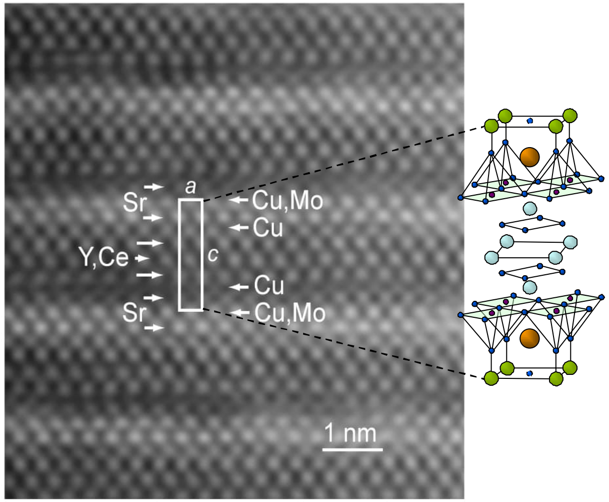
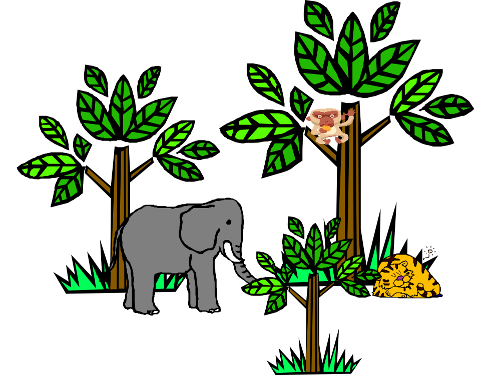
LECTURE SCHEDULE

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements (diamond)
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu & Magnetism
10.	Fri	29.09.	Cu & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2



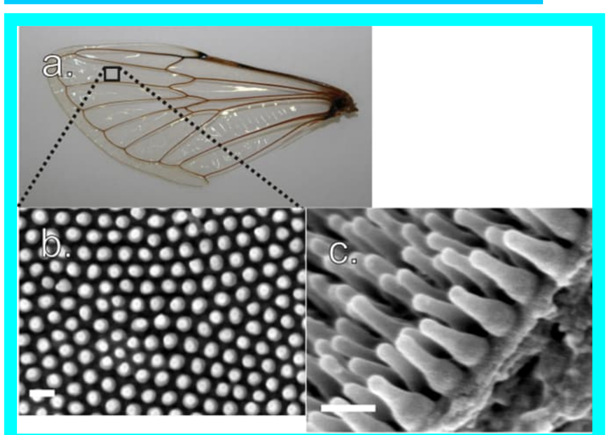


INORGANC CHEMISTRY

Aalto University
Department of Chemistry & Materials Science

Sustainable energy materials

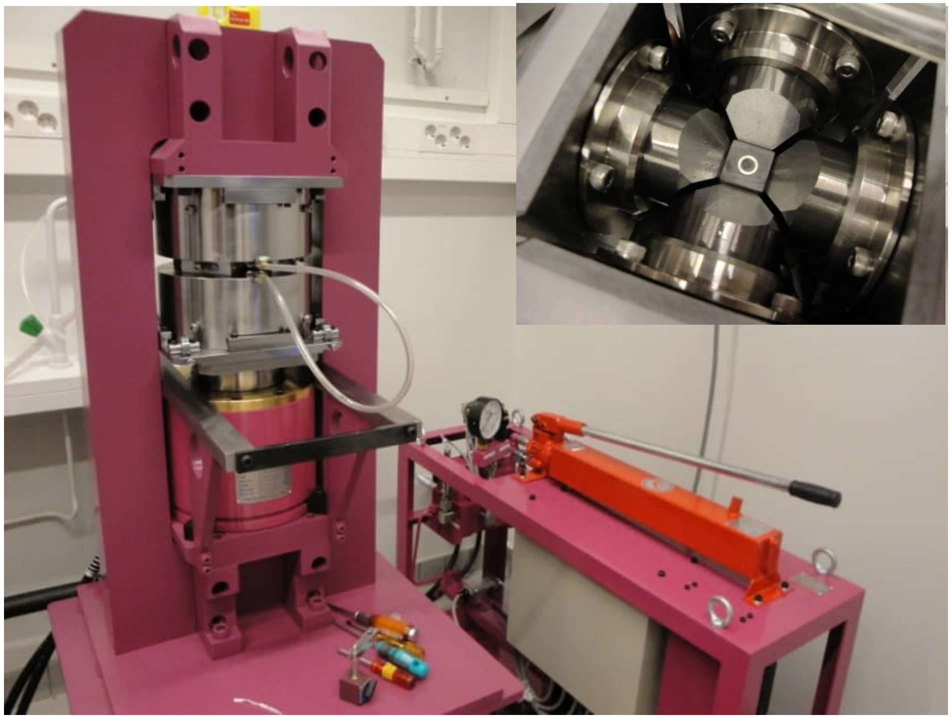
- **Novel Functional (bulk) Oxide Materials**
  - high-T_c superconductors
  - thermoelectric materials
  - exotic magnetic materials
  - ionic conductors (fuel cell, battery, oxygen storage)

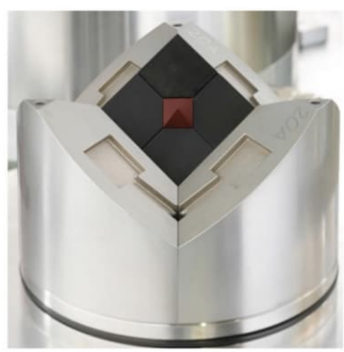


- **ALD (Atomic Layer Deposition) Thin Films**
  - complex (ternary & quaternary) oxides
  - oxide coatings on exciting surfaces (polymers, biomaterials, textiles, steel, etc.)
  - inorganic/organic hybrid materials

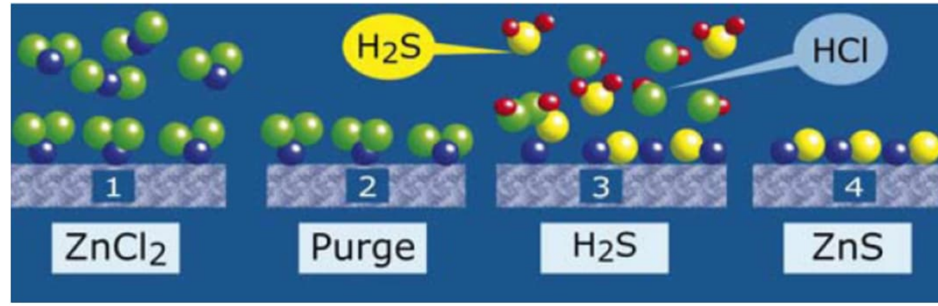
KEY CONCEPTS:
Layer-engineering & Oxygen-engineering & Nanostructuring

Ultra High-Pressure (HP) synthesis



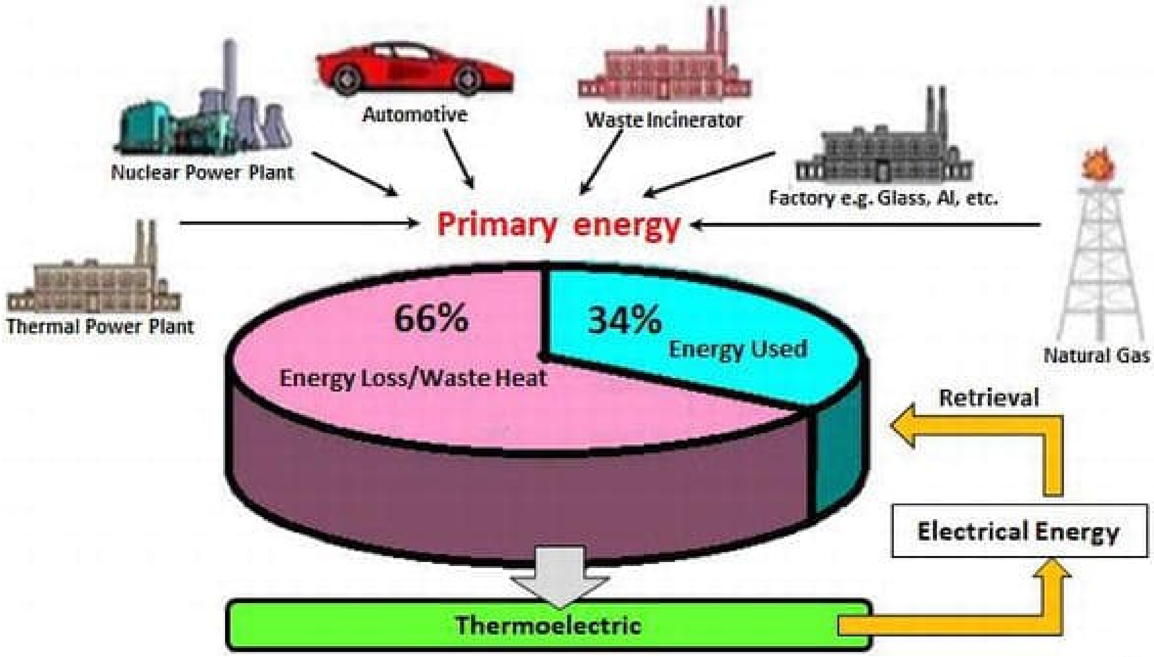


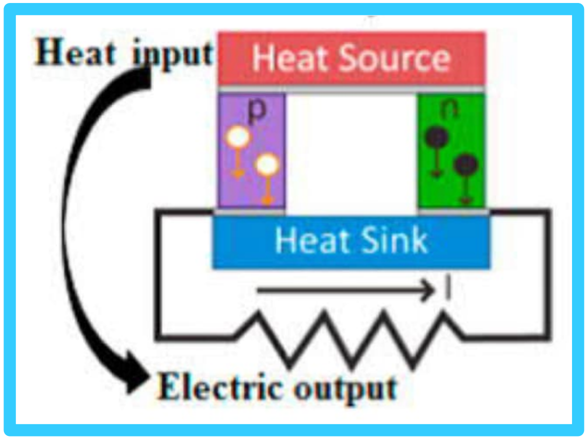
Atomic Layer Deposition (ALD) thin-film technology

