS

Takami TOHYAMA
Kyoto University

OXIDE-ION CONDUCTORS

Teruki MOTOHASHI
Hokkaido University

NEW MATERIAL RESEARCH

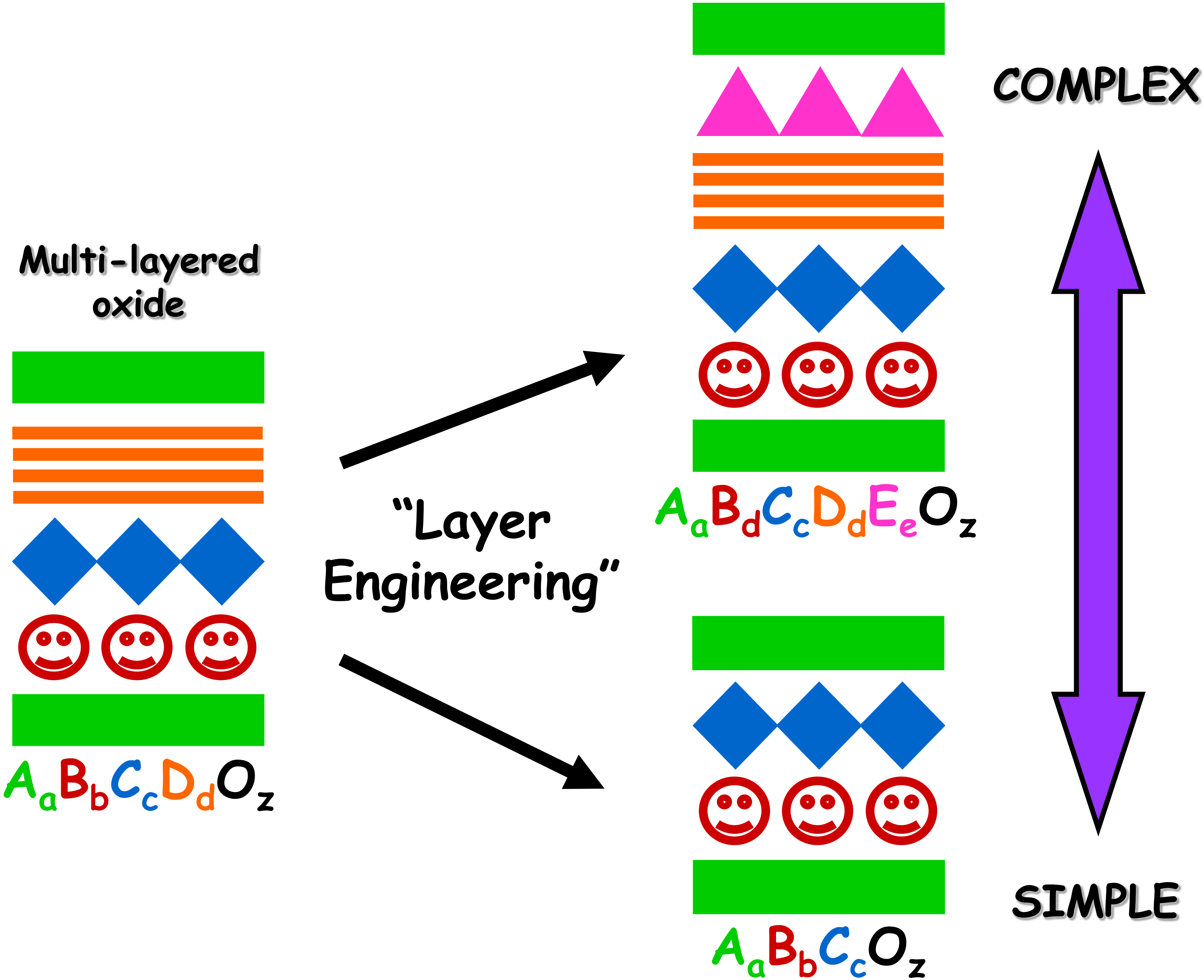
- To discover a **new compound** (with a new crystal structure and/or new chemical composition)
- To discover a **new property/function** for an already known compound
- To produce a known compound in a **new form** (single crystal, thin film, nanoparticle, *etc.*)
- To find a **new way to combine** existing materials

DISCOVERY OF NEW (oxide) COMPOUNDS

- Layer-by-Layer Design (”Layer Engineering”)
- Extreme-Condition Synthesis Techniques
  - e.g. High-Pressure Synthesis

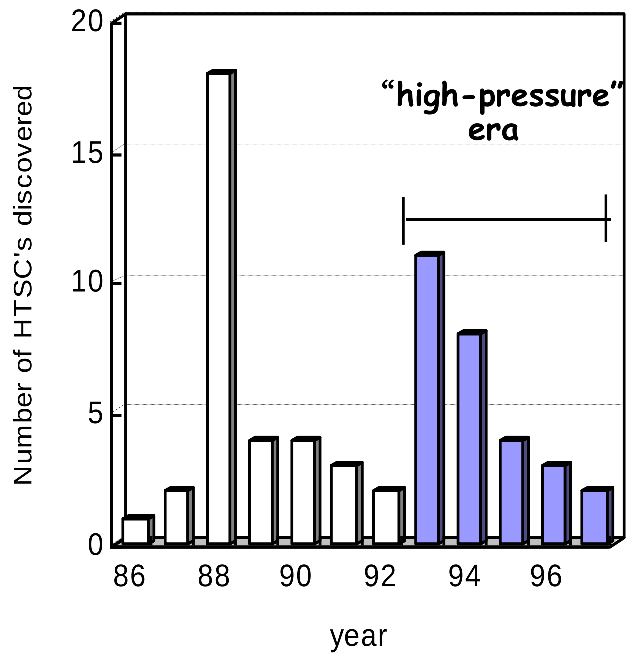
TAILORING OF MATERIALS PROPERTIES

- ”NanoStructuring”
- ”Oxygen Engineering”

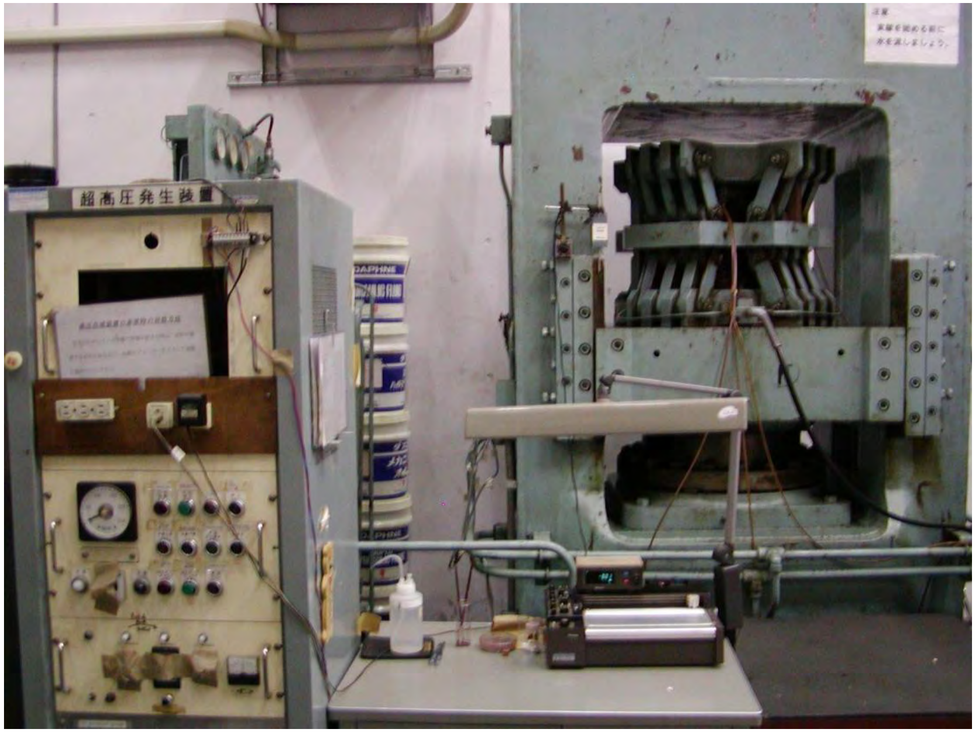

Multi-layered oxide
$A_aB_bC_cD_dO_z$
"Layer Engineering"
$A_aB_dC_cD_dE_eO_z$
$A_aB_bC_cO_z$
COMPLEX
SIMPLE

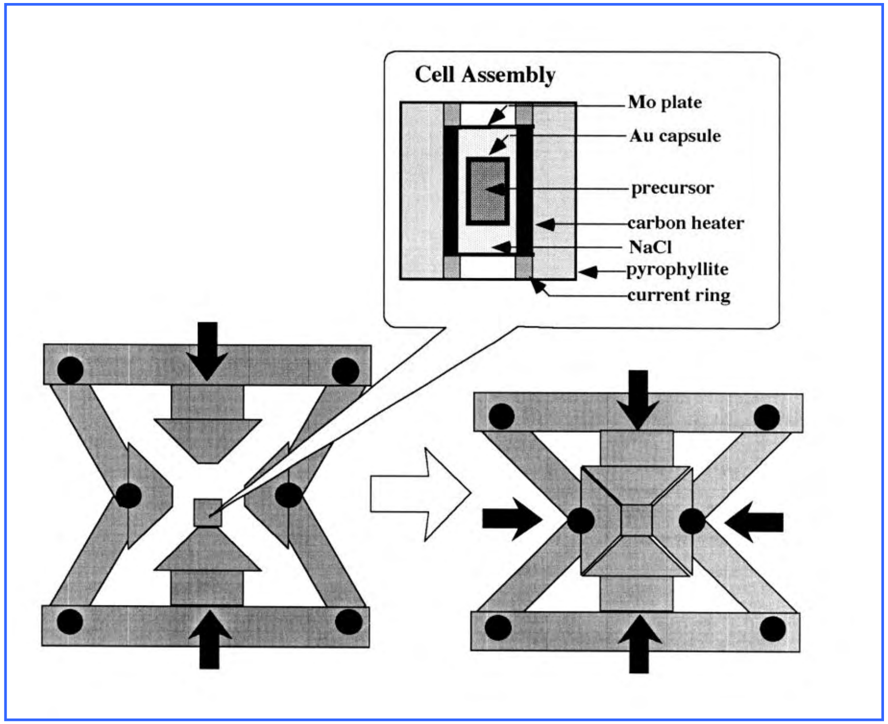
High-Pressure Synthesis

- ~5 GPa
- ~1000 °C
- ~30 min
- ~50 mg

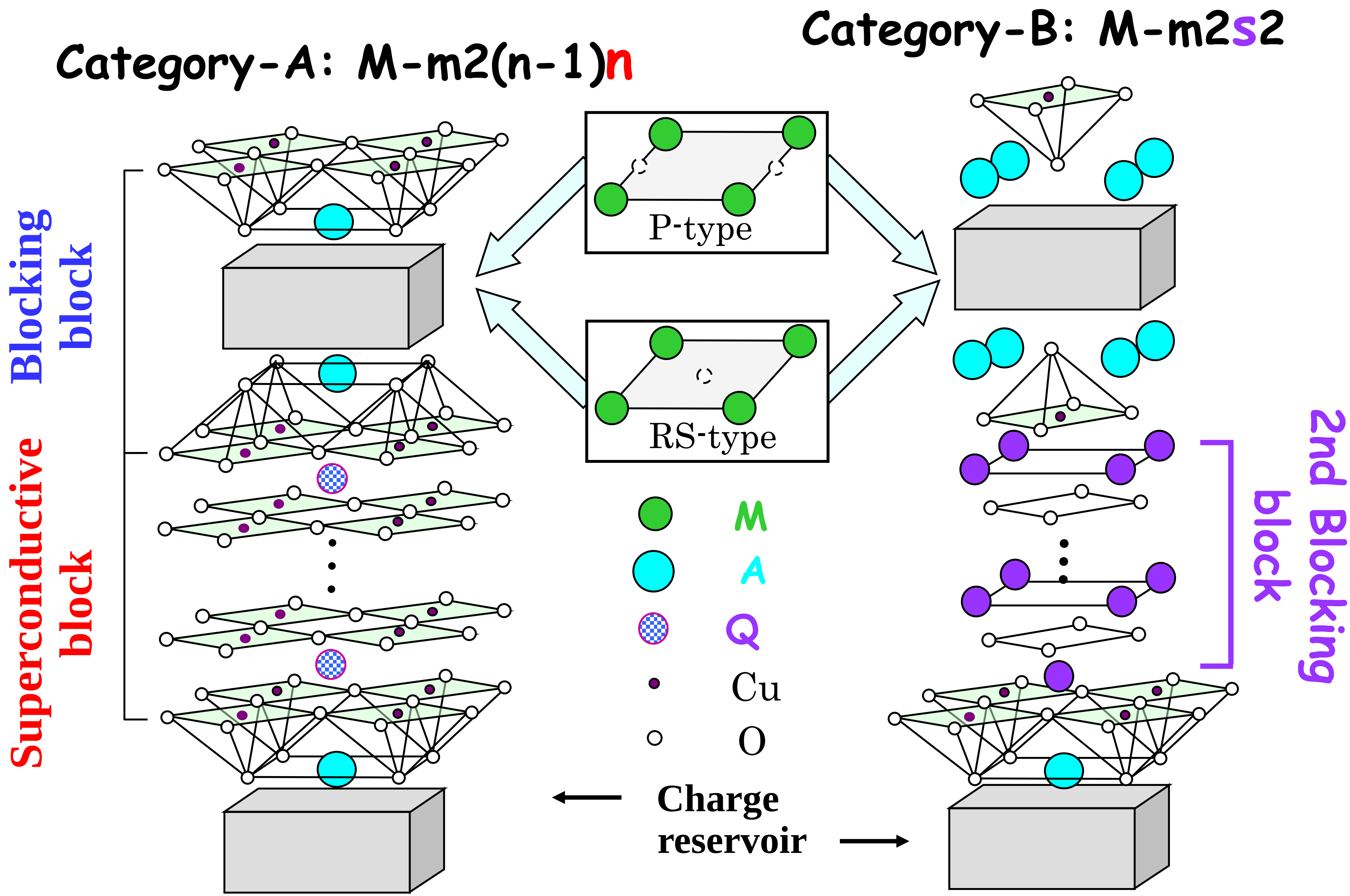


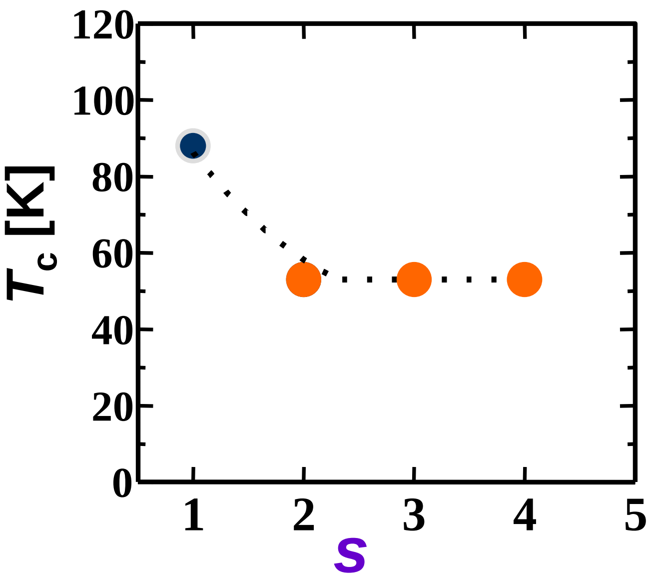
H. Yamauchi & M. Karppinen, *Supercond. Sci. Technol*. **13**, R33 (2000).



