LECTURE SCHEDULE

		Date	Topic
1.	Wed	07.09.	Course Introduction & Short Review of the Elements
2.	Fri	09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon	12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri	16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon	19.09.	Transition Metals: General Aspects & Pigments
6.	Wed	21.09.	Redox Chemistry
7.	Fri	23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon	26.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
9.	Wed	28.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
10.	Fri	30.09.	Mn, Cu, Ru
11.	Mon	03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Fri	07.10.	Lanthanoids + Actinoids & Luminescence
13.	Mon	10.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
14.	Wed	12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri	14.10.	Inorganic Materials Chemistry Research

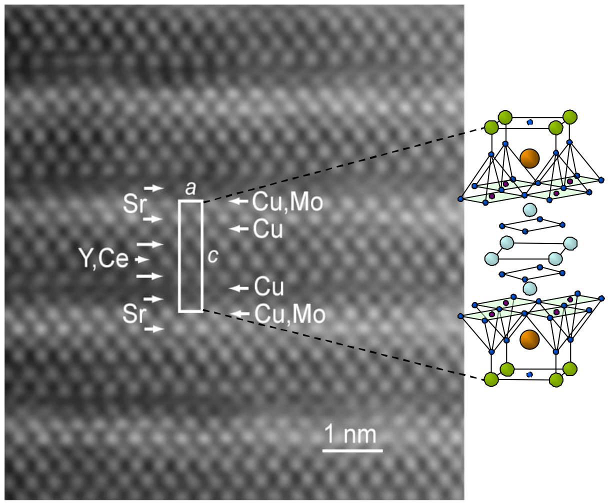
EXAM: Tuesday Oct. 18, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Fri 16.09.	Zn:	Rautakorpi, Stenbrink & Hyvärinen
Mon 26.09.	Nb:	Souza, Rahikka & Tong
Wed 28.09.	Mo:	Alimbekova & Tran (Nhi)
	Ti:	Mäki & Israr
Fri 30.09.	Mn:	Tao & Song (Zonghang)
	Cu:	Marechal, Weppe & Ishtiaq
	Ru:	Järvinen & Verkama
Fri 07.10.	Eu:	Bardiau, Wolfsberger & Klingerhöfer
	Nd:	Helminen, Olsio & Keskimaula
Mon 10.10.	U:	Airas & Holopainen
Wed 12.10.	In:	Antila & Wallius
	Te:	Peussa & Heylen
Fri 14.10.	Co:	Song (Yutong) & Lone

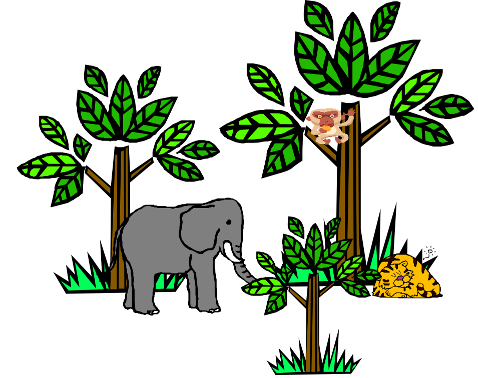
QUESTIONS: Lecture 15

Explain shortly why ZnO:organic superlattice thin films are better thermoelectric materials than ZnO thin films, especially for future wearable applications., and why the ALD/MLD technique is an highly advantageous technique for the fabrication of these films.



INORGANC CHEMISTRY

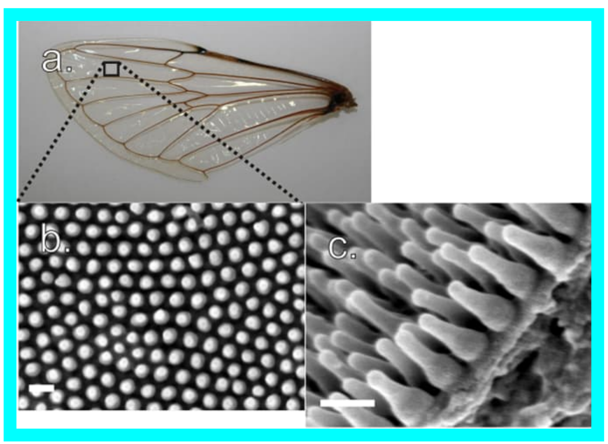
Aalto University
Department of Chemistry & Materials Science