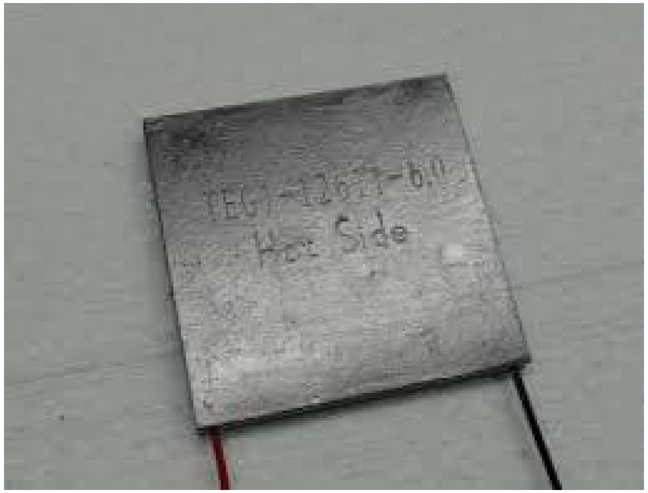


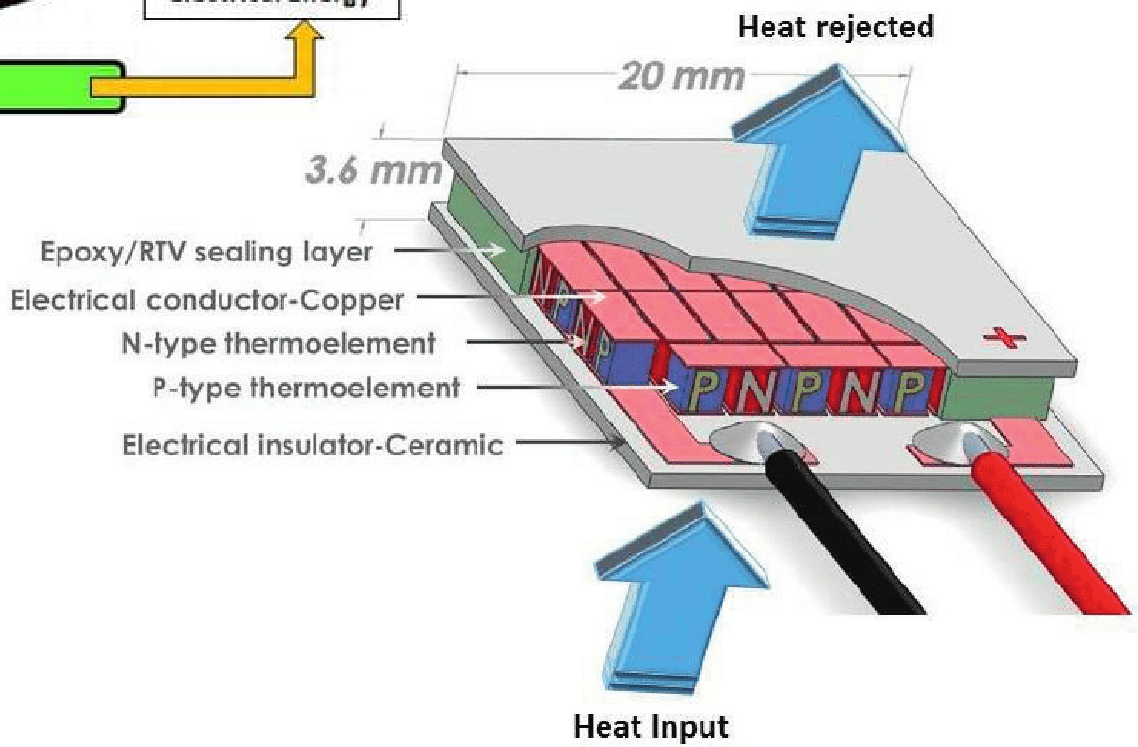
SYNTHESIS TECHNIQUES

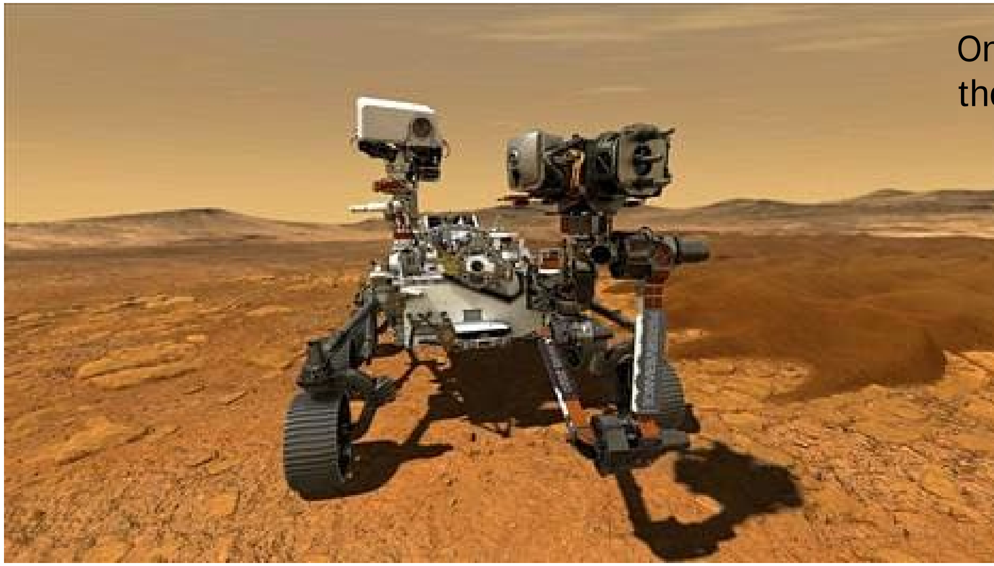
THERMOELECTRICS: Electricity from (waste) Heat







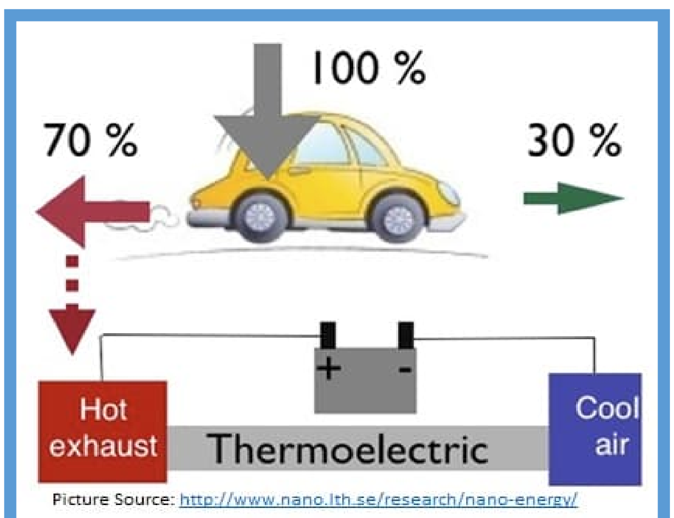




One of the three radioisotope thermoelectric generators on Cassini

EXAMPLES of CONVENTIONAL TE APPLICATIONS

- **Space crafts: ^{238}Plutonium radioactive decay as continuous heat source**
- **Cars: Exhaust gas heat**



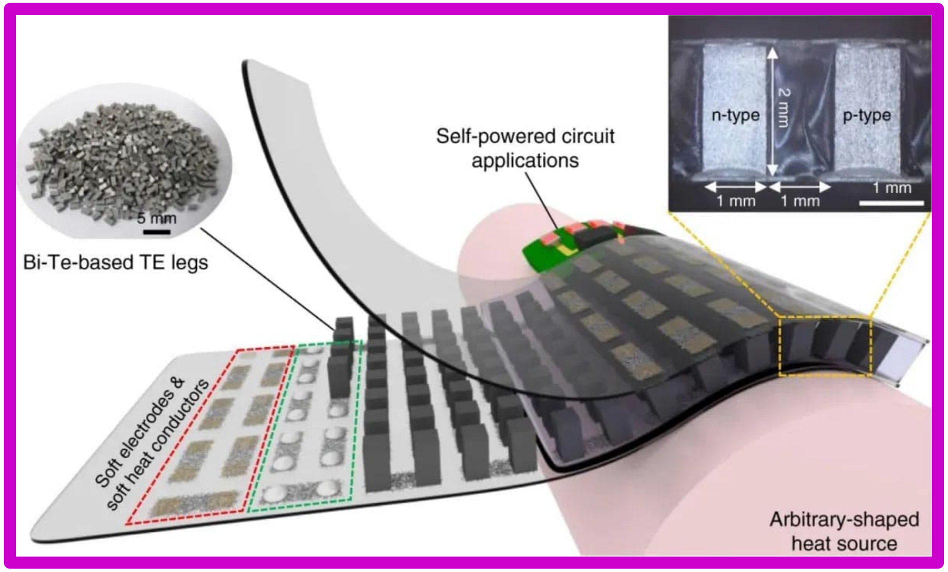
FLEXIBLE / WEARABLE THERMOELECTRICS

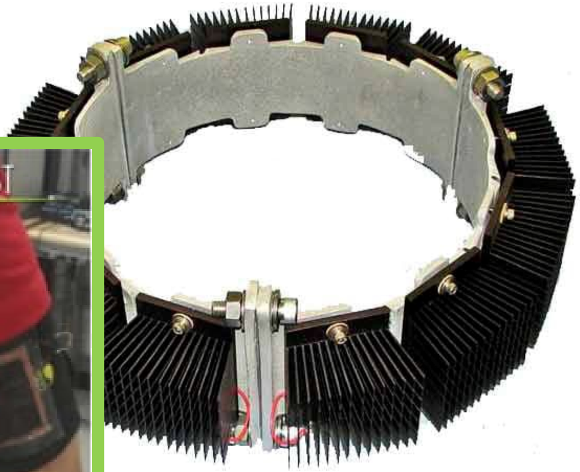
- **Flexibility needed:**

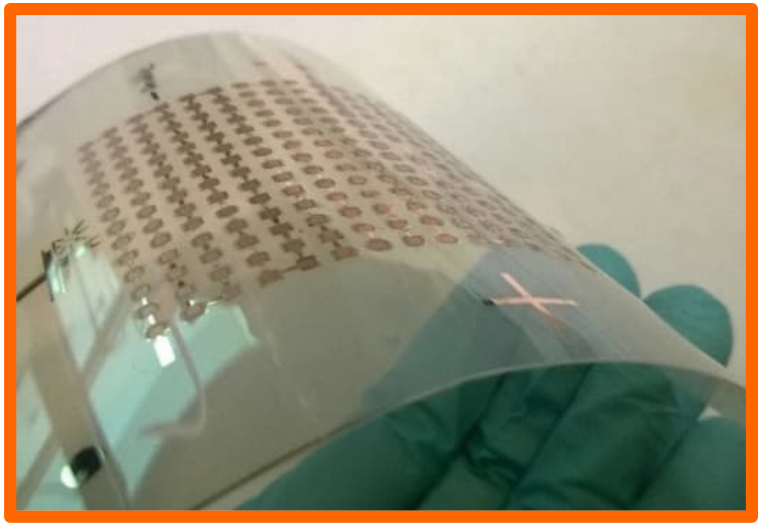
  (i) better fit with round heat sources

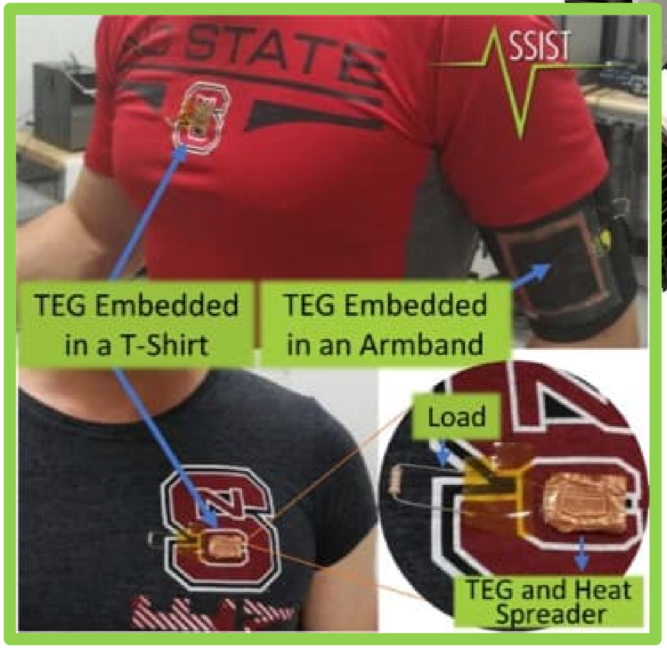
  (ii) wearable devices

- **Micro-energy-harvesters in the power range of 10-1000 µW (e.g. body-implanted pacemakers, sensors)**