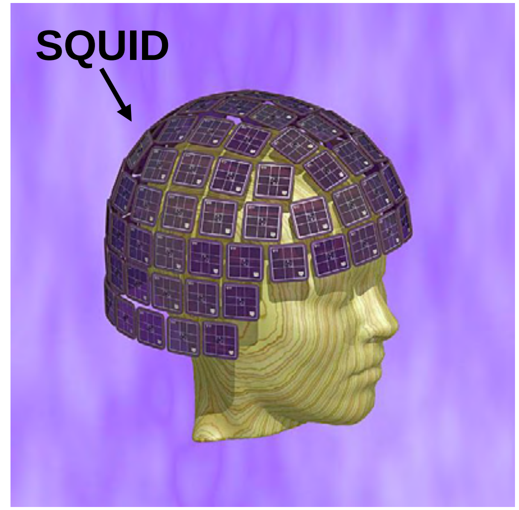


MULTI-LAYERED COPPER OXIDES: High-Tc Superconductivity



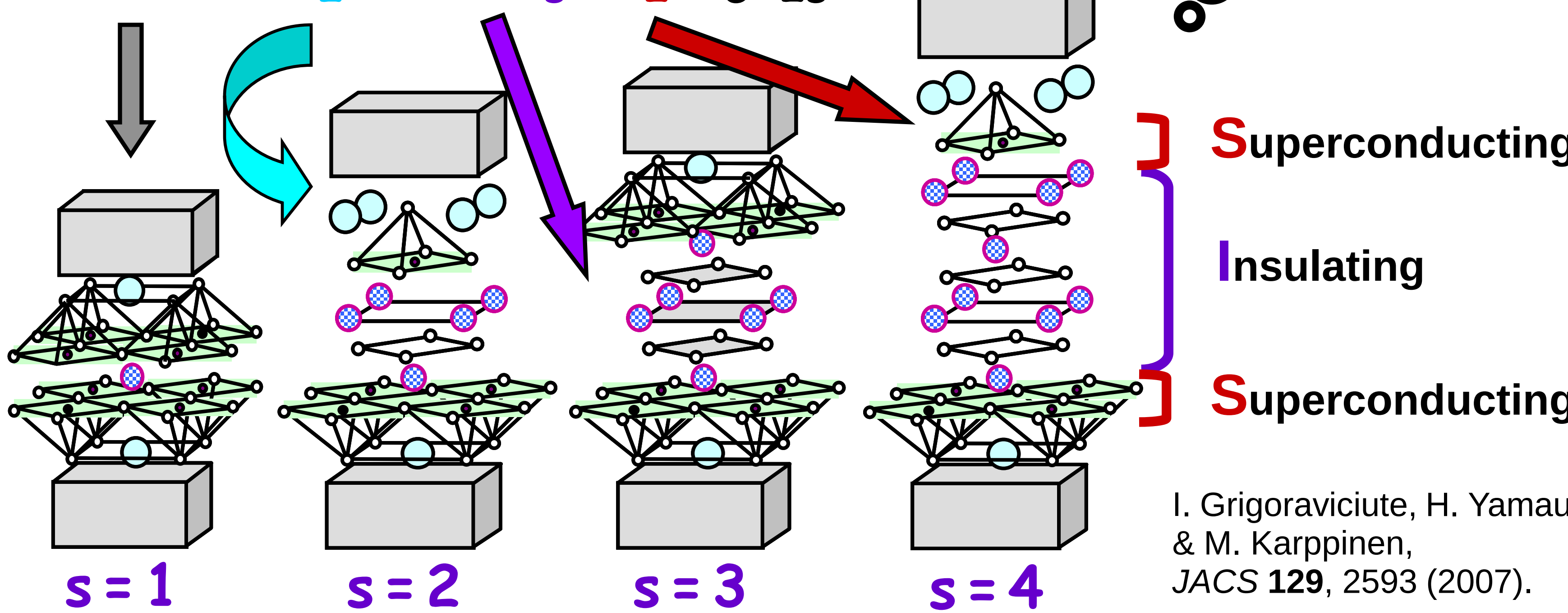


Low-*T* laboratory, TKK



INTRINSIC
SIS
JOSEPHSON
JUNCTION

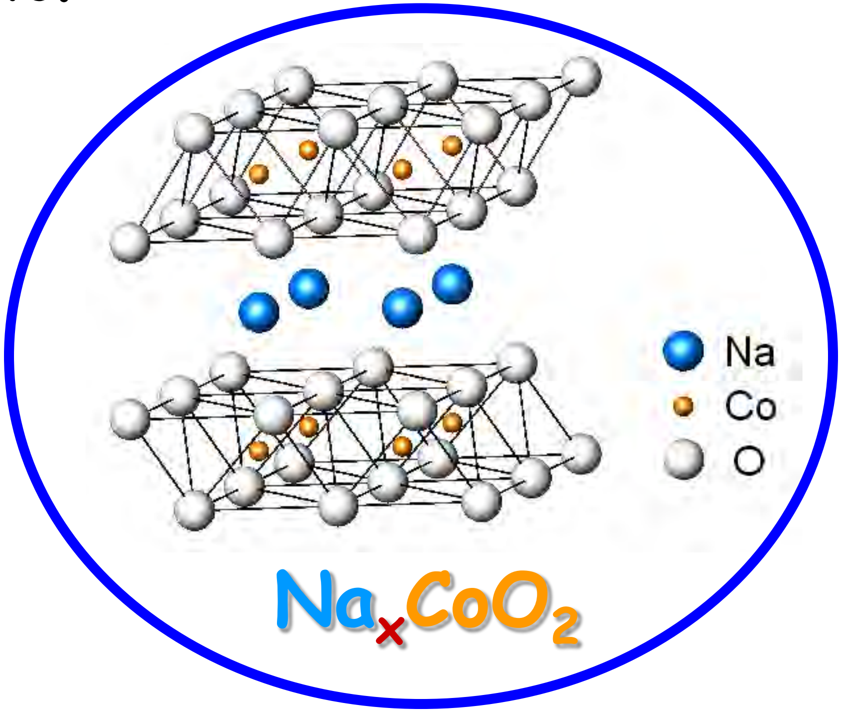
$(Cu,Mo)Sr_2(Ce,Y)_sCu_2O_{5+2s}$



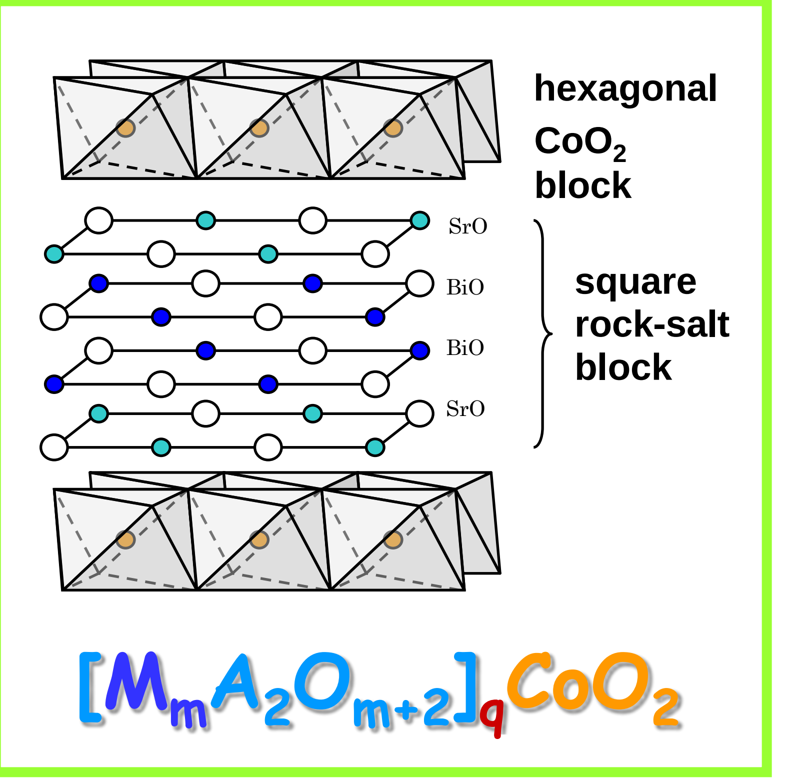
I. Grigoraviciute, H. Yamauchi & M. Karppinen, *JACS* **129**, 2593 (2007).

MULTI-LAYERED COBALT OXIDES

- cation (Na^+/Li^+ ion) conductivity
- thermoelectricity
- superconductivity
- etc.

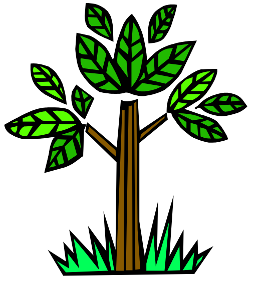


Misfit-layered oxides



THERMOELECTRICS

- Thermal current ⇔ Electric current
- Electric power from waste heat without CO_2 emission
- Refrigeration directly with electricity without Freons



Seebeck

Thermoelectric generator using waste heats
(*Energy Conservation Center, Japan*)

Peltier

Multi-stage Peltier cooler (T_{low} ~ 160 K)
(*Marlow Industries, USA)*

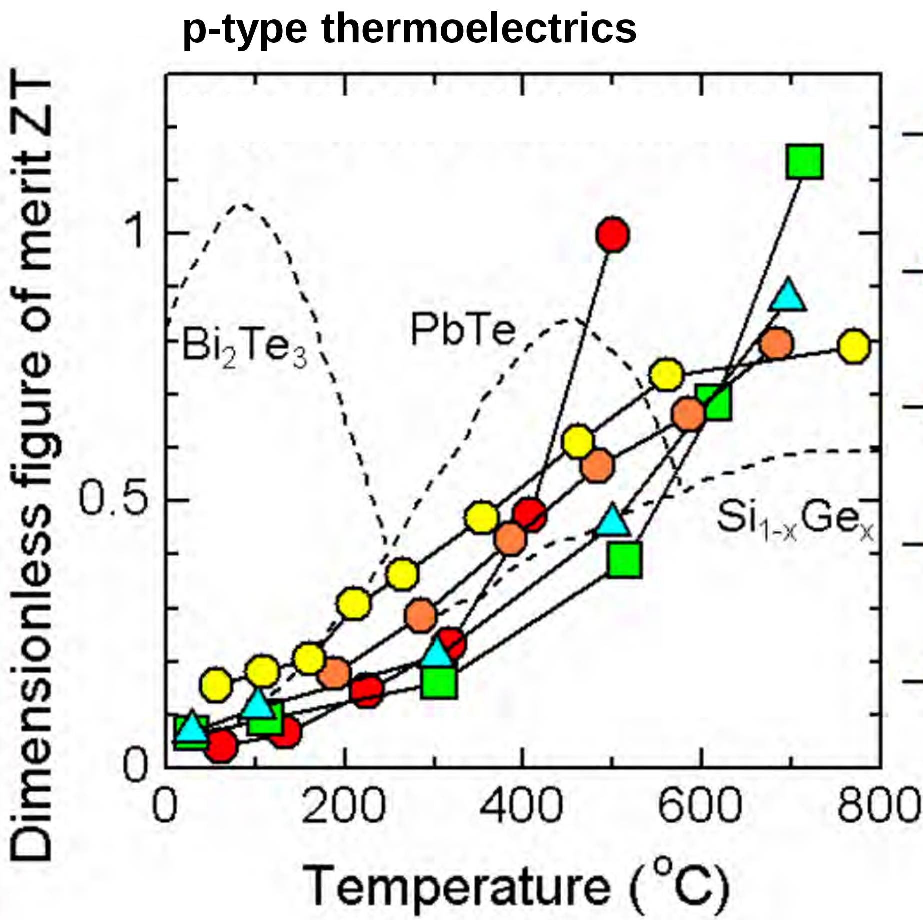
Radioisotope thermoelectric generator for spaceships
(NASA & NASM, USA)

Thermoelectric refrigerator (T = 0 ~ 45°C):
Vibration-free, Noiseless, CFC-free
(*Mitsubishi Electric, Japan*)

Figure-of-Merit: $Z \equiv \sigma S^2/\kappa$ [K^{-1}]