Sustainable energy materials

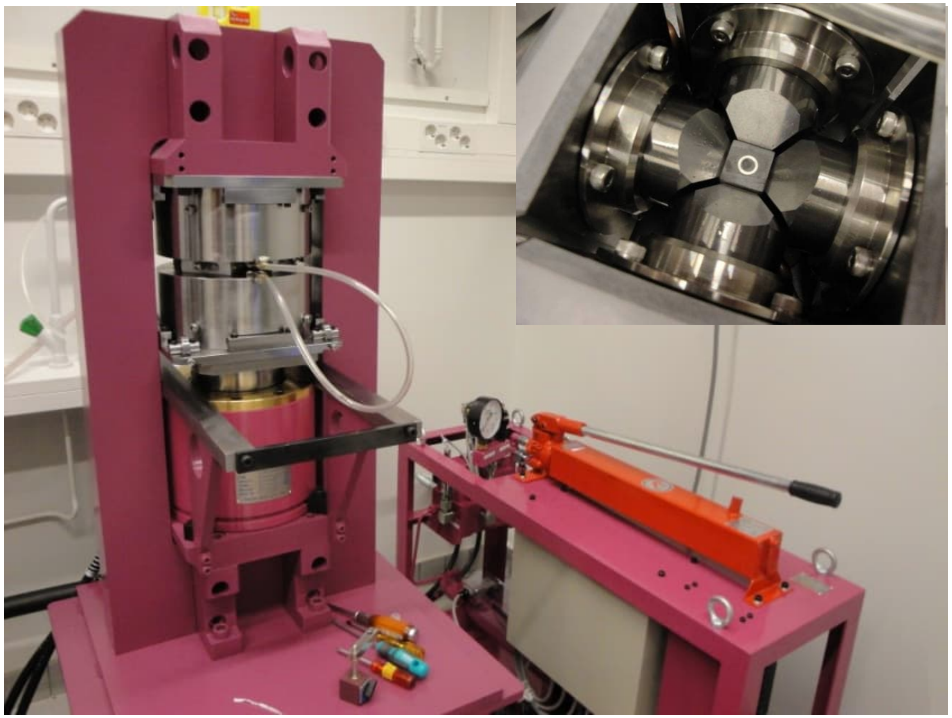
- **Novel Functional (bulk) Oxide Materials**
  - high-T_c superconductors
  - thermoelectric materials
  - exotic magnetic materials
  - ionic conductors (fuel cell, battery, oxygen storage)

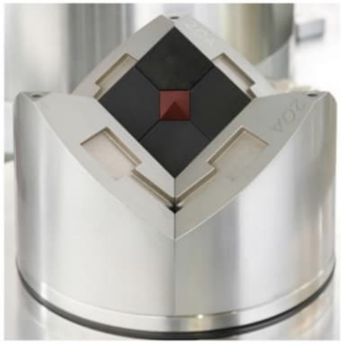
- **ALD (Atomic Layer Deposition) Thin Films**
  - complex (ternary & quaternary) oxides
  - oxide coatings on exciting surfaces (polymers, biomaterials, textiles, steel, etc.)
  - inorganic/organic hybrid materials



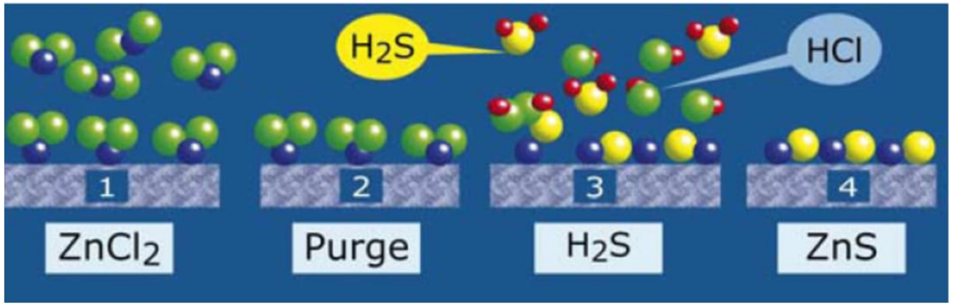
KEY CONCEPTS:
Layer-engineering & Oxygen-engineering & Nanostructuring