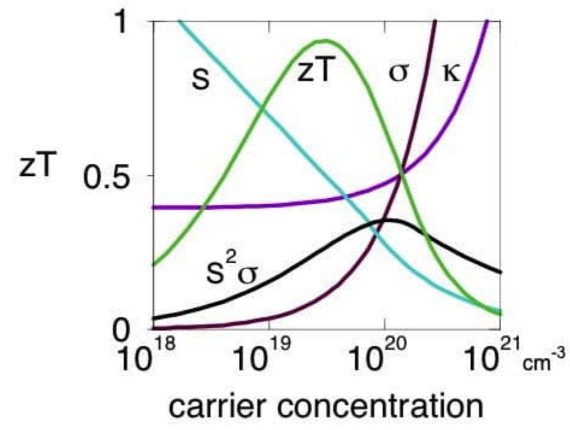


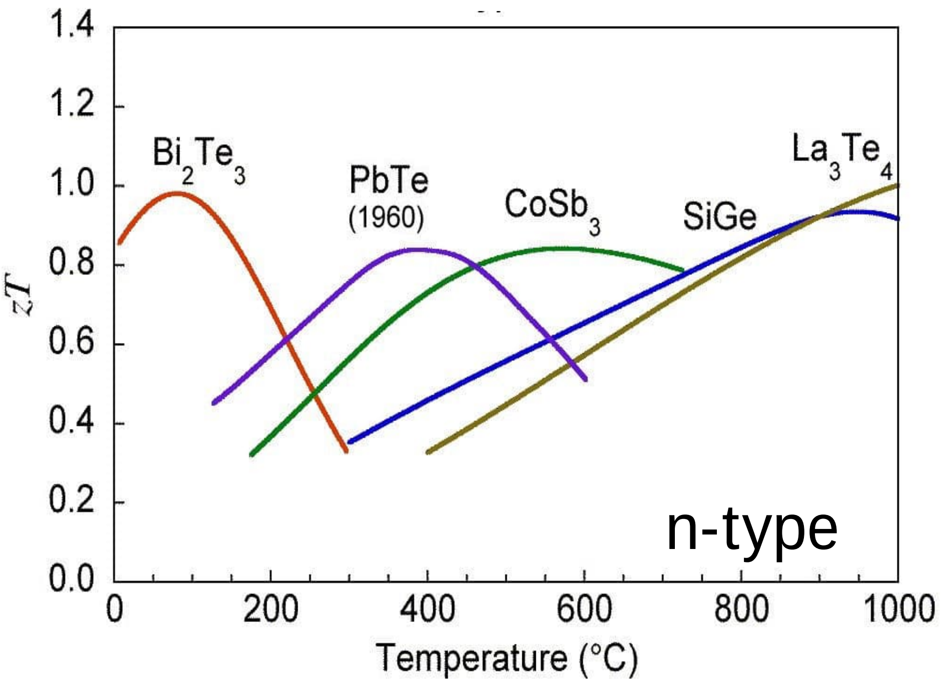


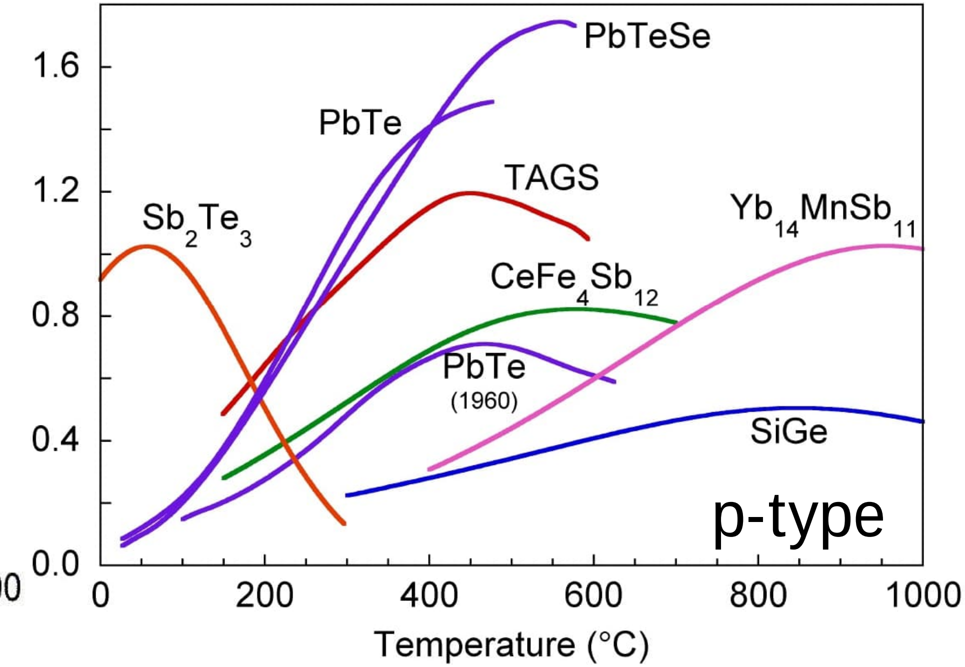
THERMOELECTRIC MATERIALS

$$ZT = \frac{S^2\sigma}{\kappa}T, \;\; \kappa = \kappa_e + \kappa_L$$

- Heat-to-electricity conversion efficiency: **Figure-of-Merit (ZT)**
- ZT increases by increasing electrical conductivity (σ) & decreasing thermal conductivity (κ) → **DIFFICULTY**
- Two terms for κ: electronic (κ_e) and lattice (κ_L)
- Currently: strong efforts to decease





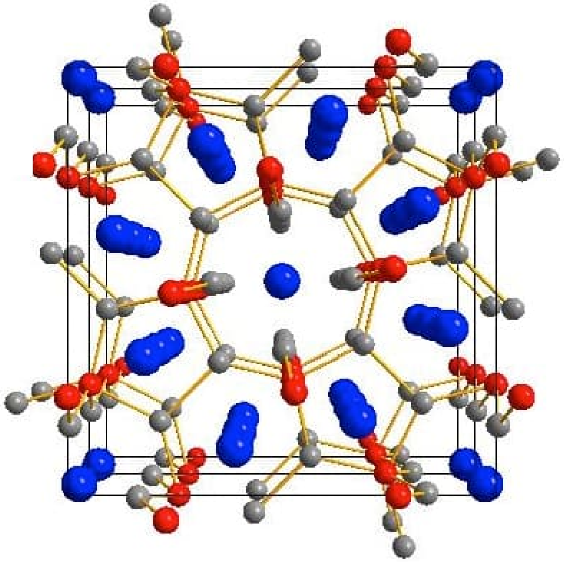


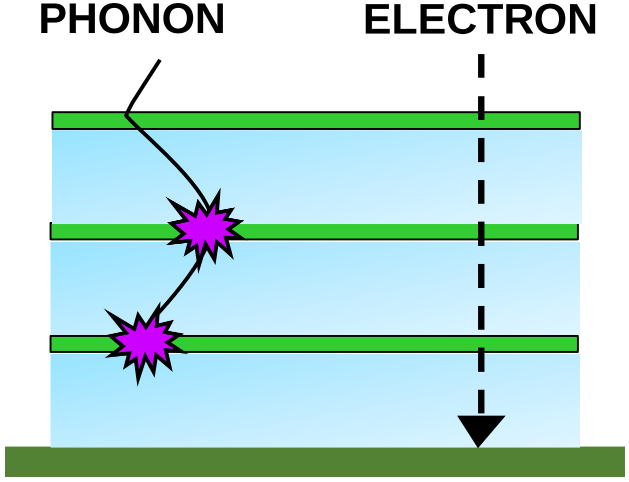
http://thermoelectrics.matsci.northwestern.edu/graphics/thermoelectrics/n-zT.jpg

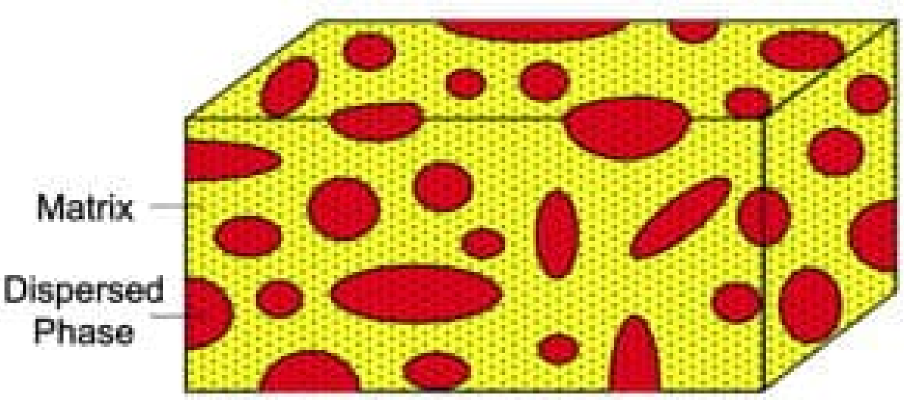
$$ZT = \frac{S^2\sigma}{\kappa}T, \ \kappa = \kappa_e + \kappa_L$$

HOW TO DECREASE LATTICE THERMAL CONDUCTIVITY (ref. Diamond)

- **Heavy elements (often the rarest !)**
- **Complex crystal structure**
- **Defects / Nanostructures / Superlattices**