S: Seebeck coefficient
σ: electrical conductivity
κ: thermal conductivity

- For practical application: ZT > 1

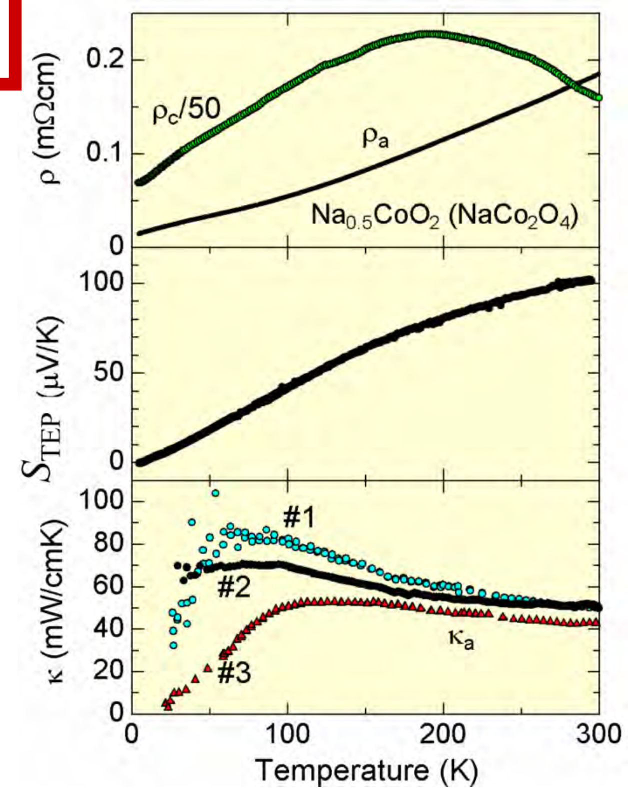


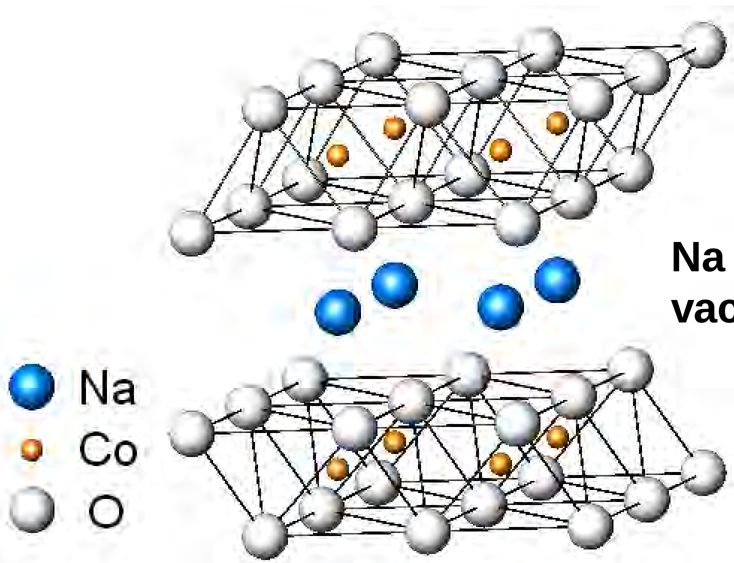
First Oxide Thermoelectrics: Na_xCoO_2

I. Terasaki, *et al.*, *PRB* **56**, R12685 (1997).

Crystal structure of Na_xCoO_2

- Layered structure with alternating Na and CoO_2 layers
- Large nonstoichiometry in the Na content
- Na^+ ions randomly distributed in the Na layer
- "**Electron Crystal**" & "**Phonon Glass**"

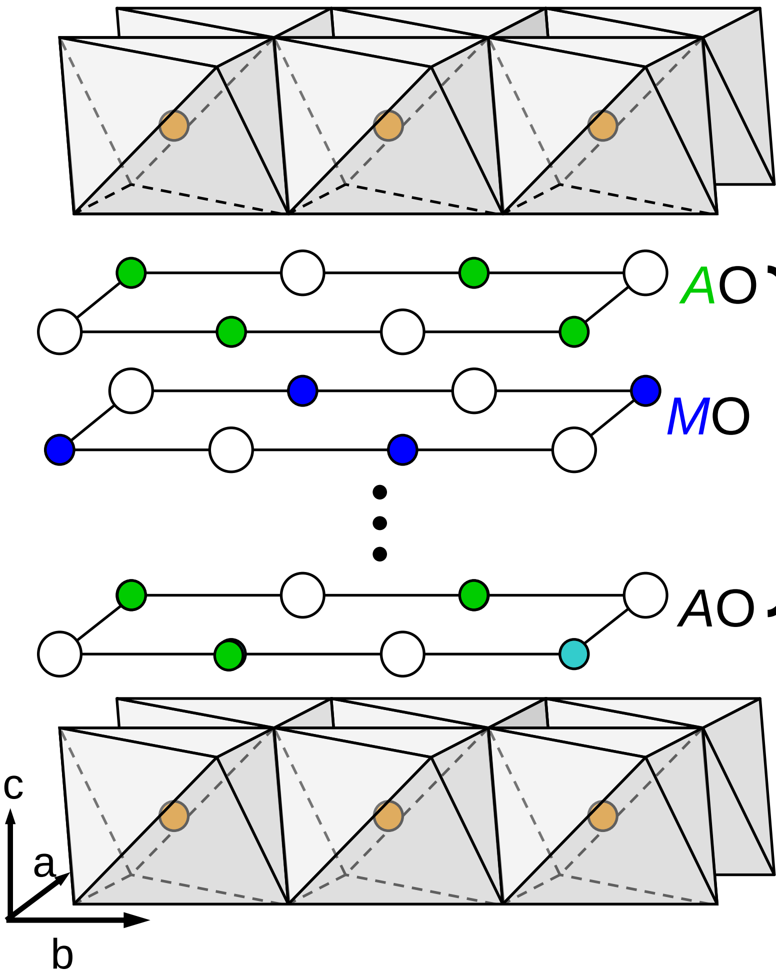




Na ions & vacancies

Strongly-correlated conducting layer	→ Low ρ, High S
Disordered insulating layer	→ Low κ
Strongly-correlated conducting layer	

Thermoelectric Misfit-Layered Cobalt Oxides



Hexagonal CoO_2

High electrical conductivity !!!

Square $[M_m A_2 O_{m+2}]$

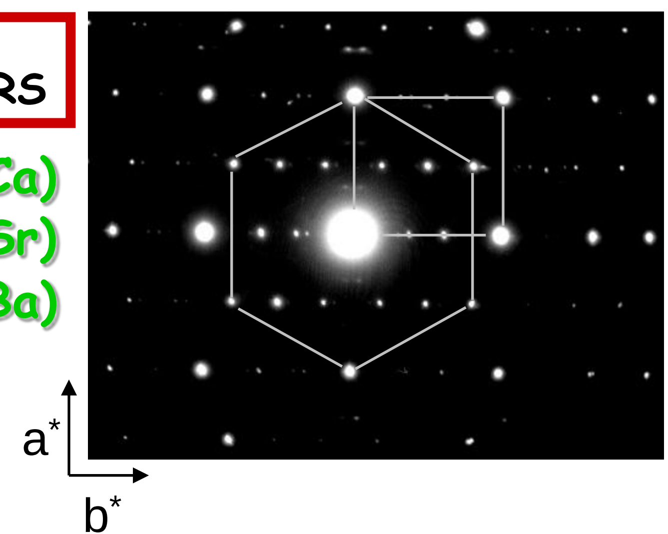
A: Ca, Sr, Ba

M: Co, Pb, *etc.*

Low thermal conductivity !!!

$$q = b_{Hex} / b_{RS}$$

$\approx$ 0.62 (A=Ca)
0.56 (A=Sr)
0.50 (A=Ba)



$$[M_m A_2 O_{m+2}]_q CoO_2$$

Misfit-Layered Cobalt Oxides

$[(MO_{1\pm\omega})_x]_m[(AO_{1\pm\varepsilon})_y]_2[CoO_2]$

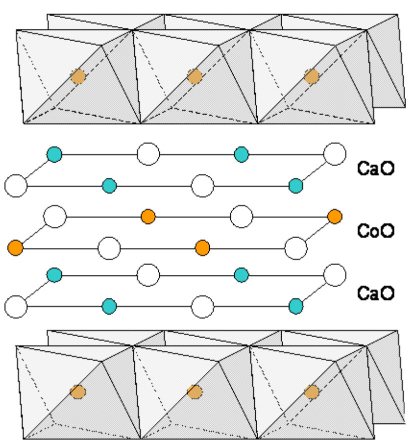
m = 0

$[A_2O_2]_qCoO_2$

?

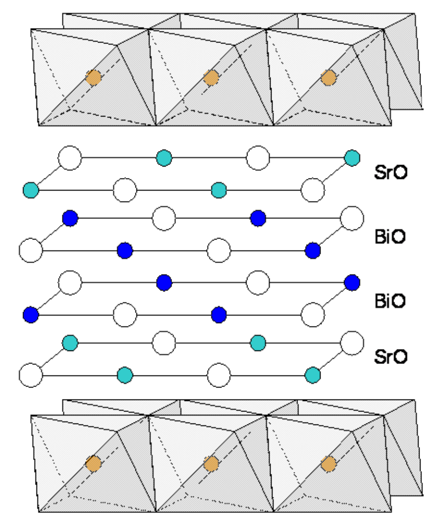
m = 1

$[CoCa_2O_3]_{0.62}CoO_2$



m = 2

$[Bi_2Sr_2O_4]_{0.56}CoO_2$



$[SrO-SrO]_{0.5}CoO_2$

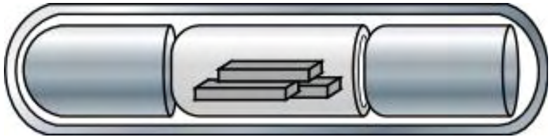
SYNTHESIS

excess-oxygen source

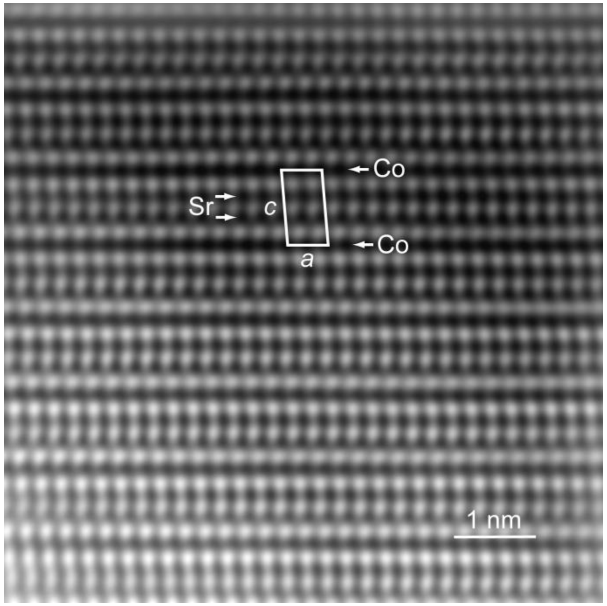
Co_3O_4 + 3 SrO_2

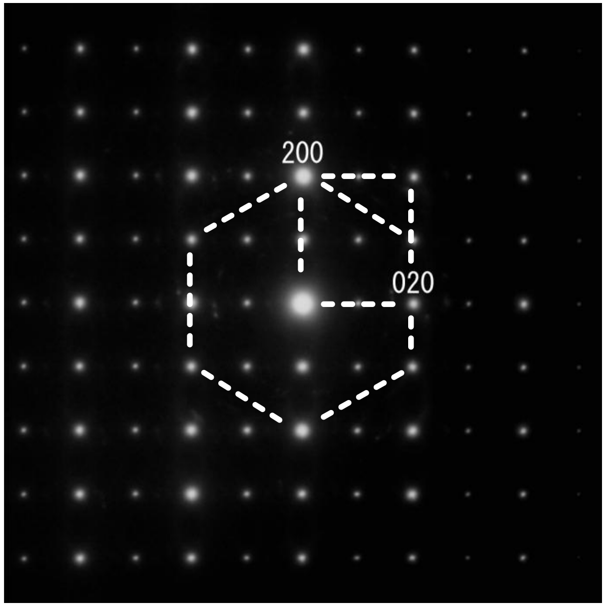
850 °C, 24 h

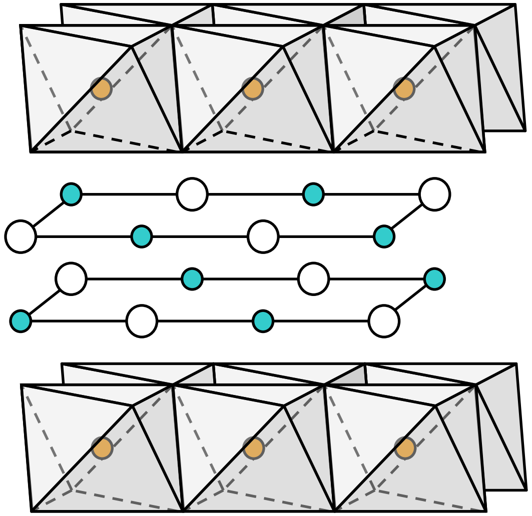
(in a closed silica ampoule)



H. Yamauchi, K. Sakai, T. Nagai, Y. Matsui & M. Karppinen,
Japanese Patent, Feb. 14, 2005;
Chem. Mater. 18, 155 (2006).







- electrical conductivity somewhat enhanced
- Seebeck coefficient remains the same
- thermal conductivity higher ?

THERMOELECTRICS & NANOTECHNOLOGY

- **Mean free path longer for phonons (>100 nm) than for electrons/holes (<10 nm)**
- **Nanostructuring of thermoelectric materials: dimensions should be smaller than the mean free path for phonons but larger than that for electron/hole**
  → thermal conductivity (κ_{latt}) is reduced but electrical conductivity not
- **Nanostructuring approaches so far reported only for conventional thermo-electric materials**

  M.S. Dresselhaus, *et al*., *Adv. Mater*. **19**, 1043 (2007).
  A.I. Boukai, *et al*., *Nature* **451**, 168 (2007).