Ultra High-Pressure (HP) synthesis

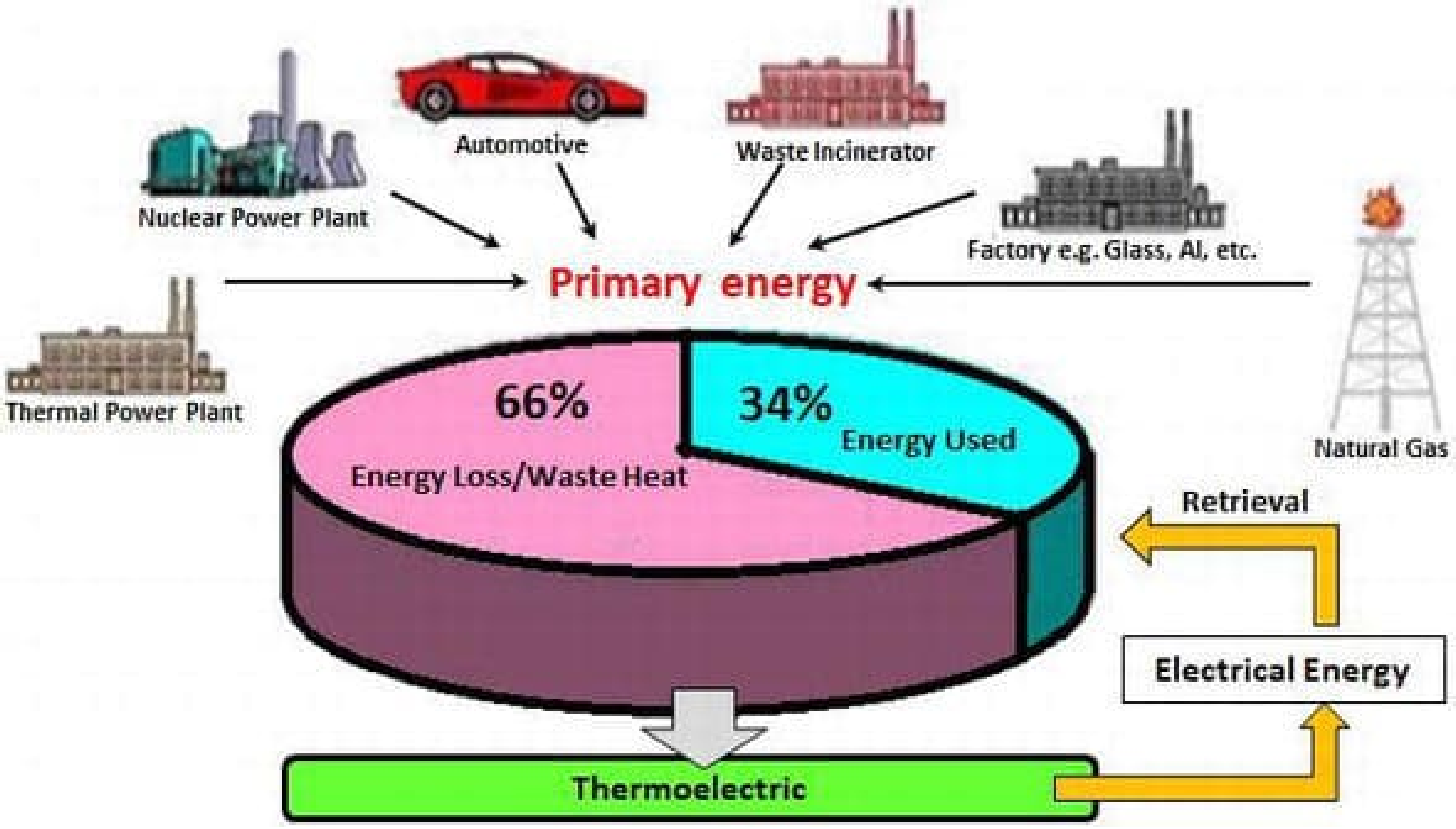


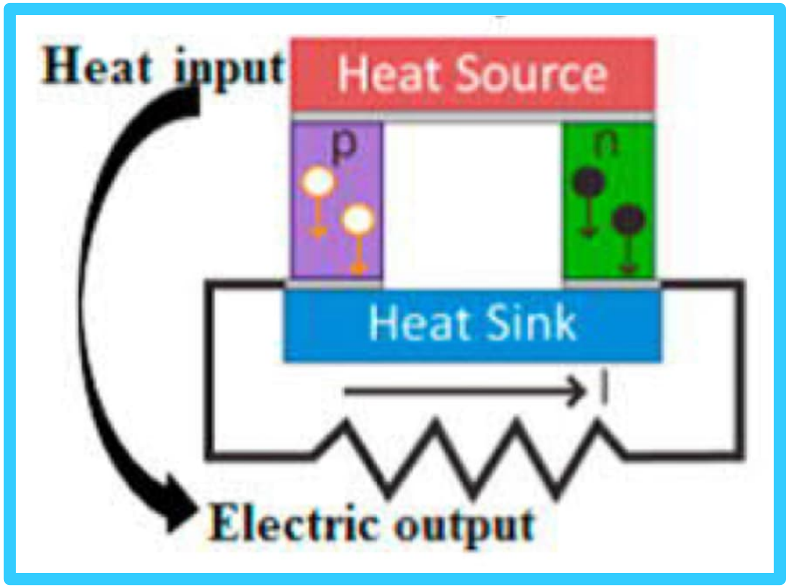


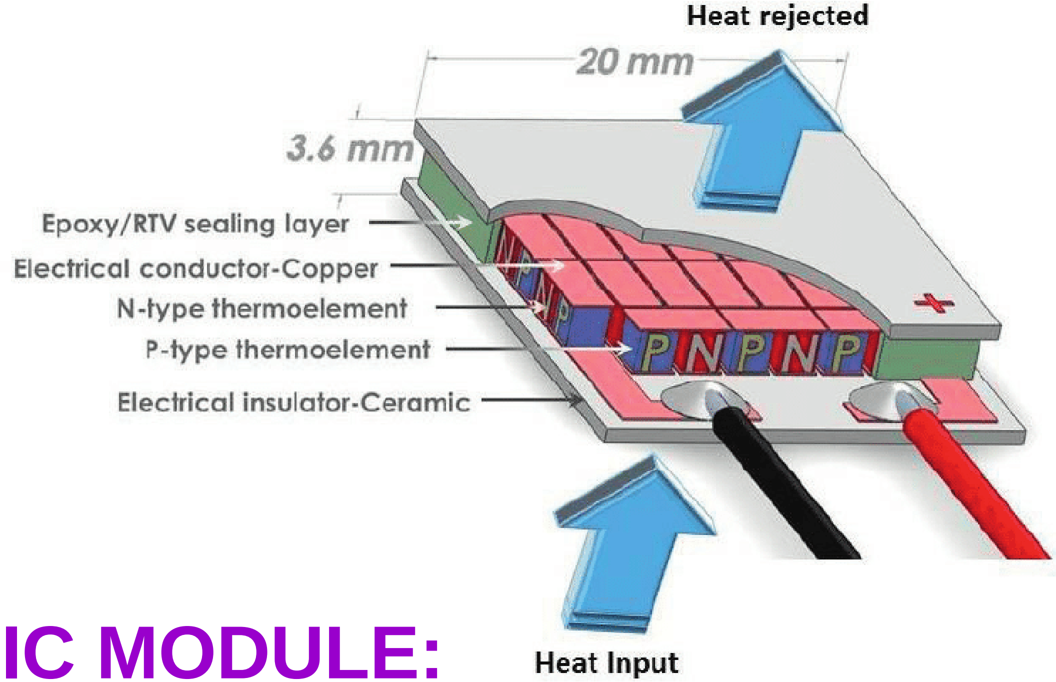
Atomic Layer Deposition (ALD) thin-film technology



SYNTHESIS TECHNIQUES