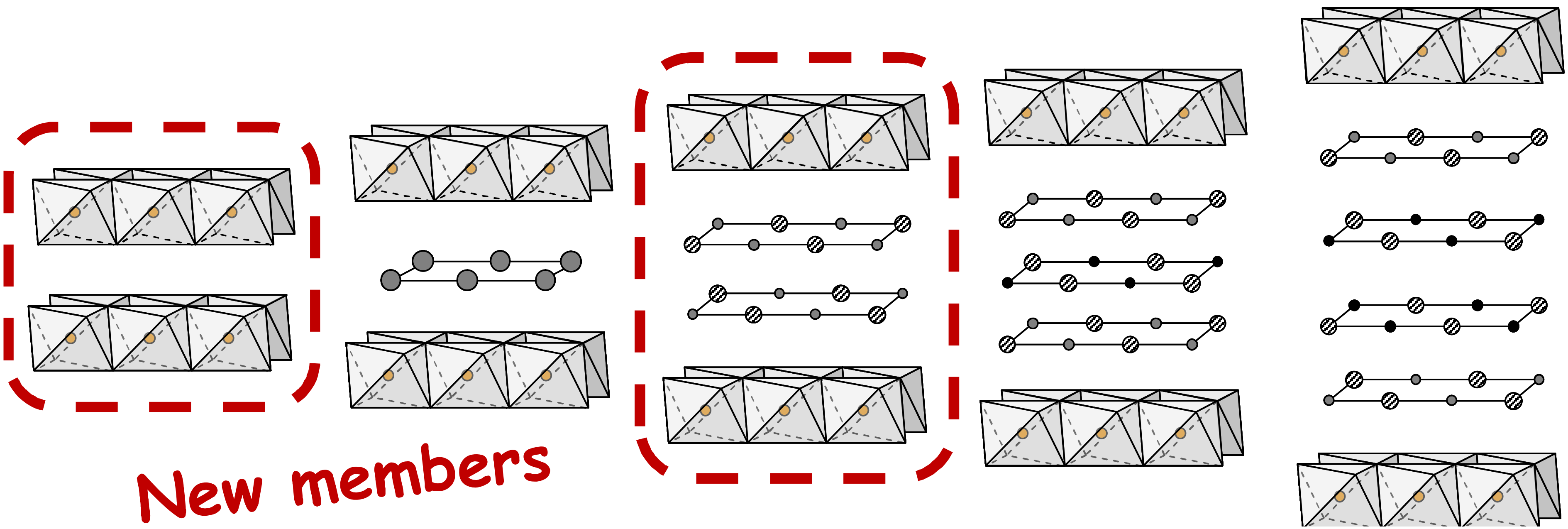


THERMOELECTRICS SUMMARY

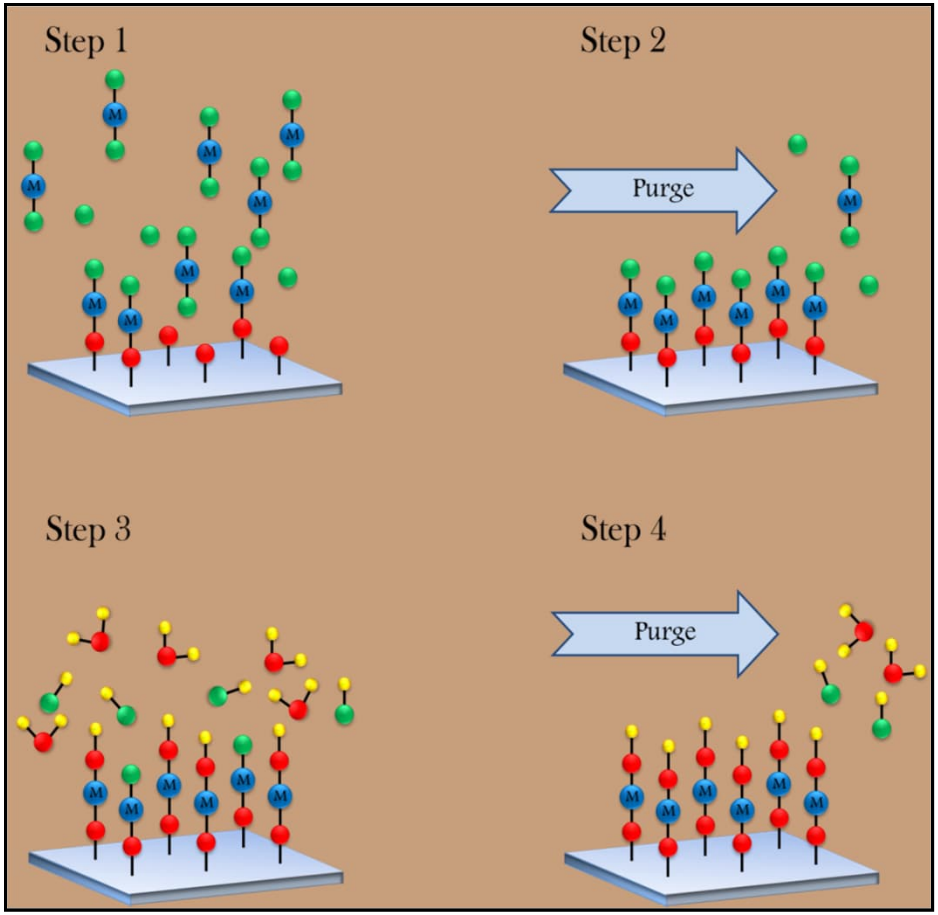
- Over 65% of all energy produced is lost as waste heat
- Thermoelectric power generators, which are semiconductor-based electronic devices, can turn this heat into electricity via the Seebeck effect
- These devices are simple to construct (just two different solid materials), easy to scale-up & long-term reliable
- However, we need MATERIALS that are good electrical conductors but have extremely low thermal conductivity → This is a very tricky combination to achieve (but a materials chemists dream research topic)
- Moreover, the devices should stand heat sources as hot as 500 °C
- Also, mechanical flexibility desired
- True commercialization of thermoelectric technology has been seriously limited by the low ZT values and the presence of toxic elements (e.g. Pb) or rare elements (e.g. Te)
- Minimum criterion: $ZT > 1$
  So far reached: $ZT \approx 2$
  Dream-of-the-Dream: $ZT > 4$

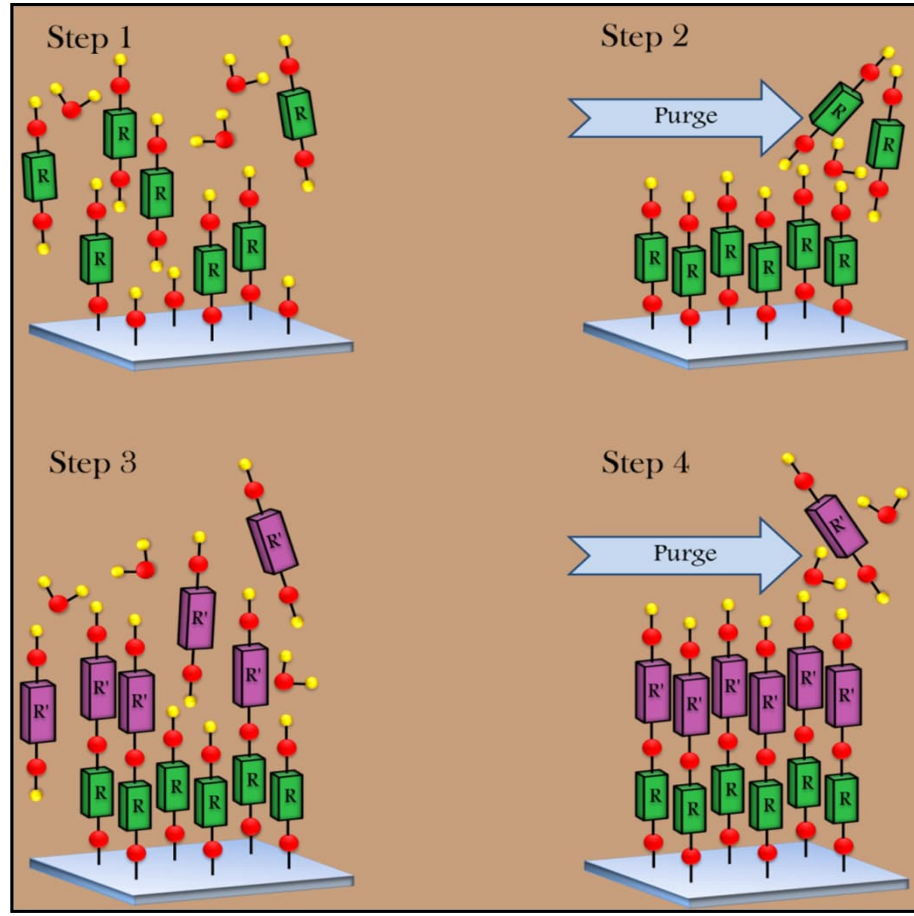
Thermoelectric Misfit Oxides: $[(MO)_m(AO)_k]_qCoO_2$

- **First oxide thermoelectric material: Na_xCoO_2** (similar to Li_xCoO_2 battery cathode)
- **Thermoelectric $[CoCa_2O_3]_qCoO_2$ and $[Bi_2Sr_2O_4]_qCoO_2$ CoO_2 discovered later**
- **CoO_2 layers with mixed-valent cobalt → electrical conductivity**
- **”Misfitting” intermediate (metal or metal oxide) layers → Low thermal cond.**



CoO_2	Na_xCoO_2	$[Sr_2O_2]_{0.5}CoO_2$	$[CoCa_2O_3]_qCoO_2$	$[Bi_2Sr_2O_4]_qCoO_2$
k=0, m=0	**k=1, m=0**	**k=2, m=0**	**k=2, m=1**	**k=2, m=2**





ALD (Atomic Layer Deposition)

MLD (Molecular Layer Deposition)

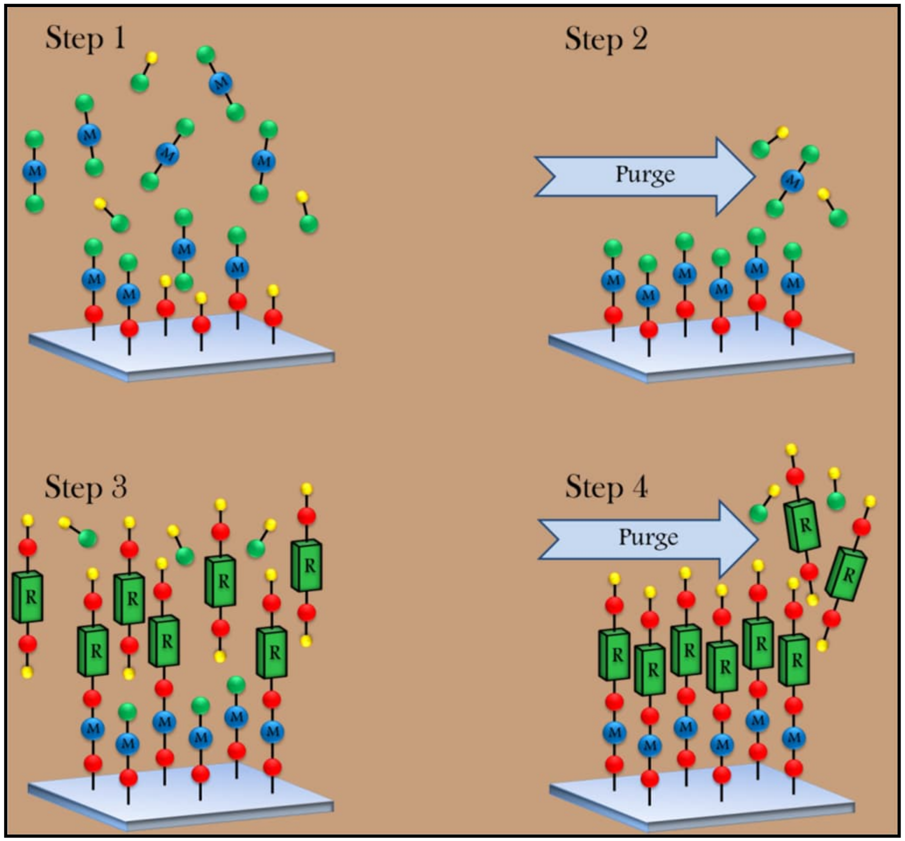
High-quality INORGANIC thin films with atomic level control for microelectronics and beyond

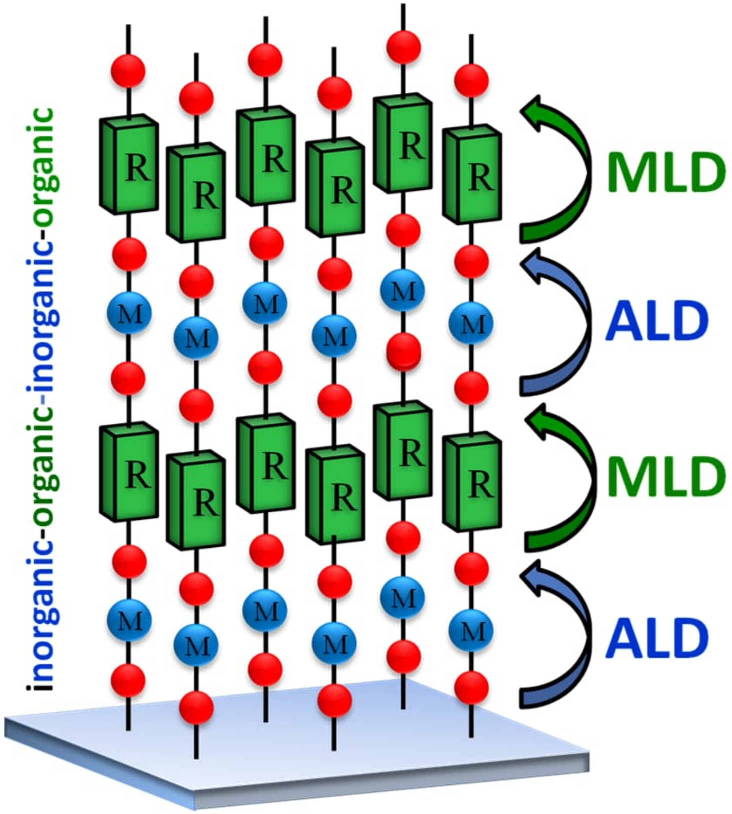
ORGANICS !