Our Fin-Jpn Project (Terasaki-Karppinen):

"Novel Tailor-Made Oxide Thermoelectrics"

"Thermoelectric oxides are engineered into various nano-scale forms (thin film structures and template-based nanostructures) taking advantage of the Finnish ALD (atomic-layer-deposition) coating technique. This approach is unique in the world."

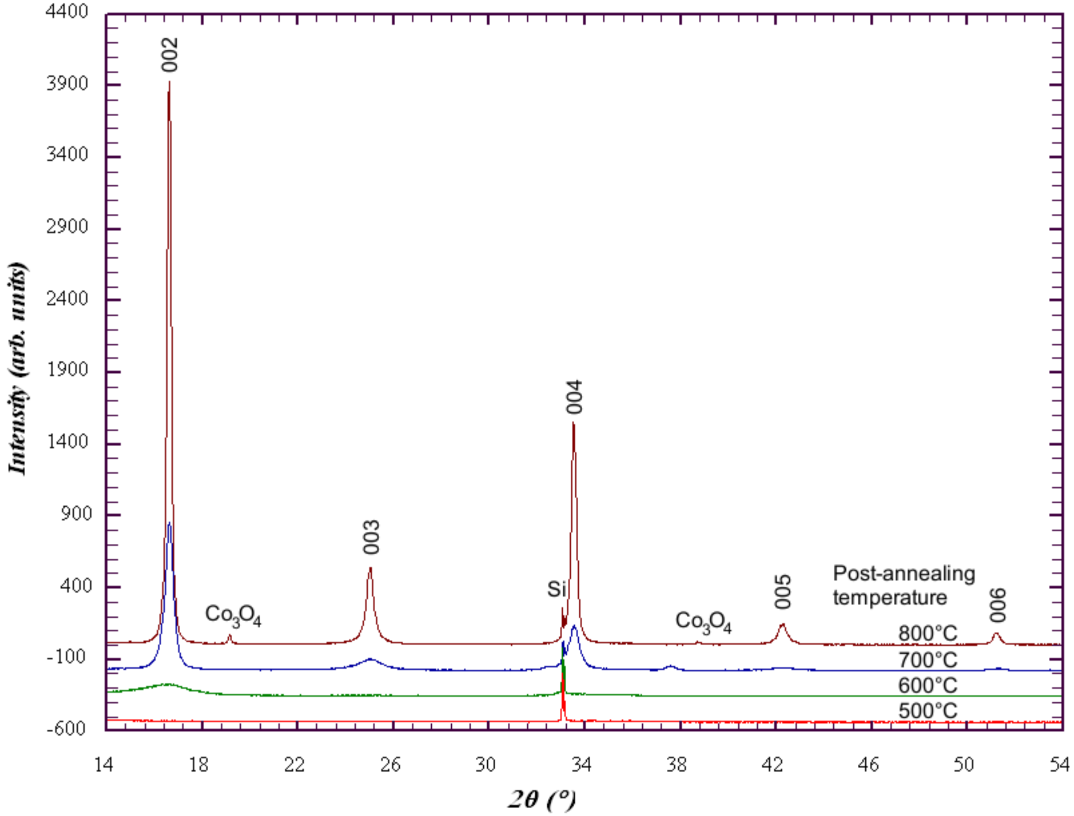
ALD of thermoelectric oxide $[CoCa_2O_3]_{0.62}CoO_2$

- Ca(thd) + ozone + Co(thd) + ozone

  (thd = 2,2,6,6-tetramethyl-3,5-heptanedione)

- Deposition conditions: 200 ^{o}C, 2 mbar, N_2 as a carrier and purging gas, 600 cycles, Si (100) substrate

- as-deposited films amorphous → post-annealing in O_2



M. Valkeapää, T. Viitala & M. Karppinen, manuscript (2009).

OXYGEN NONSTOICHIOMETRY

(1) Interstitial oxygen atoms

- $La_2CuO_{4+\delta}$
- other RP-phases: $La_{n+1}T_nO_{3n+1+\delta}$ (T = Cu, Ni, Co)

(2) Cation vacancies

- $La_{1-x}Mn_{1-x}O_3$

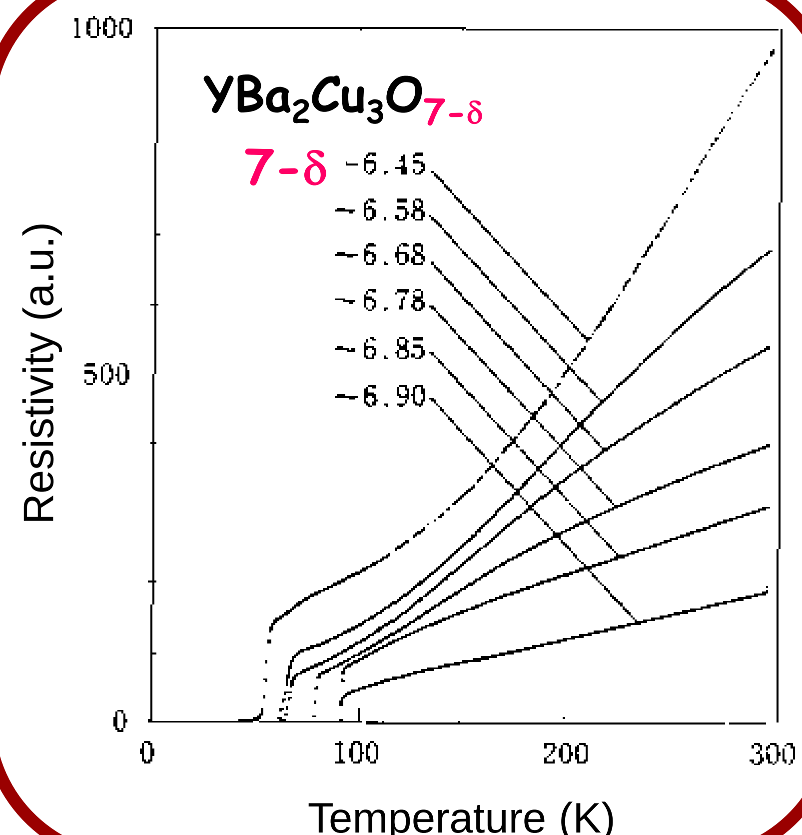
(3) Oxygen vacancies

- $YBa_2Cu_3O_{7-\delta}$
- other HTSCs

(4) Interstitial cations

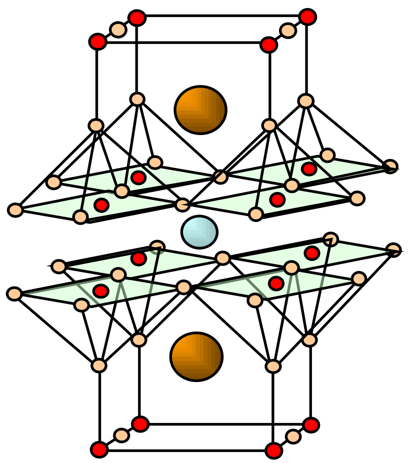
- $Zn_{1+x}O$

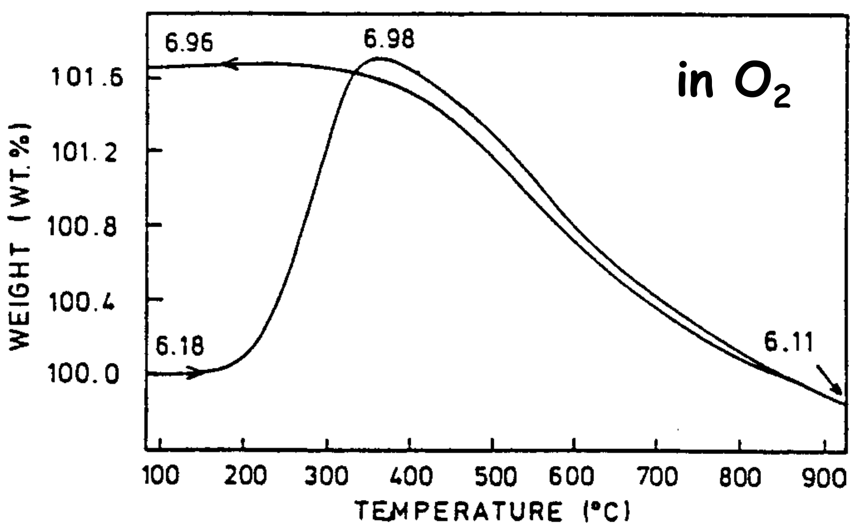
Oxygen Engineering !



SUPERCONDUCTORS

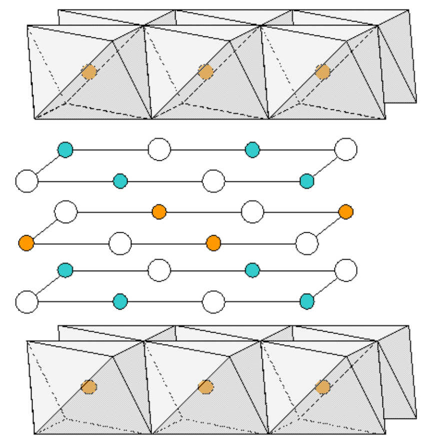
$YBa_2Cu_3O_{7-\delta}$

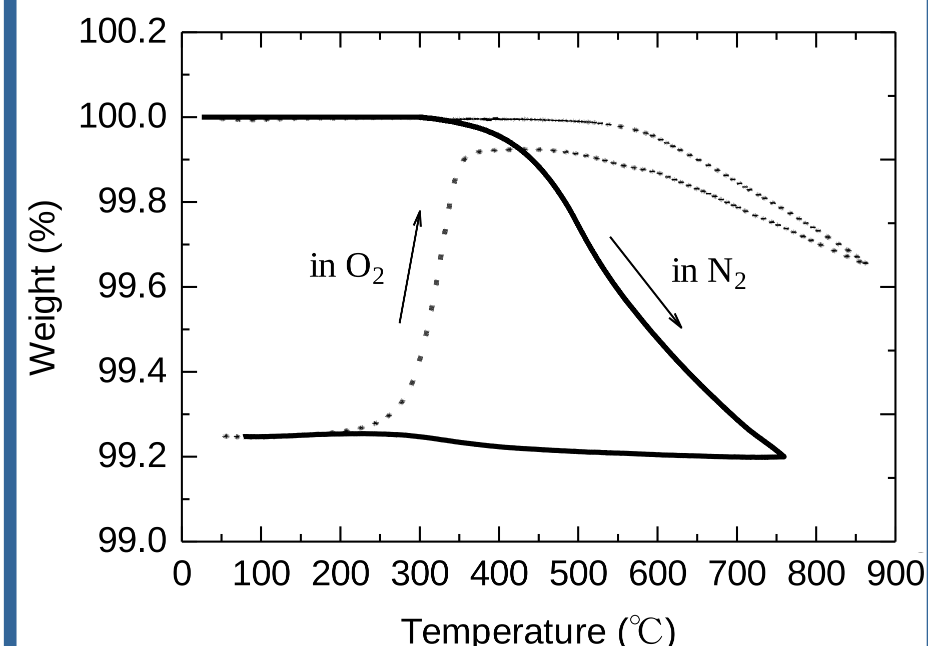




THERMOELECTRICS

$[CoCa_2O_{3-\delta}]_{0.62}CoO_2$





OXYGEN ENGINEERING

- Presice Control of the Oxygen Content
- Accurate Determination of the Oxygen Content

↓

DEVELOPMENT OF

A VERSATILE ARSENAL OF TECHNIQUES OF

CHEMICAL ANALYSIS AND MANIPULATION

TKK

M. Karppinen & H. Yamauchi,
Oxygen engineering for functional oxide materials,
In: International Book Series: Studies of High Temperature Superconductors,
Vol. **37**, A.V. Narlikar (Ed.), Nova Science Publishers, New York 2001, pp. 109-143.

M. Karppinen & H. Yamauchi,
Chemical design of copper-oxide superconductors: Homologous series and oxygen engineering,
In: Frontiers in Superconducting Materials,
A.V. Narlikar (Ed), Springer Verlag, Berlin 2005, pp. 255-294.

DISCOVERY OF NEW FUNCTIONS

- e.g. unique oxygen absorption/desorption properties for $YBaCo_4O_{7+\delta}$

$\rightarrow$ New Oxygen-Storage Material

Oxygen-Storage Materials

- **$CeO_{2-\delta}$: $Ce^{III/IV}$**
- **$(Ce,M)O_{2-\delta}$: *M* = Zr, Ti, Bi, etc. (commercial)**
- **$(Ce_{2/3}Cr_{1/3})O_{2+\delta}$: $Ce^{III/IV}$ and $Cr^{III/VI}$**

  [P. Singh, M.S. Hegde & J. Gopalakrishnan, *Chem. Mater*. **20**, 7268 (2008)]
- **$R_2O_2SO_4$: $S^{-II/VI}$**

  - large OSC, but too high operation temperature (> 600 °C)

  [M. Machida *et al*., *Chem. Mater*. **17**, 1487 (2005); **19**, 954 (2007); **20**, 6697 (2008)]
- **$RBaCo_4O_{7+\delta}$: $Co^{II/III}$**

  - large OSC, low operation temperature (250 ~ 400 °C)

  [M. Karppinen *et al*., *Chem. Mater*. **18**, 490 (2006);

  Int. Patent Appl. PCT/JP2006313436, filed June 6, 2006]
- **$Pb_2Sr_2RCu_3O_{8+\delta}$: $Cu^{I/II}$ and $Pb^{II/IV}$**

  - resembles $RBa_2Co_4O_{7+\delta}$, but less attractive OSC characteristics

  [M. Lehtimäki, H. Yamauchi & M. Karppinen, manuscript (2009)]

OSC (oxygen-storage capacity): μmol O / g

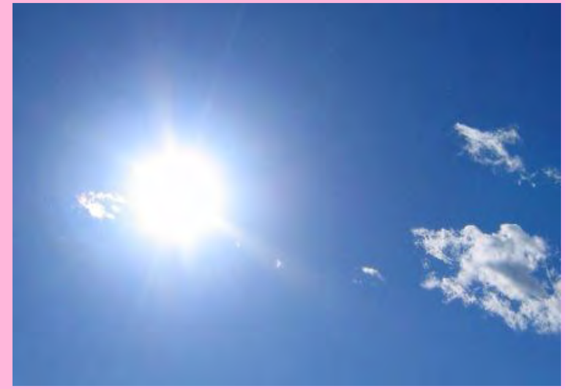
Examples of Applications

$P(O_2)$ sensitivity

Redox catalyst for autoexhaust

TOKYO ROKI Co. Ltd.