T. Yoshimura, S. Tatsuura & W. Sotoyama,
Polymer films formed with monolayer growth steps by molecular layer deposition,
Appl. Phys. Lett. 59, 482 (1991).

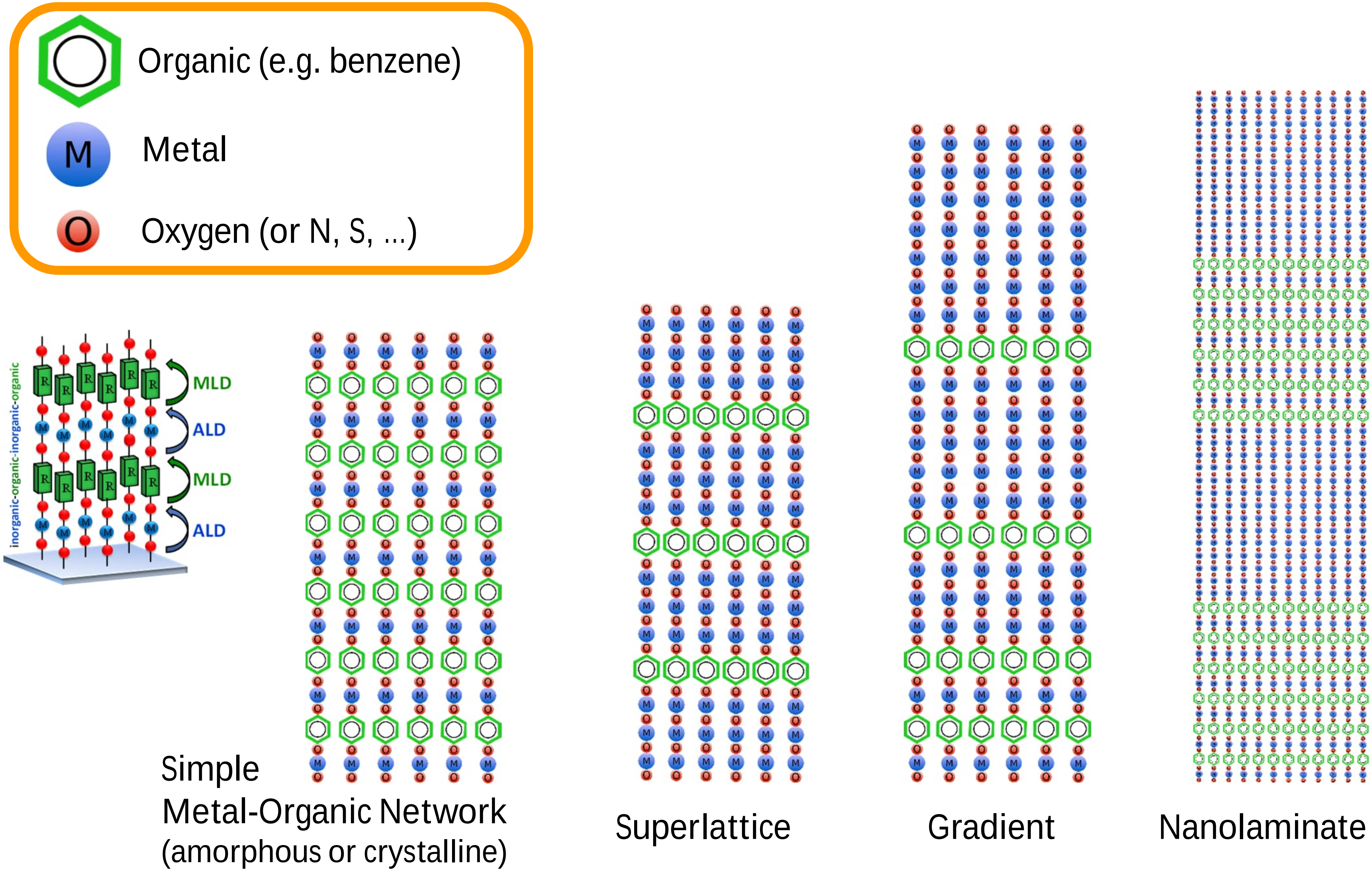
Inorganic-Organic (Metal-Organic) Thin Films

by Combined ALD/MLD



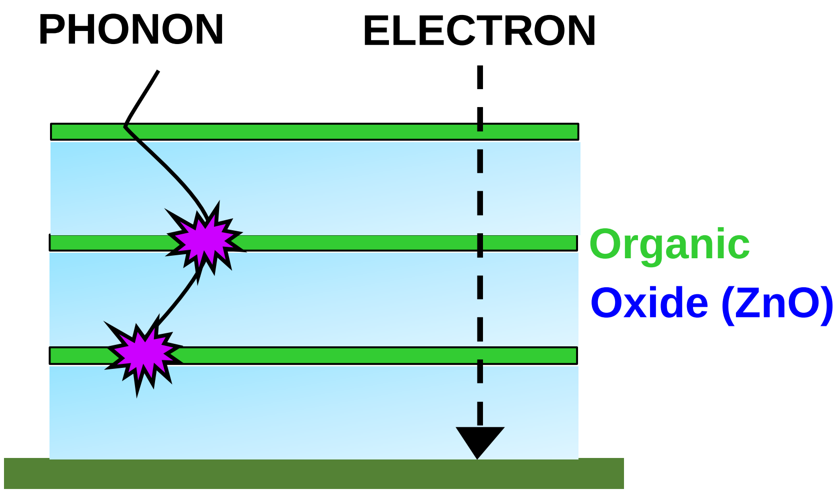


NOVEL FLEXIBLE MULTIFUNCTIONAL HYBRID MATERIALS



DIFFERENT LAYER SEQUENCES BY DESIGN

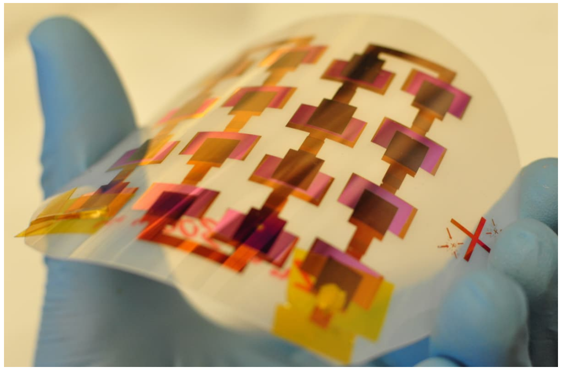
TEXTILE THERMOELECTRICS: ALD/MLD ZnO:organic



Organic layers in ZnO:org superlattices reduce thermal conductivity (into 1 / 50) without lowering electrical conductivity

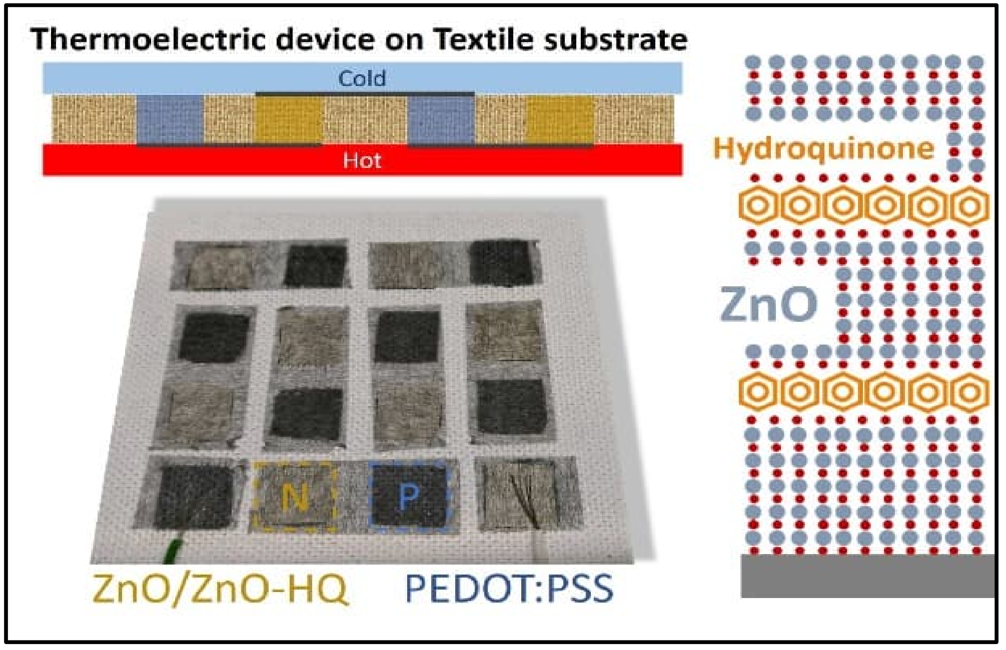
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, *J. Mater. Chem. A* 2, 12150 (2014).

Flexible TE "device" on plastics

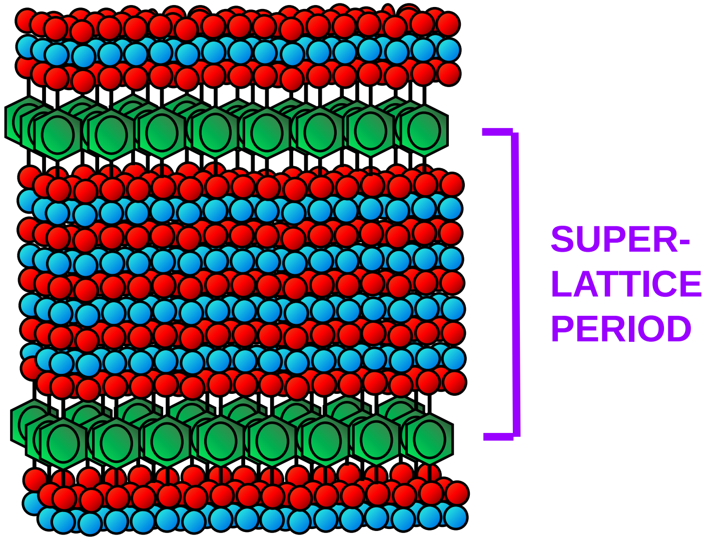


Textile-integrated thermoelectrics

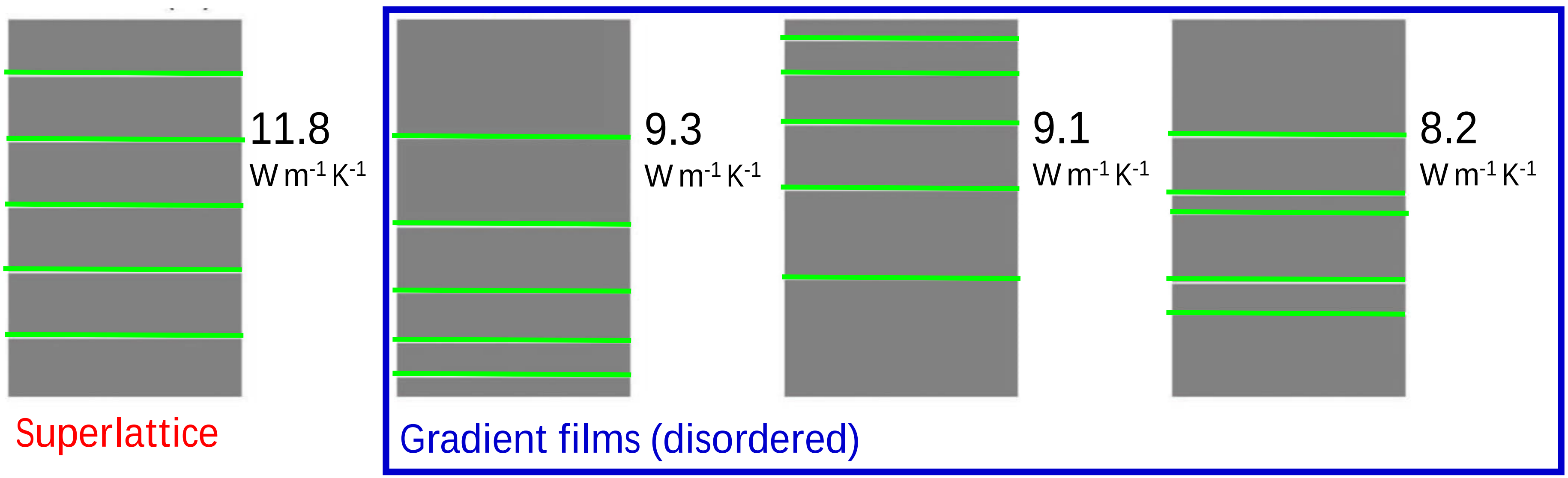
ZnO:org film grows in a conformal manner on textile fibers so that the entire textile piece becomes an active part of the device