Gas selectivity



H_2/O_2 separator for photo-catalysts

Domen Lab. (Univ. of Tokyo) website

Oxygen storage capability

Oxygen enrichment

National (Panasonic)

Fast oxygen diffusion

Oxygen selective membrane in SOFC

NISSAN Motor Co. Ltd.

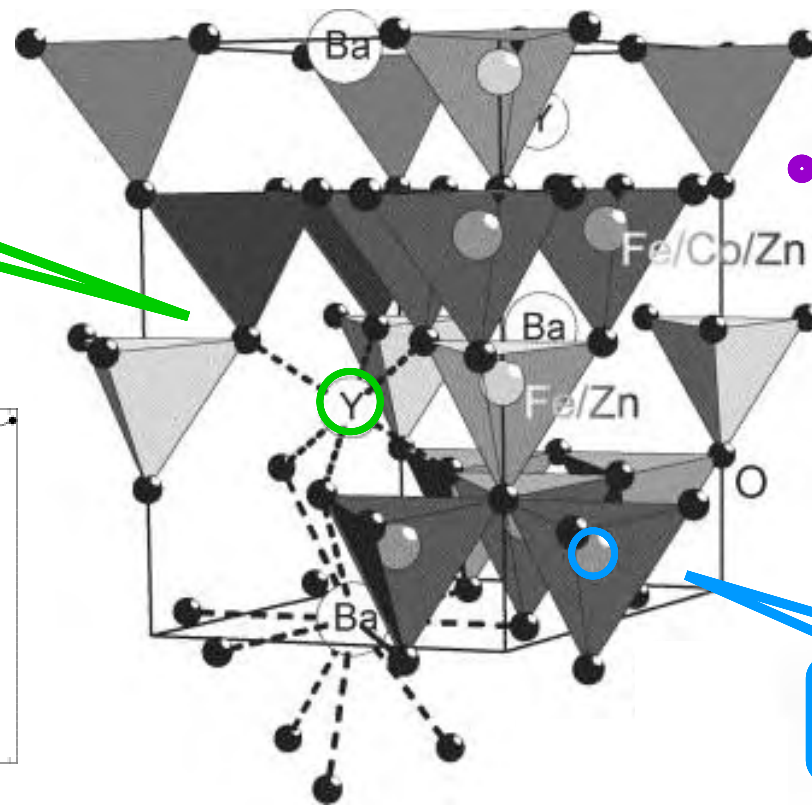
$YBaCo_4O_7$

- **discovered in 2002 in Sweden**

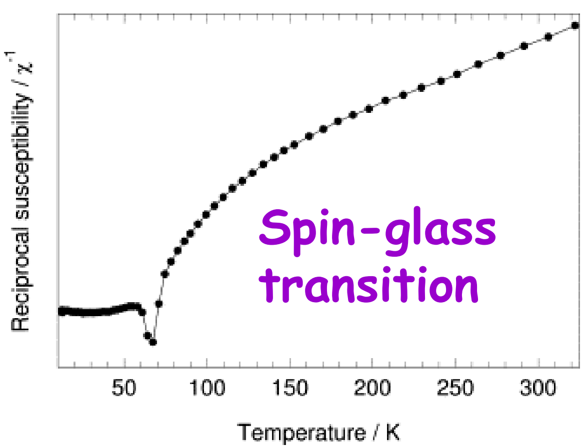
  [M. Valldor & M. Andersson, *Solid State Sci.* 4, 923 (2002).]
- **investigated for TE properties** **(hexagonal cobalt oxide)**
- **investigated for magnetic properties** **(frustrated Kagome-lattice)**

OXYGEN ???

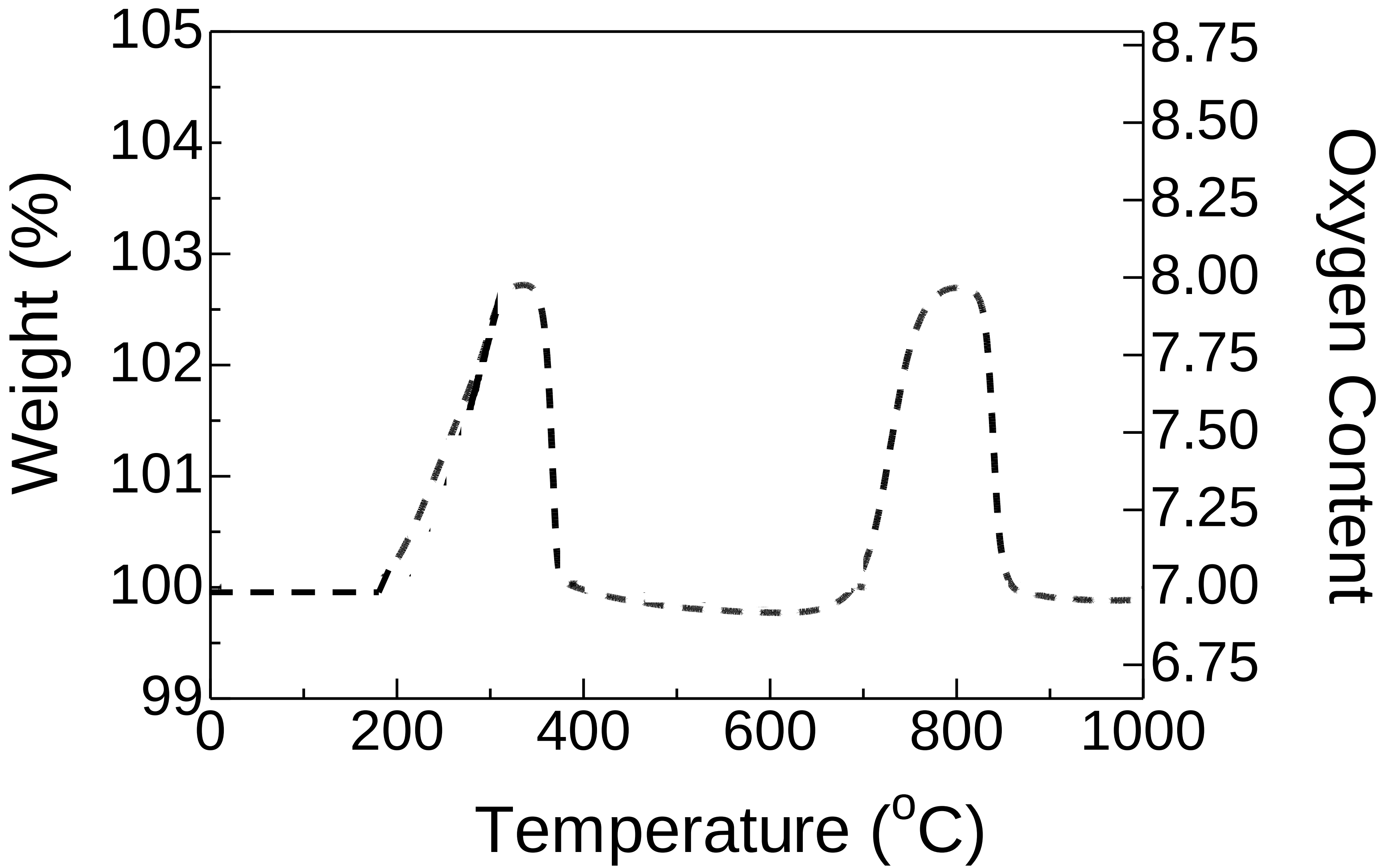
Y, Dy ~ Lu, Ca, In

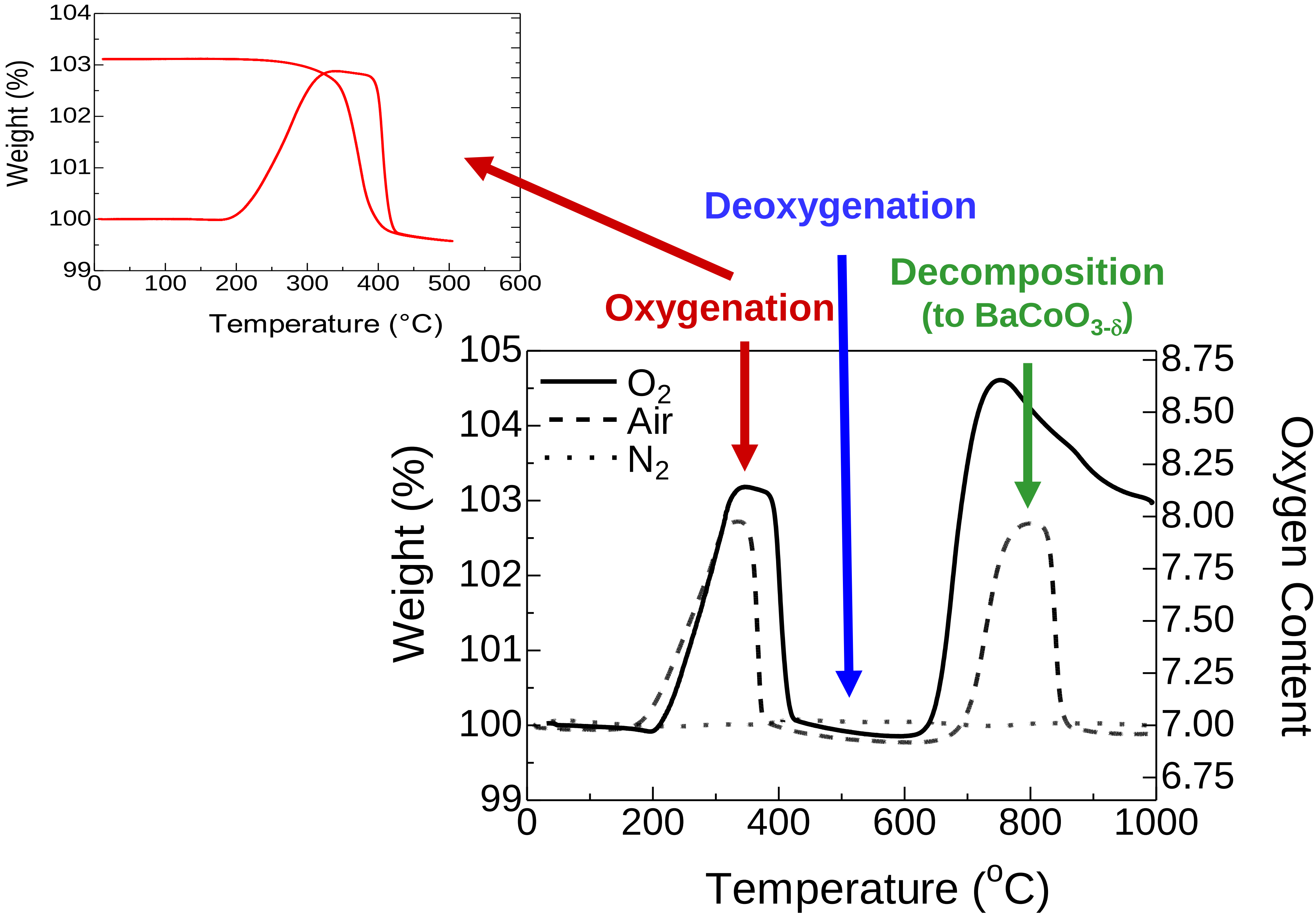


Co, Al, Zn, Fe



$YBaCo_4O_7$: heating in air in a thermobalance





M. Karppinen, H. Yamauchi, S. Otani, T. Fujita, T. Motohashi, Y.-H. Huang, M. Valkeapää & H. Fjellvåg, *Chem. Mater*. **18**, 490 (2006).

$YBaCo_4O_{7+\delta}$

Sample	δ	OSC (µmol-O/g)	Co valence
N_2, 1 atm, 500 °C	0.03		2.265
as-synthesized	0.13		2.315
Br_2/H_2O, 25 °C	0.38	660	2.44
air, 1 atm, 340 °C	1.01	1760	2.755
O_2, 1 atm, 340 °C	1.19	2070	2.845
O_2, 10 atm, 340 °C	1.32	2300	2.91
O_2, 100 atm, 340 °C	1.46	2540	2.98
$KClO_3$, $2 \cdot 10^4$ atm, 500 °C	1.56	2720	3.03

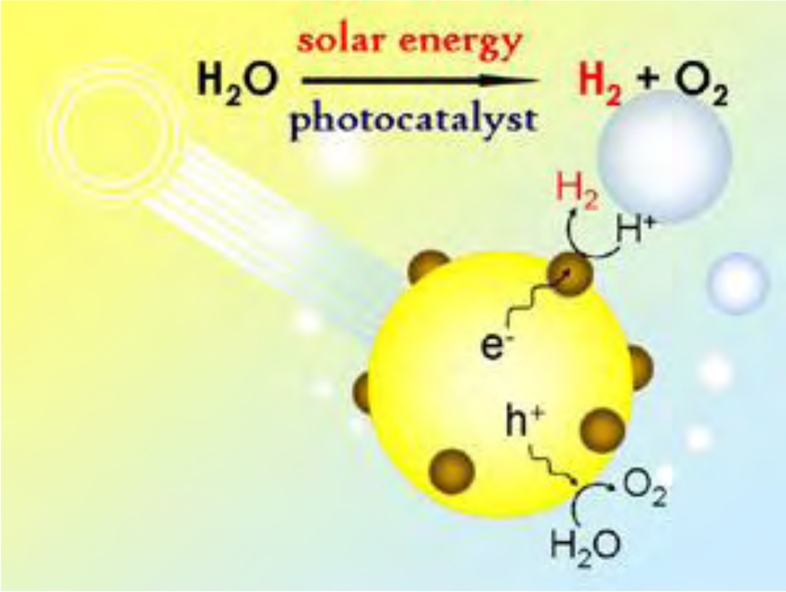
S. Räsänen, H. Yamauchi & M. Karppinen, *Chem. Lett*. **37**, 638 (2008).