G. Marin, R. Funahashi & M. Karppinen, *Adv. Eng. Mater.* 22, 2000535 (2020).



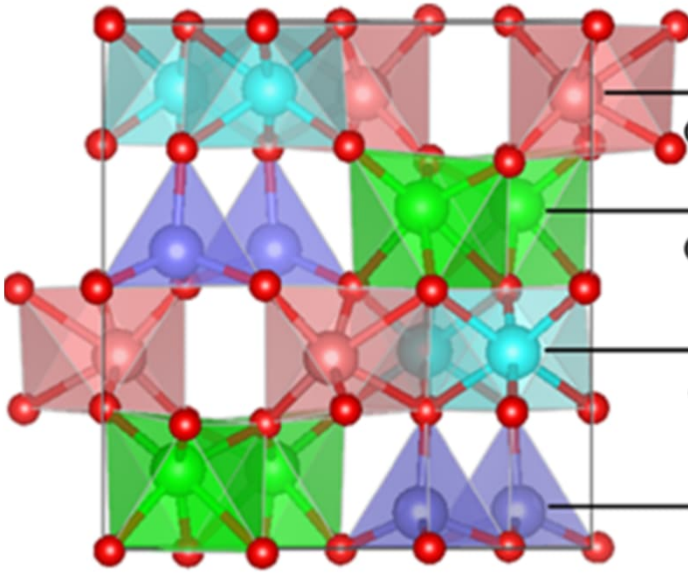
Thermal conductivity [W m^{-1} K^{-1}]	
ZnO (~100 nm)	~43
5 org. layers	11.8
6 org. layers	7.1
12 org. layers	4.1
20 org. layers	3.1
40 org. layers	1.3
80 org. layers	0.7



F. Krahl, A. Giri, J.A. Tomko, T. Tynell, P.E. Hopkins & M. Karppinen, Thermal conductivity reduction at inorganic-organic interfaces: from regular superlattices to irregular gradient layer sequences *Adv. Mater. Interfaces* 5, 1701692 (2018).

ε-Fe_2O_3

- Simple & critical-raw-material-free
- Rarest of the Fe_2O_3 polymorfs
- RT ferrimagnet ($T_C \approx 490$ K)
- Colossal coercivity
- Magnetoelectric



1934: First observed by Forestier and Guiot-Guillain

1963: Named by Schrader and Buttner

2004: Synthesis of pure ε-Fe_2O_3 with giant coercive field values (up to 2 T)
- J. Jin, S.I. Ohkoshi & K. Hashimoto, Adv. Mater. 16, 48 (2004)

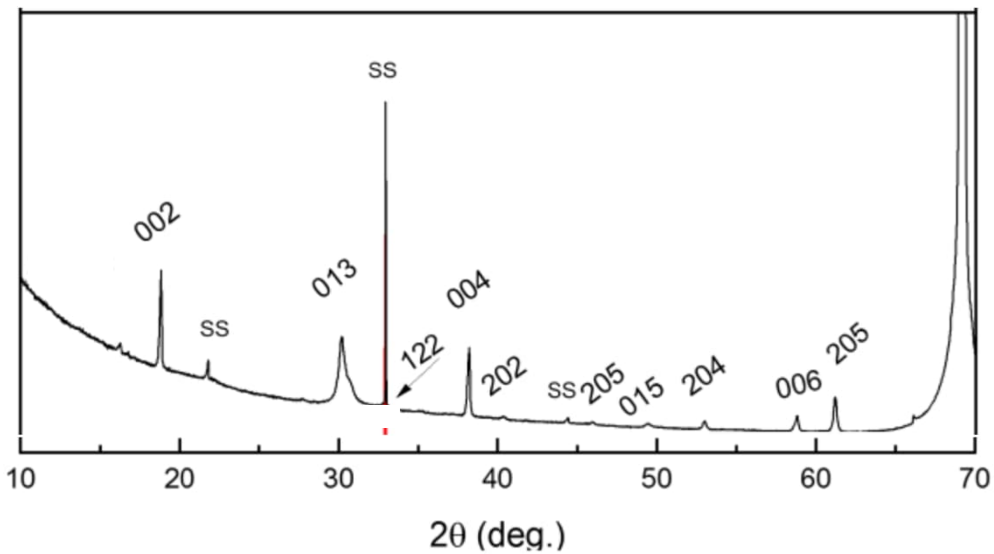
State-of-the-art: Synthesized in nano-scale/trace amounts only
- J. Tuček, R. Zbořil, A. Namai & S.I. Ohkoshi, Chem. Mater. 22, 6483 (2010)

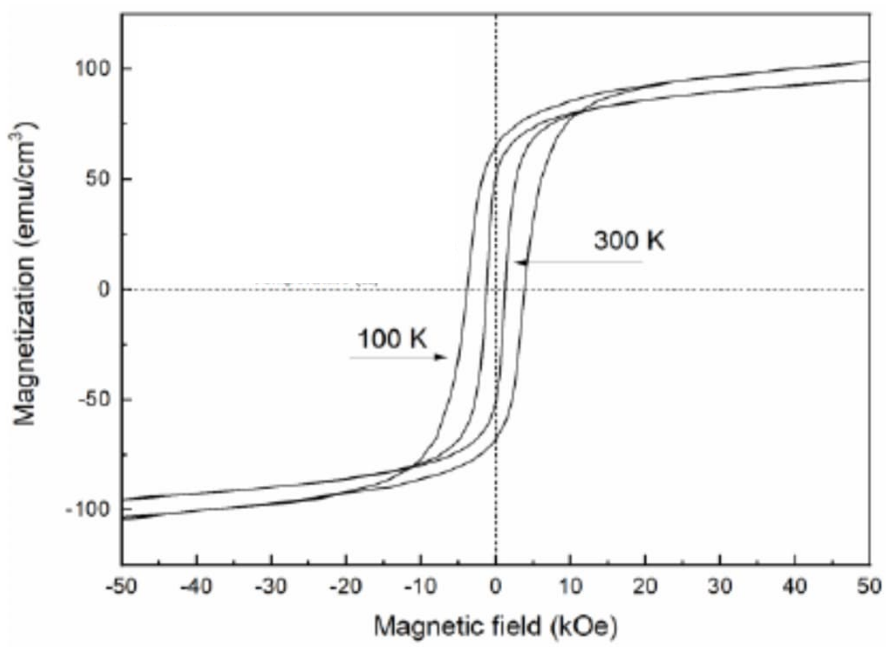
2017: ALD of ε-Fe_2O_3 thin films
- A. Tanskanen, O. Mustonen & M. Karppinen, APL Mater. 5, 056104 (2017)

Facile ALD process for stable **ε**-Fe_2O_3 thin films

- Just "most common" precursors: $FeCl_3$ & H_2O
- Deposition temperature: 280 ºC
- Substrate: silicon, flexible glass, Kapton, polyimide, etc.

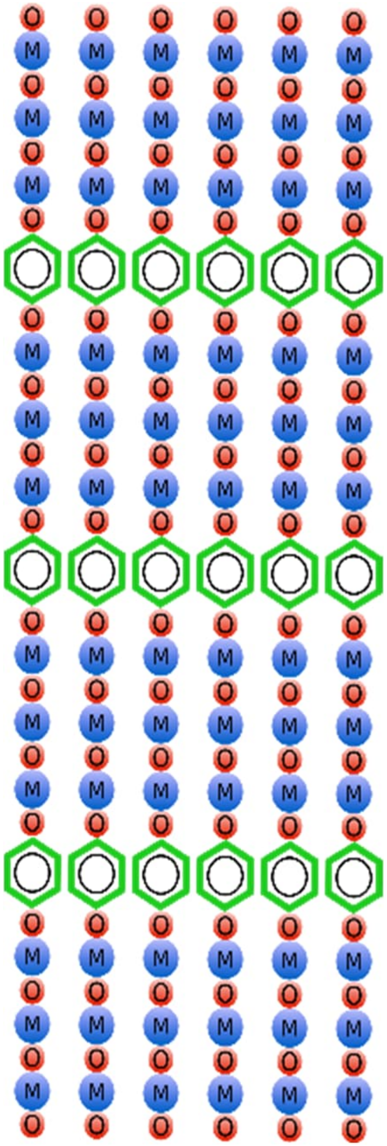
ALD: large-**area homogeneity & conformality over porous templates → "MASS production"**

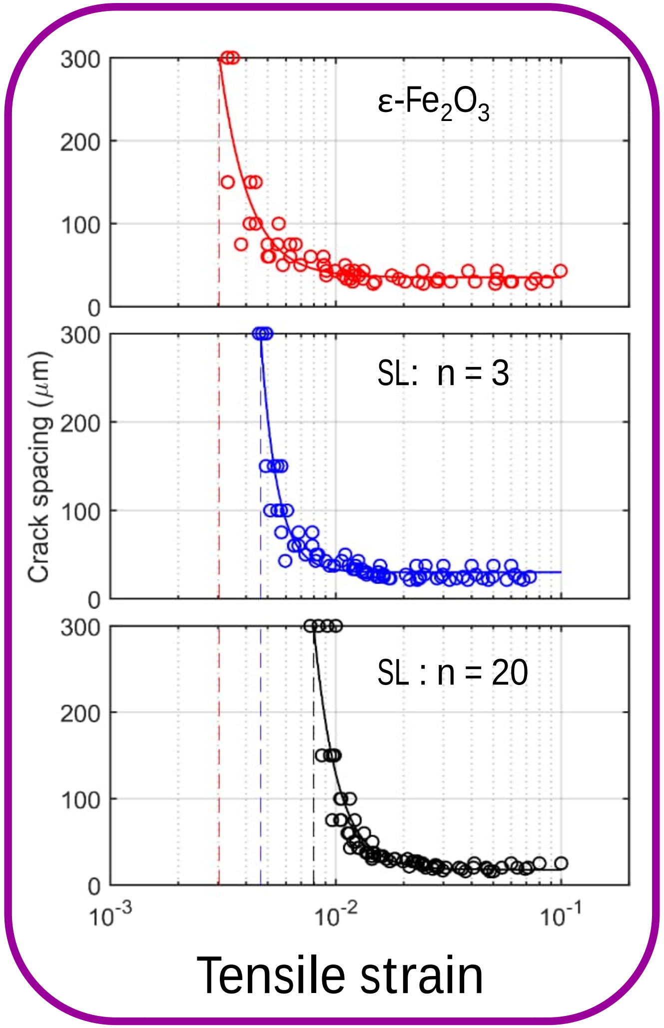




A. Tanskanen, O. Mustonen & M. Karppinen, Simple ALD process for ε-Fe_2O_3 thin films, *APL Materials* 5, 056104 (2017).

MECHANICALLY FLEXIBLE: **ε**-Fe_2O_3:org

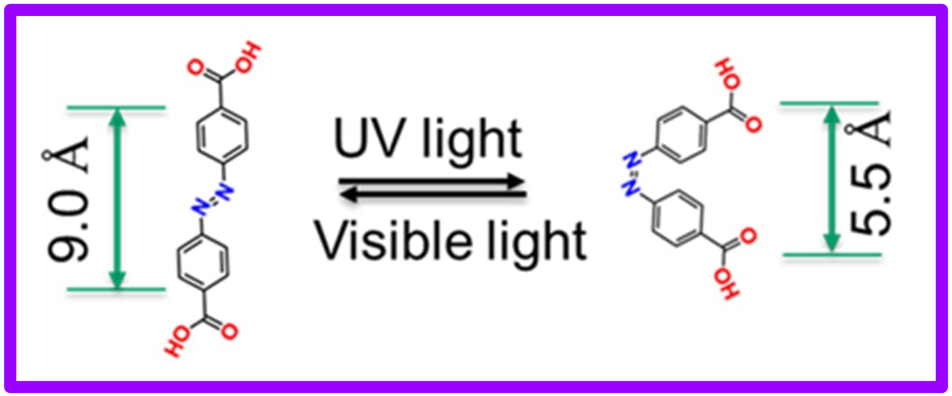


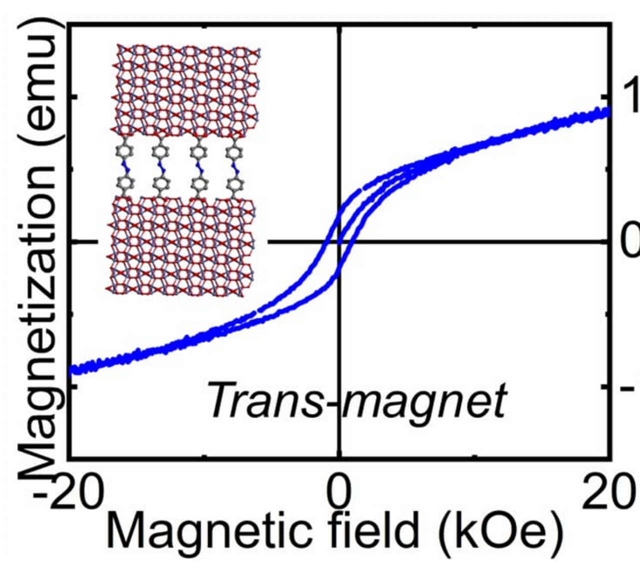


A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

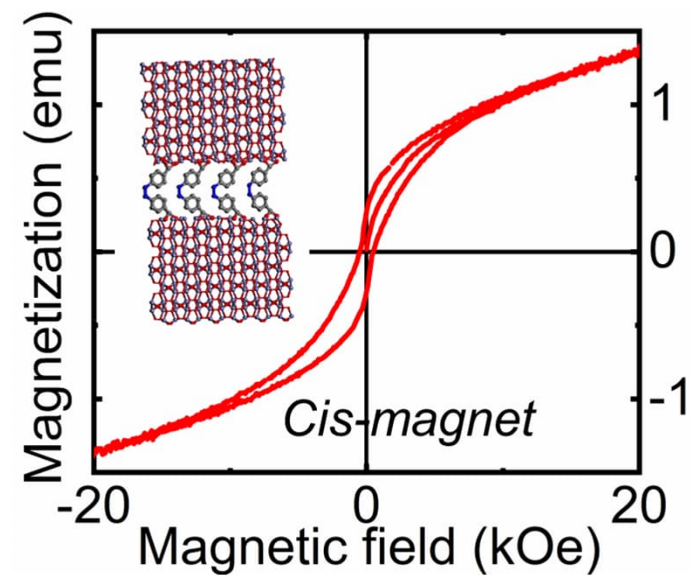
PHOTOSWITCHABLE: **ε**-Fe_2O_3:azobenzene

Trans Cis





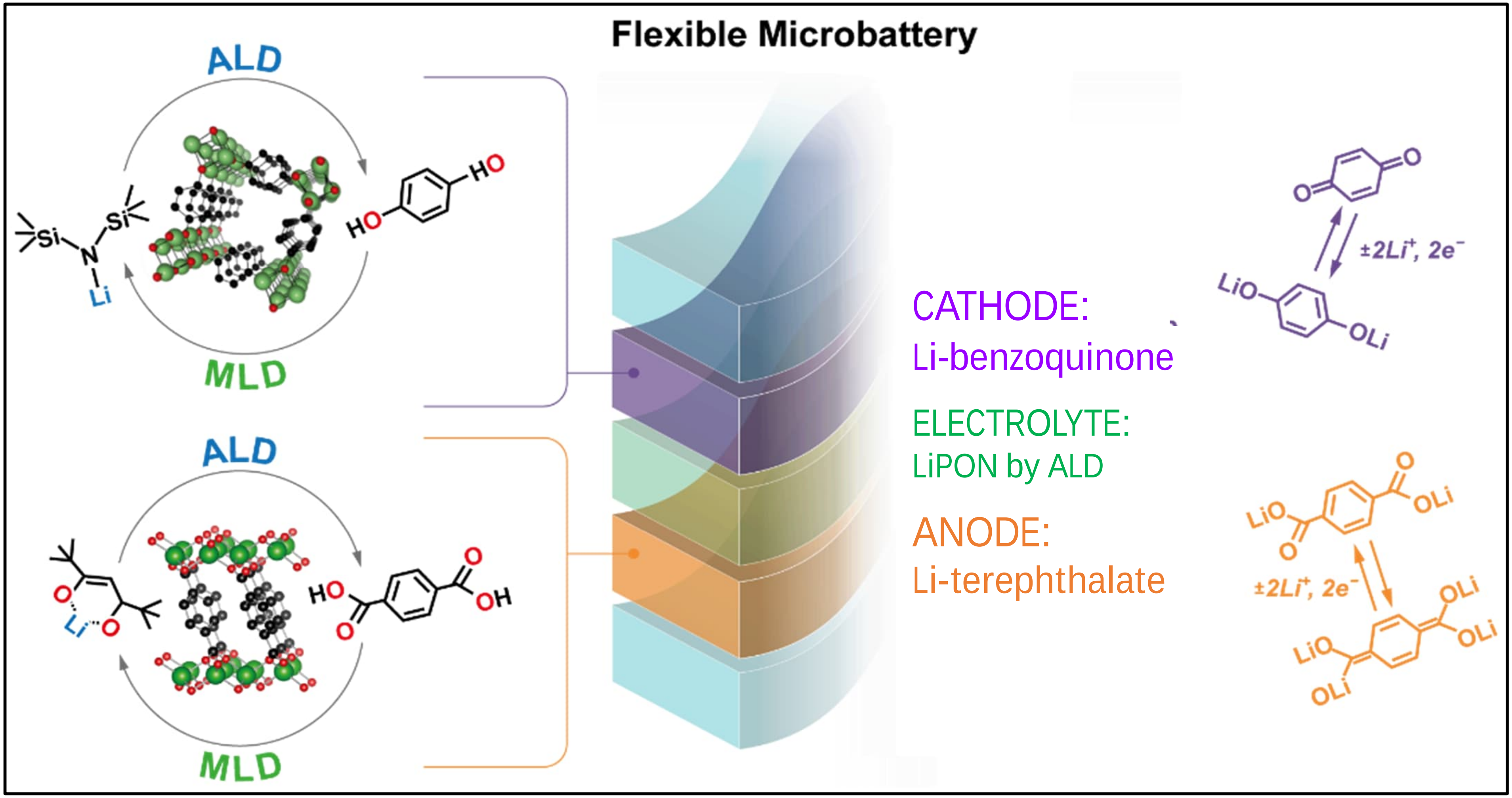
UV (365 nm)



Magnetization & Coercivity controlled by UV/vis exposures

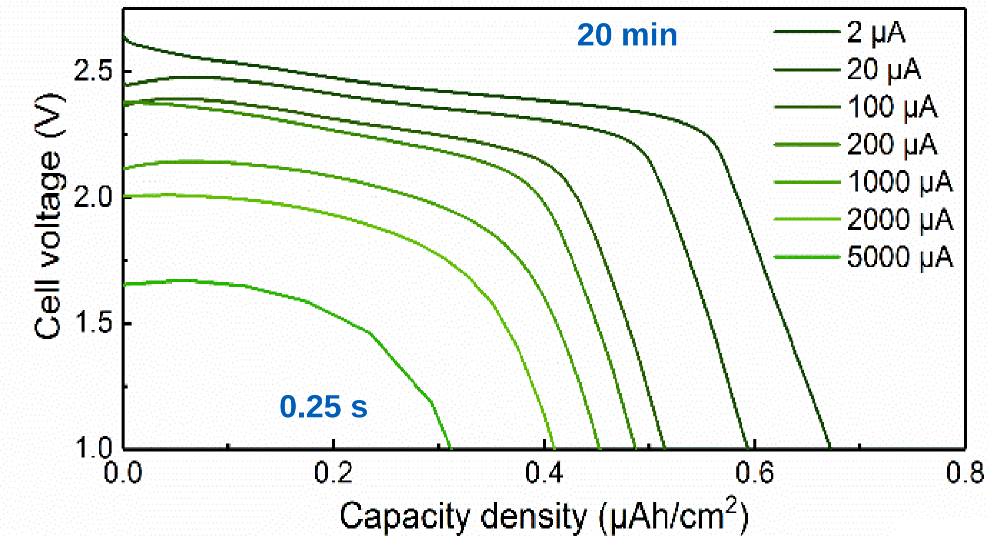
A. Philip, Y. Zhou, G.C. Tewari, S. van Dijken & M. Karppinen, Optically controlled large-coercivity room-temperature thin-film magnets, *J. Mater. Chem. C* **10**, 294 (2022).

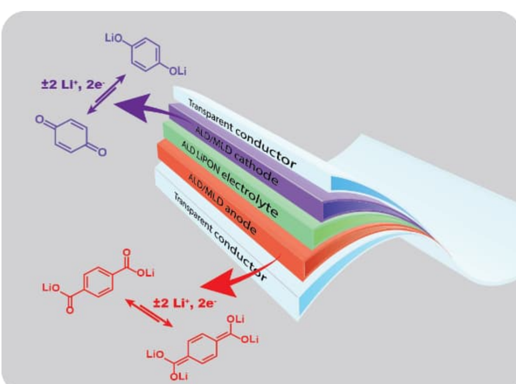
Lithium-organic microbattery

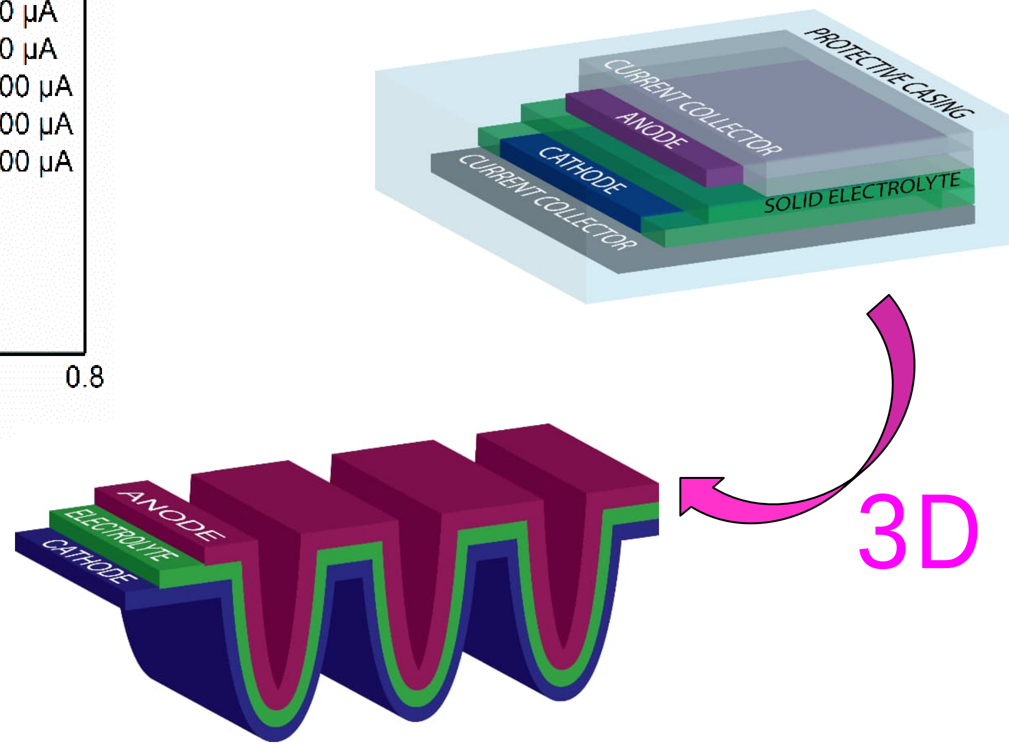


M. Nisula & M. Karppinen, In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery, *Journal of Materials Chemistry A* 6, 7027 (2018).