$YBaCo_4O_{7+\delta}$

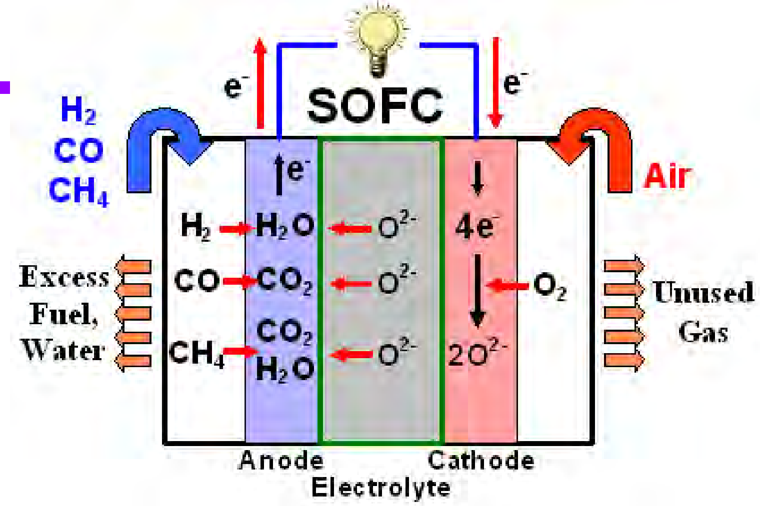
could be used for separation of H_2 from O_2

yielded through photocatalytic water splitting ?

- **Prof. K. Domen, University of Tokyo**
- **Mitsubishi Chemical Coporation**



SOLID OXIDE FUEL CELL



■ ELECTROLYTE

- oxide-ion conductor
- $(Zr,Y)O_2$ (= YSZ)
  (works well only at high operation temperatures)
- $(La_{0.2}Sr_{0.8})(Ga_{0.3}Mg_{0.7})O_{3-\delta}$ (Ga is expensive)
- **$YBaCo_4O_{7+\delta}$** [M. Karppinen, et al., *Chem. Mater*. **18**, 490 (2006)]

■ ANODE

- mixed-conductor (MIEC: mixed ionic & electronic conductor)
- Ni/YSZ composite
  (works with H_2, but not for C- and S-containing fuels)
- $(La,Sr)_{0.9}(Cr_{0.5}Mn_{0.5})O_{3-\delta}$ [S.W. Tao & J.T.S. Irvine, *Nature Mater.* **2**, 320 (2003)]
- **$Sr_2(Mg,Mn)MoO_{6-\delta}$** [Y.H. Huang, J.B. Goodenough, *et al*., *Science* **312**, 254 (2006)]

■ CATHODE

- MIEC
- $(La,Sr)MnO_{3-\delta}$ (reacts with the electrolyte)
- $(Sr,Ba)(Co,Fe)O_{3-\delta}$ [Z.P. Shao & S.Haile, *Nature* **431**, 170 (2004)]

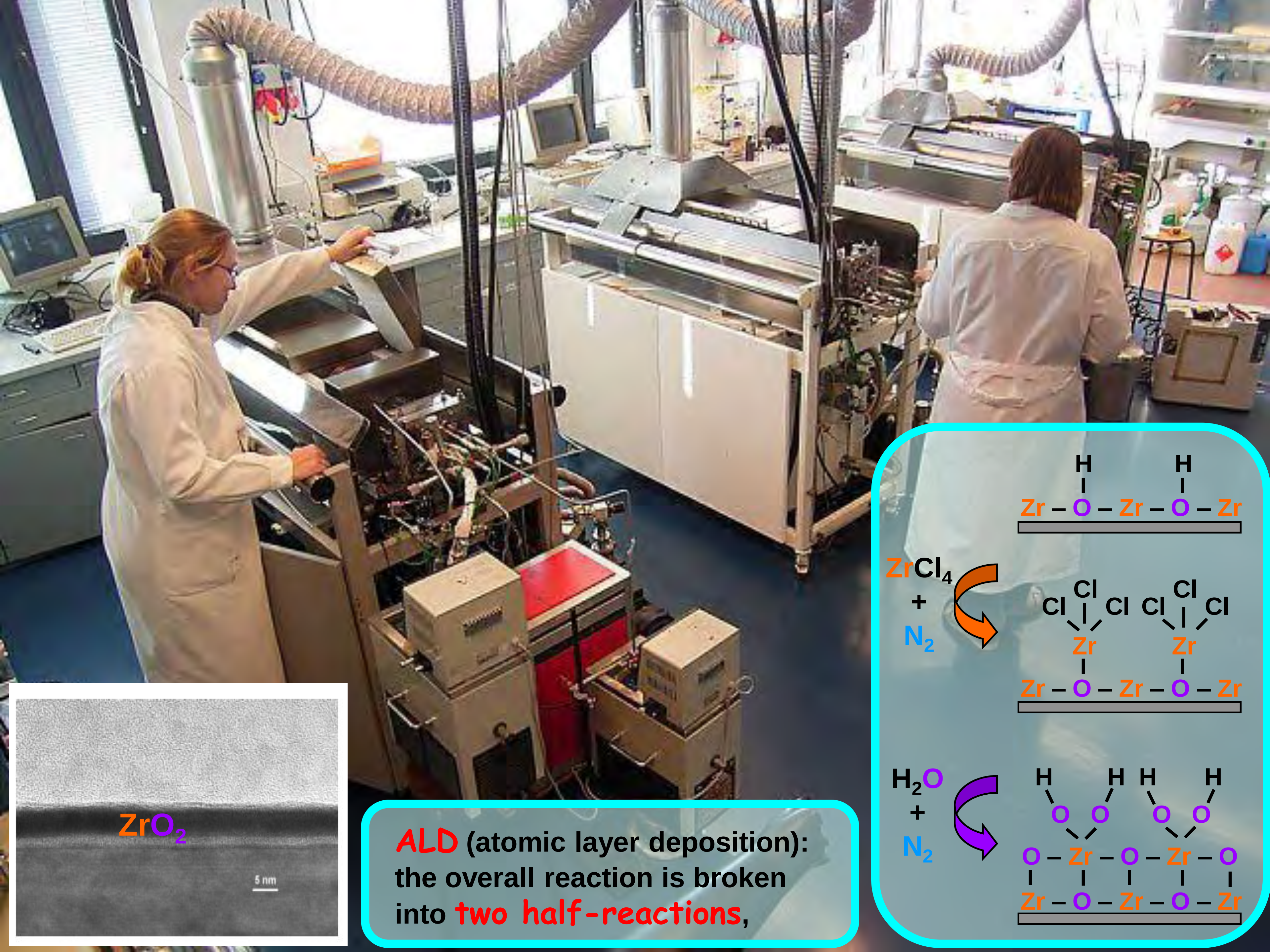
ATOMIC LAYER DEPOSITION (ALD)

- **To produce a known compound in a new form:**

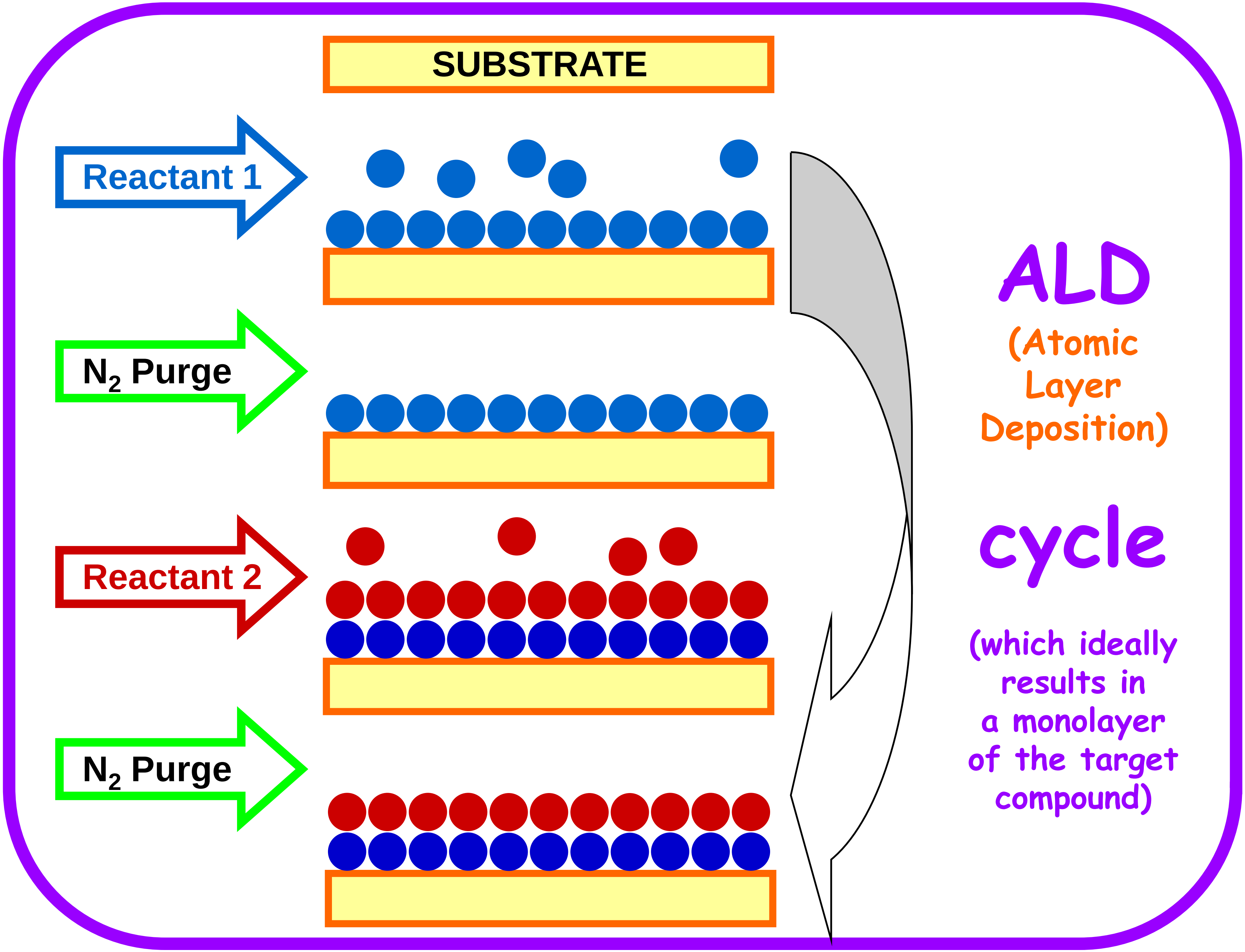
  - thin films of (complex) oxide materials, polymers, etc.

- **To find a new way to combine existing materials:**

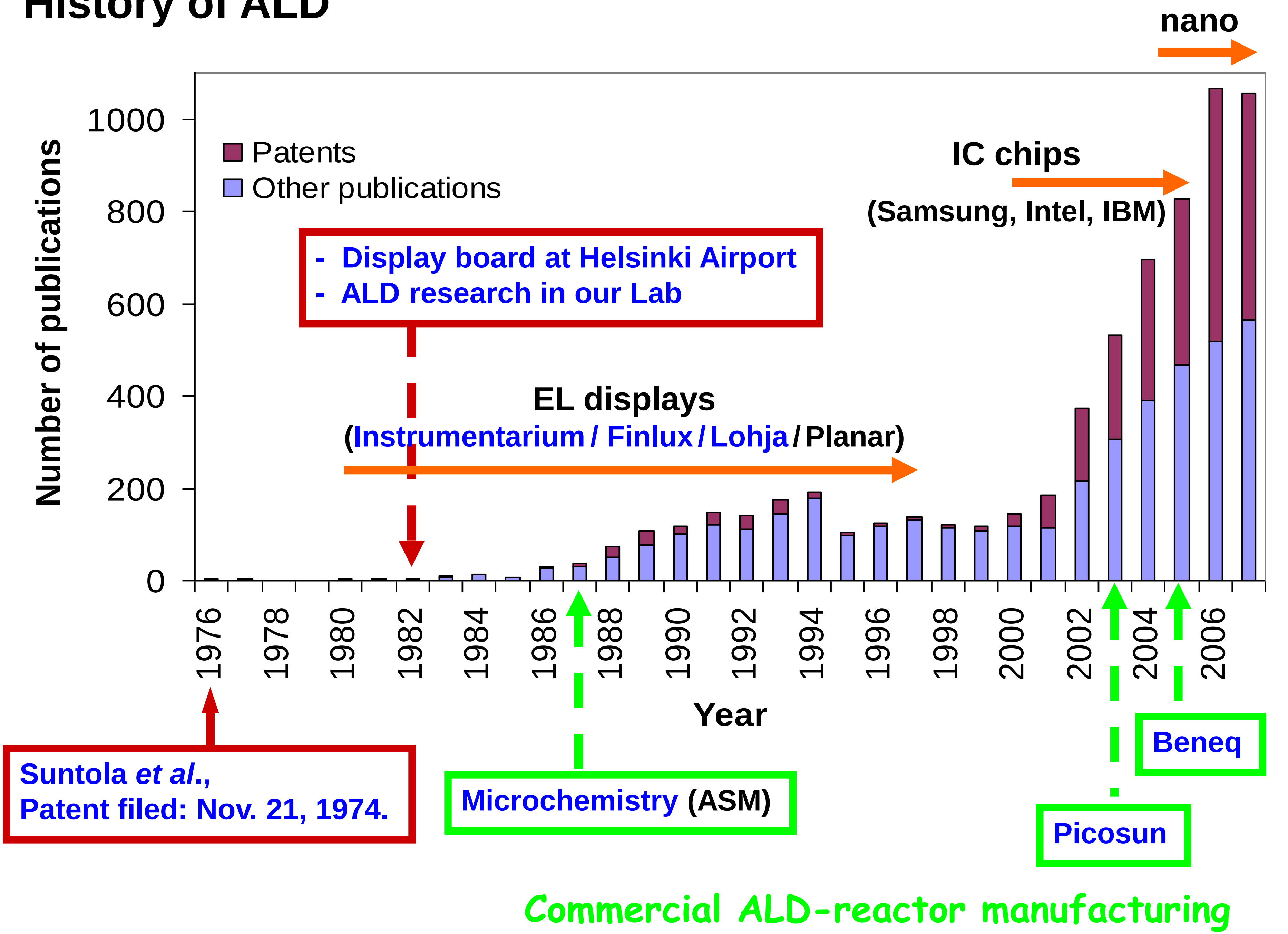
  - oxide coatings on graphene, biomaterials, paper, polymers, etc.
  - inorganic/organic hybrid materials