- **Charging/discharging: extremely fast**
- **Power density: ~500 W/cm^3**
- **Energy density: ~100 mWh/cm^3**



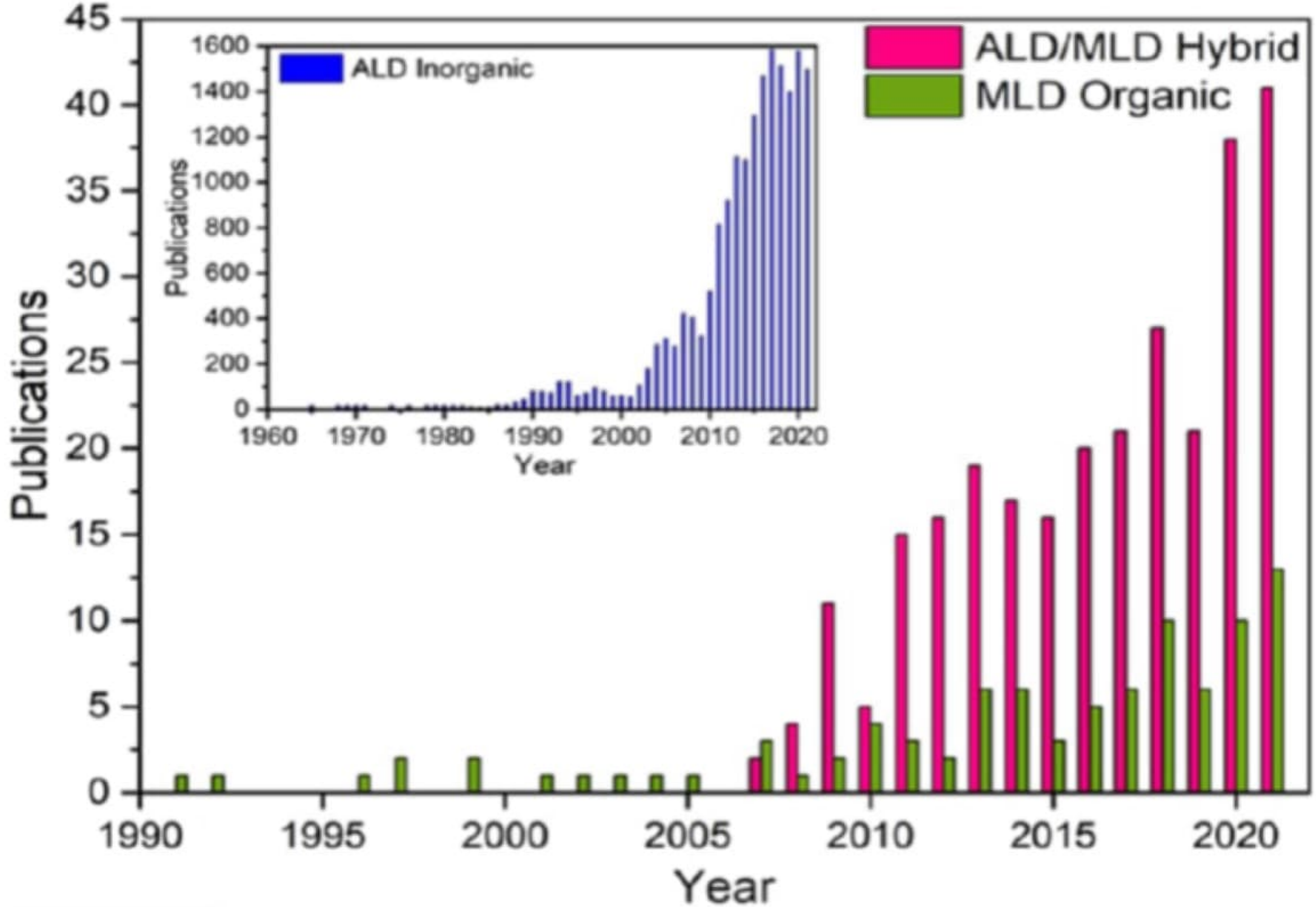




HIGH POWER & ENERGY DENSITY

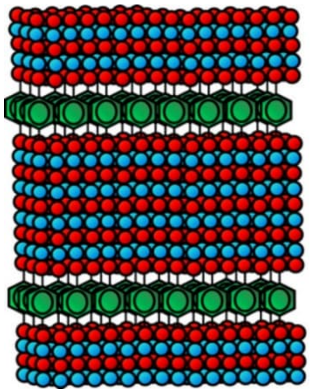
- M. Nisula, Y. Shindo, H. Koga & M. Karppinen, *Chem. Mater.* 27, 6987 (2015).
- M. Nisula & M. Karppinen, *Nano Lett.* 16, 1276 (2016).
- M. Nisula & M. Karppinen, *J. Mater. Chem. A* 6, 7027 (2018).
- J. Heiska, M. Nisula & M. Karppinen, *J. Mater. Chem. A* 7, 18735 (2019).

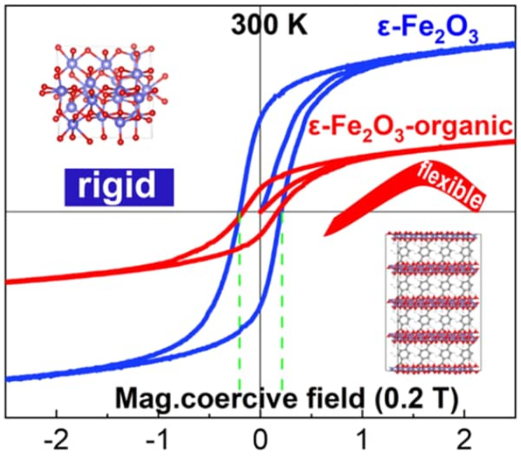
Annually published papers:
MLD & ALD/MLD

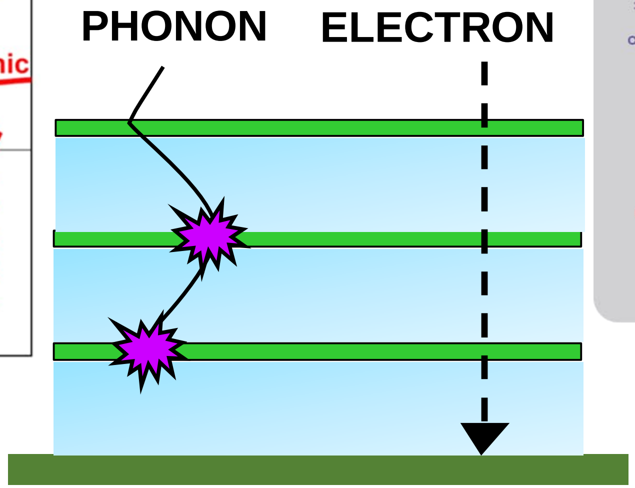


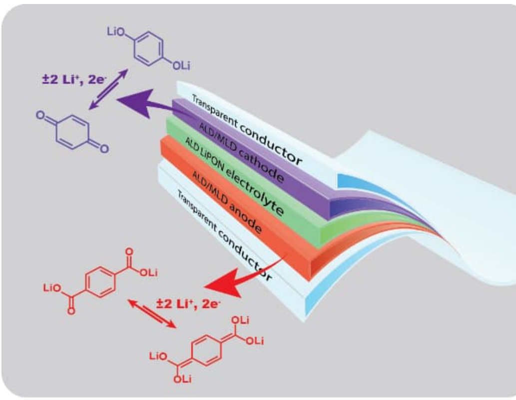
Yoshimura, Tatsuura & Sotoyama, *Appl. Phys. Lett.* **1991,** *59,* 482.
Yoshimura, Tatsuura, Sotoyama, Matsuura & Hayano, *Appl. Phys. Lett.* **1992,** *60,* 268.
Lee, Ryu, Choi, Lee, Im & Sung, *J. Am. Chem. Soc.* **2007,** *129,* 16034.
Smirnov, Zemtsova, Belikov, Zheldakov, Morozov, Polyachonok & Aleskovskii, *Dokl. Phys. Chem.* **2007,** *413,* 95.
Nilsen, Klepper, Nielsen & Fjellvåg, *ECS Trans.* **2008,** *16,* 3.
Dameron, Seghete, Burton, Davidson, Cavanagh, Bertrand & George, *Chem. Mater.* **2008,** *20,* 3315.

J. Multia & M. Karppinen, Atomic/molecular layer deposition for designer's functional metal-organic materials, ***Applied Materials Interfaces*** 9, 202200210 (**2022**).

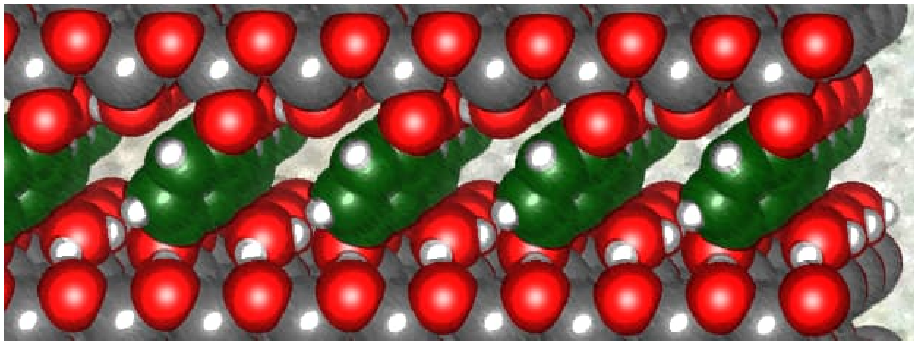


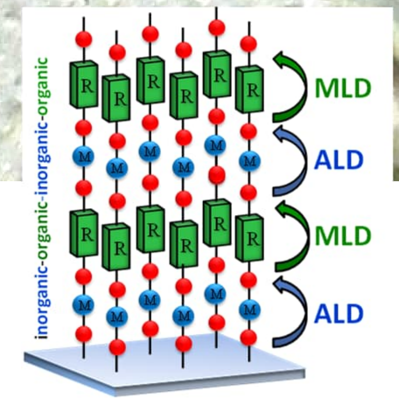






- **ALD/MLD can yield various new types of hybrid materials: new MOFs & layer-engineered superlattice and gradient materials**
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties have been discovered and much more expected !!!**





LECTURE SCHEDULE

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu & Magnetism
10.	Fri	29.09.	Cu & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2