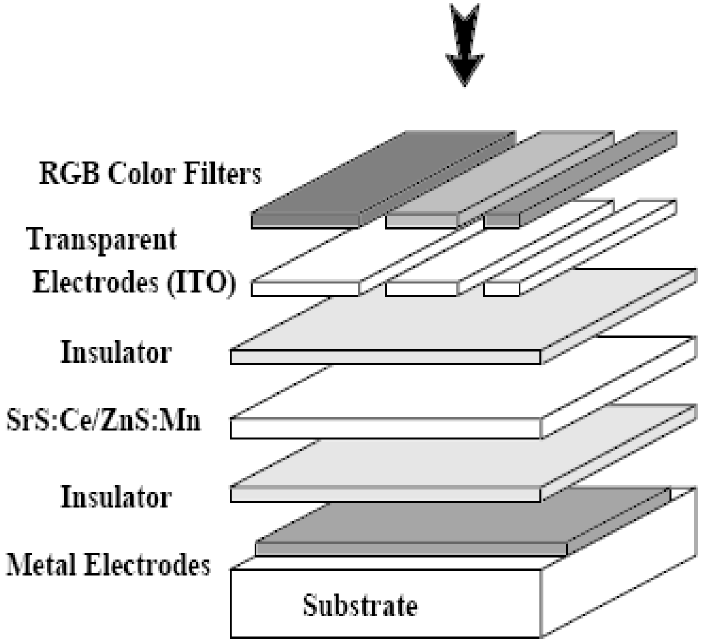


ZrO2
5 nm
ALD (atomic layer deposition): the overall reaction is broken into two half-reactions,
H H
Zr – O – Zr – O – Zr
ZrCl4 + N2
Cl Cl Cl Cl Cl Cl
Zr Zr
Zr – O – Zr – O – Zr
H2O + N2
H H H H
O O O O
O – Zr – O – Zr – O
Zr – O – Zr – O – Zr


SUBSTRATE
Reactant 1
N2 Purge
Reactant 2
N2 Purge
ALD
(Atomic Layer Deposition)
cycle
(which ideally results in a monolayer of the target compound)

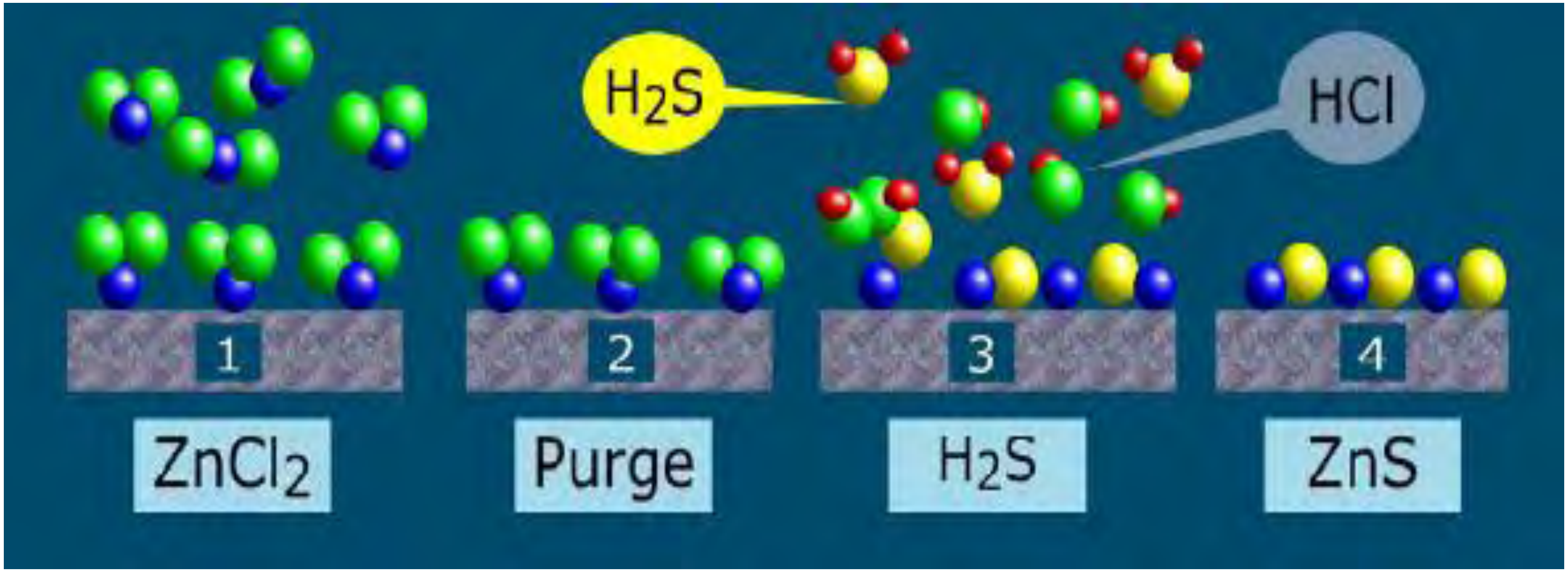
History of ALD





Electroluminescent display

Instrumentarium/Finlux/Lohja/Planar



Kalevala Koru (Finland):

- **traditional (silver) jewelry**

Beneq (Finland):

- **Al_2O_3 coating by ALD**

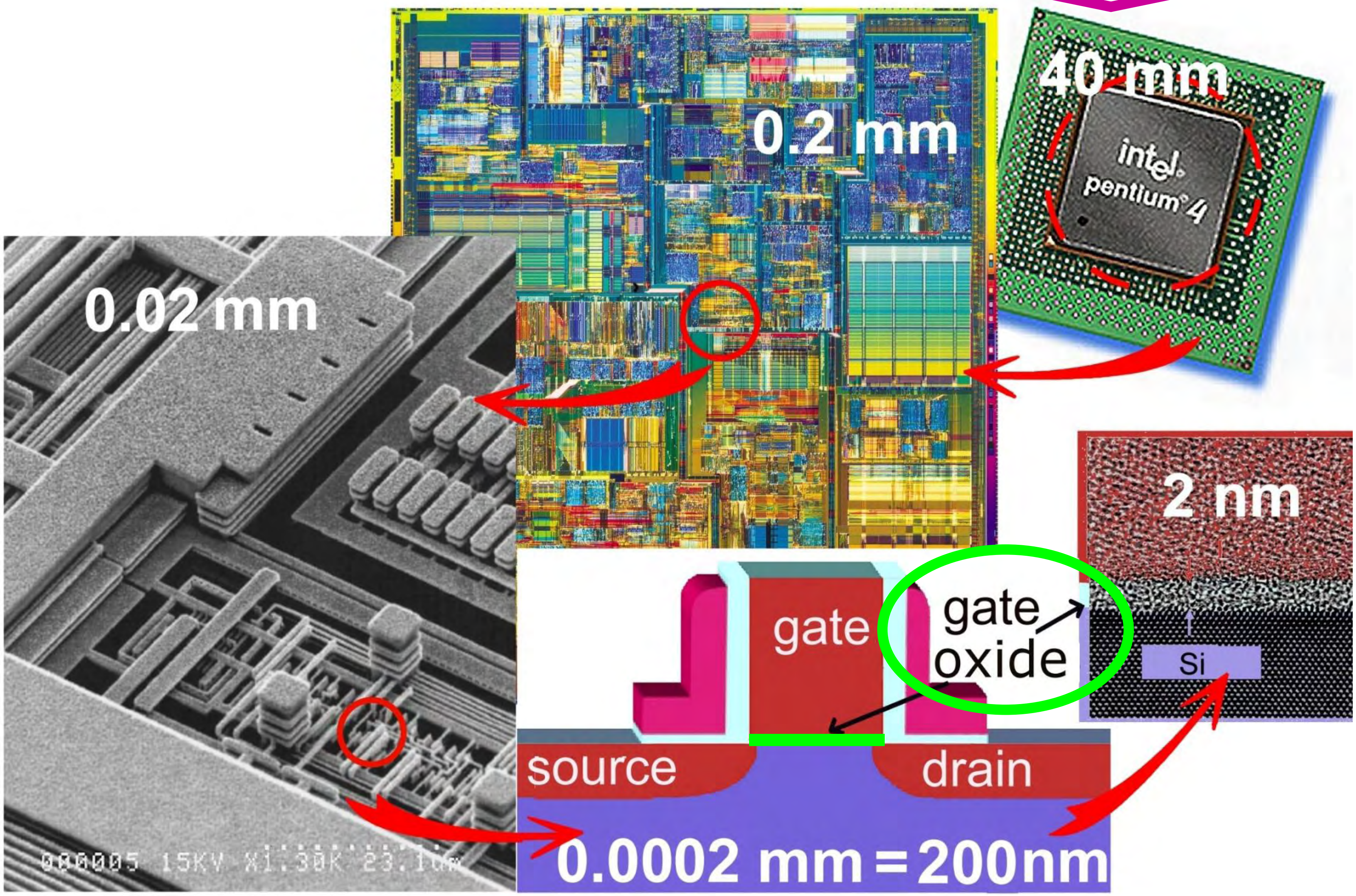
uncoated | **Al_2O_3-coated**

BEFORE | **AFTER TARNISHING TEST**

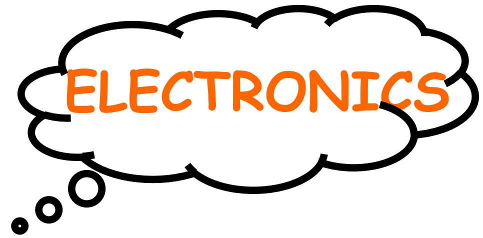
Dense, pinhole-free & highly conformal Al_2O_3-nanocoating efficiently protects silver jewelries from tarnishing

CMOS transistor

smaller transistors → lower gate voltage
same electric fields → thinner dielectric
SiO_2 → **HIGH-*k* DIELECTRICS**

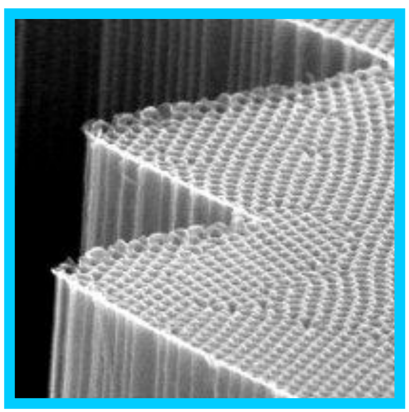


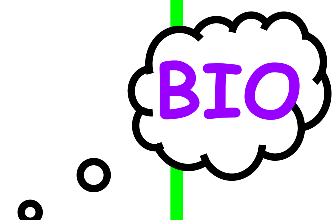
Advantages of ALD



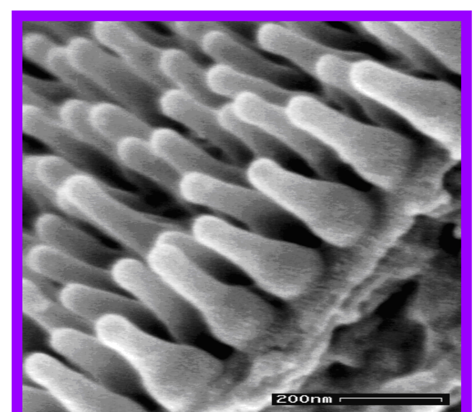
- Inexpensive method
- Excellent repeatability
- Dense and pinhole-free films
- Accurate and simple thickness control
- Doping easily achieved
- Large area uniformity

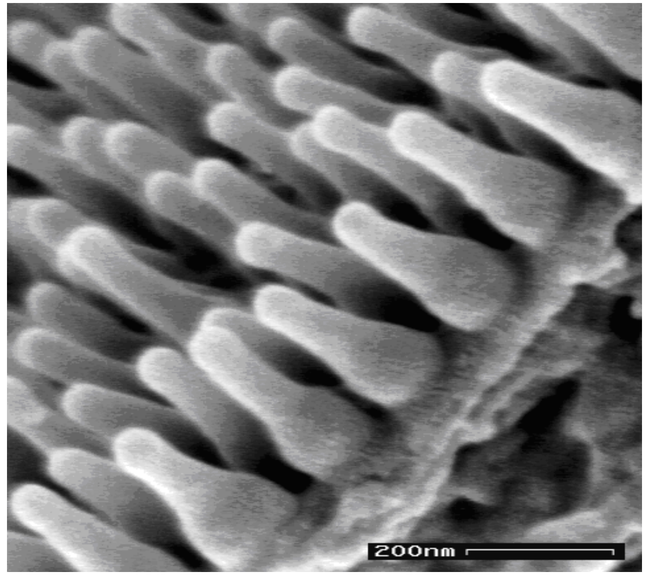
- Excellent conformality





- Low deposition temperature
- Gentle deposition process





CICADA WING

- **Peculiar surface-nanostructure**

  200-nm high nanopillars coated with a waxy layer

- **superhydrofobic**

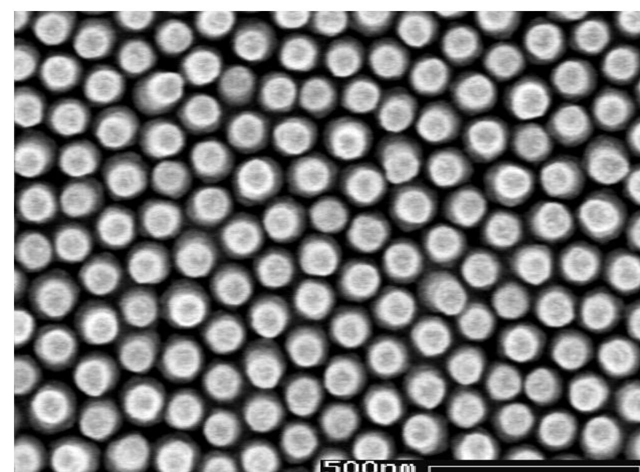
ZnO

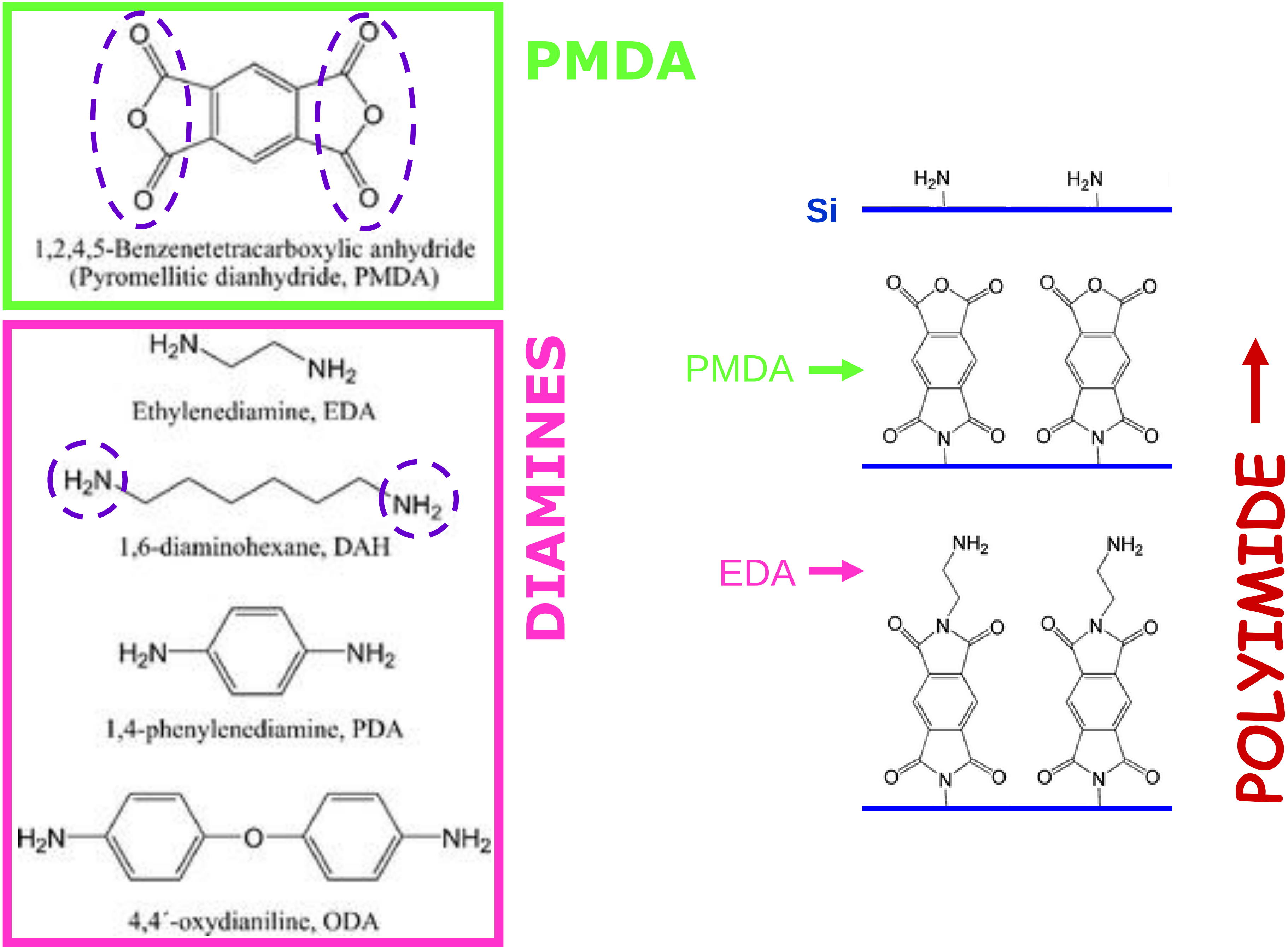
- **Reversible change from hydrofobic to hydrophilic upon UV-radiation**

CICADA WING + ZnO

- **Conformal coating of the wing by a thin layer of ZnO (~10 nm) by means of ALD**
- **Reversible change from superhydrofobic to hydrophilic upon UV-radiation**

Sahramo, Malm, Raula, Ras & Karppinen, manuscript (2009).

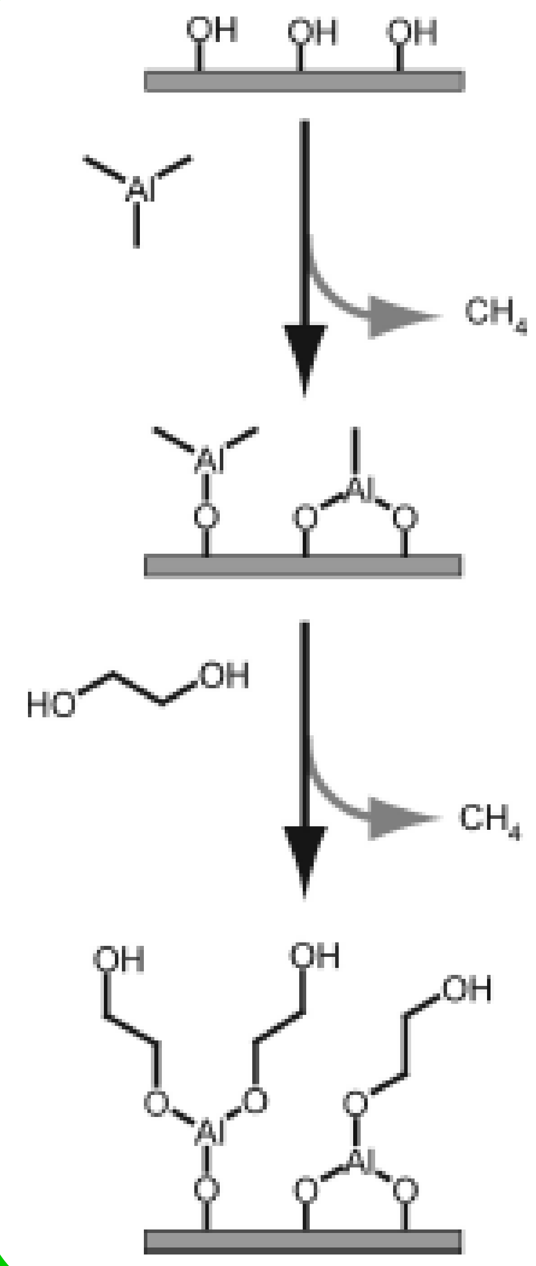




Putkonen, Harjuoja, Sajavaara & Niinistö, *J. Mater. Chem*. **17**, 664 (2007).

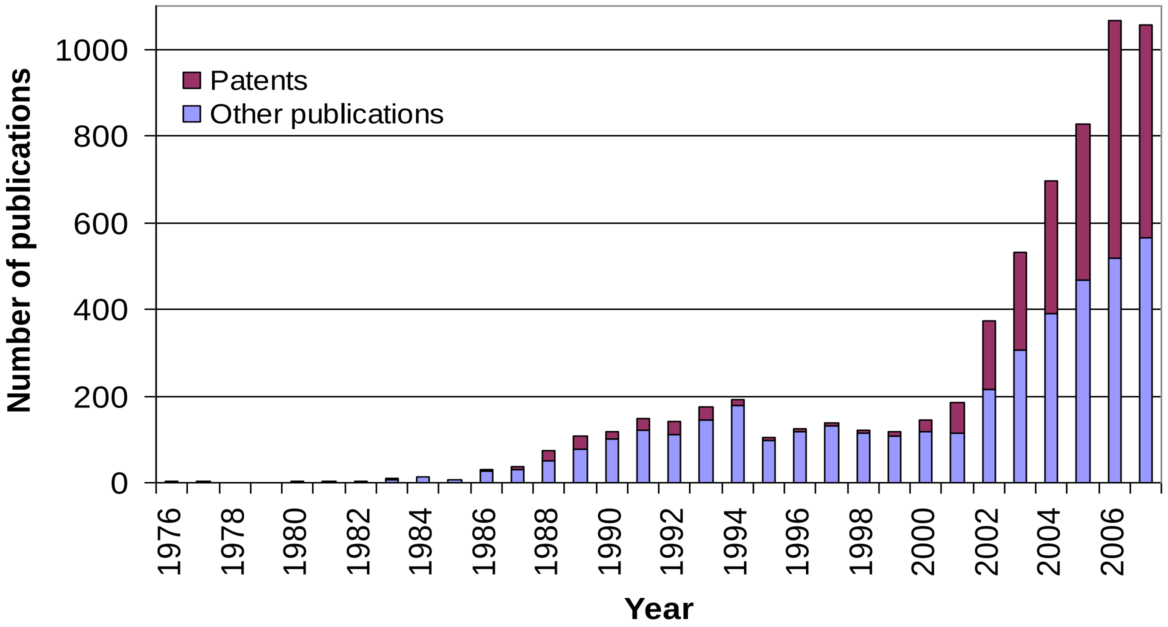
Inorganic-Organic Hybrids

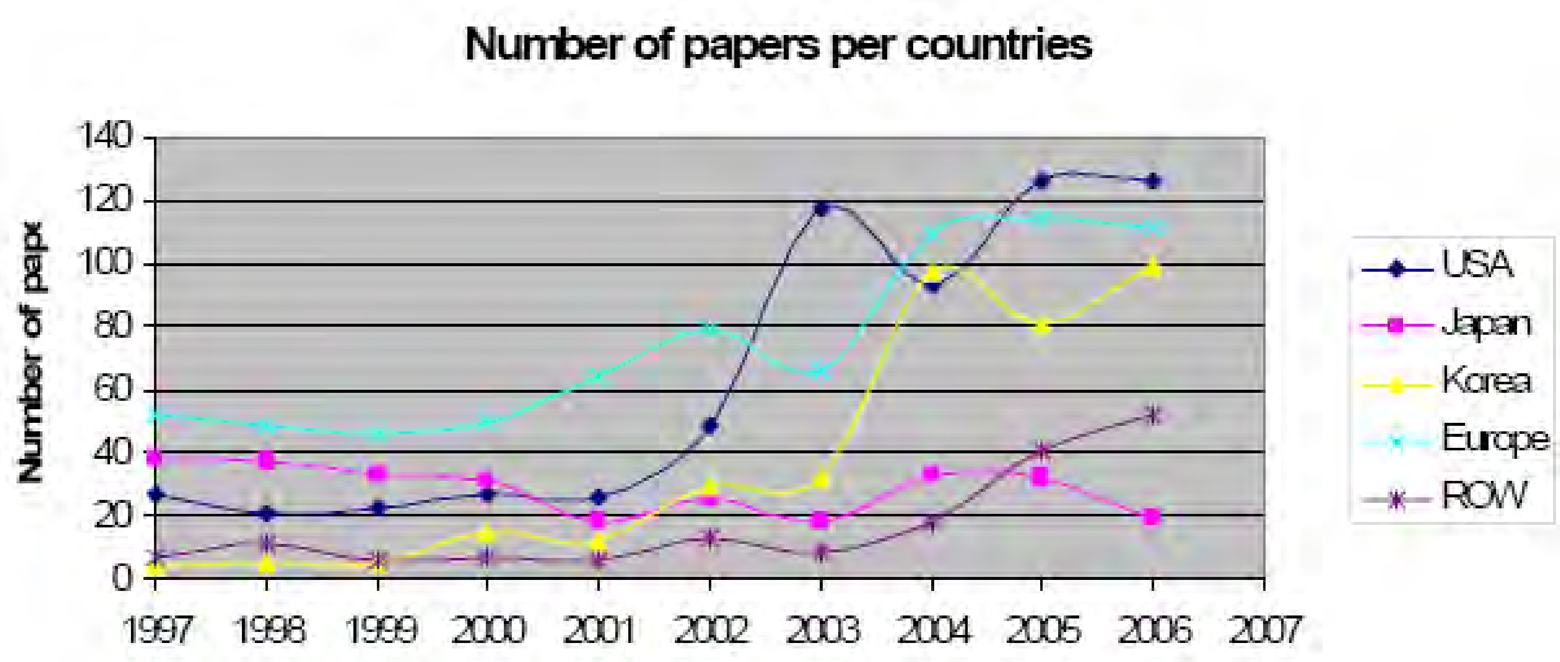
- Proof-of-Concept:
  - $Al(CH_3)_3 + HO\text{-}(CH_2)_2\text{-}OH$
- Future Challenges:
  - $M\text{-}R_x$ + HO-Org-OH
  - m(Inorg) + n(Org)



TOP-11 in Japan

Semicond Leading Edge Technol
Univ Tokyo
Tohoku Univ
Hiroshima Univ
Semicond Res Inst
Univ Shizuoka
Natl Inst Adv Ind Sci & Technol
Kobe Univ
Univ Tsukuba
NEC Elect Corp
Tokyo Inst Technol





Jarmo Skarp / Arrivac, March 6, 2007

SUMMARY

Non-Accidental Expansion of the Material Frontier

NEW MATERIALS
NEW KNOWLEDGE
NEW FUNCTIONS

Layer-by-Layer Design

- additional layers
- the simplest "zero phases"

Layer-by-Layer Deposition

- polymers
- inorganic-organic hybrids
- inorganic/bio-nano combinations

Material-Property Tailoring

- oxygen-engineering
- nanoengineering

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