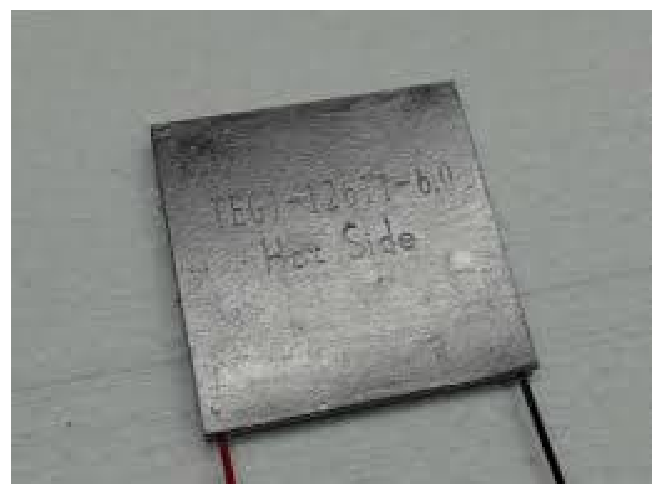

Nuclear Power Plant
Automotive
Waste Incinerator
Factory e.g. Glass, Al, etc.
Thermal Power Plant
Primary energy
Natural Gas
66%
Energy Loss/Waste Heat
34%
Energy Used
Retrieval
Electrical Energy
Thermoelectric





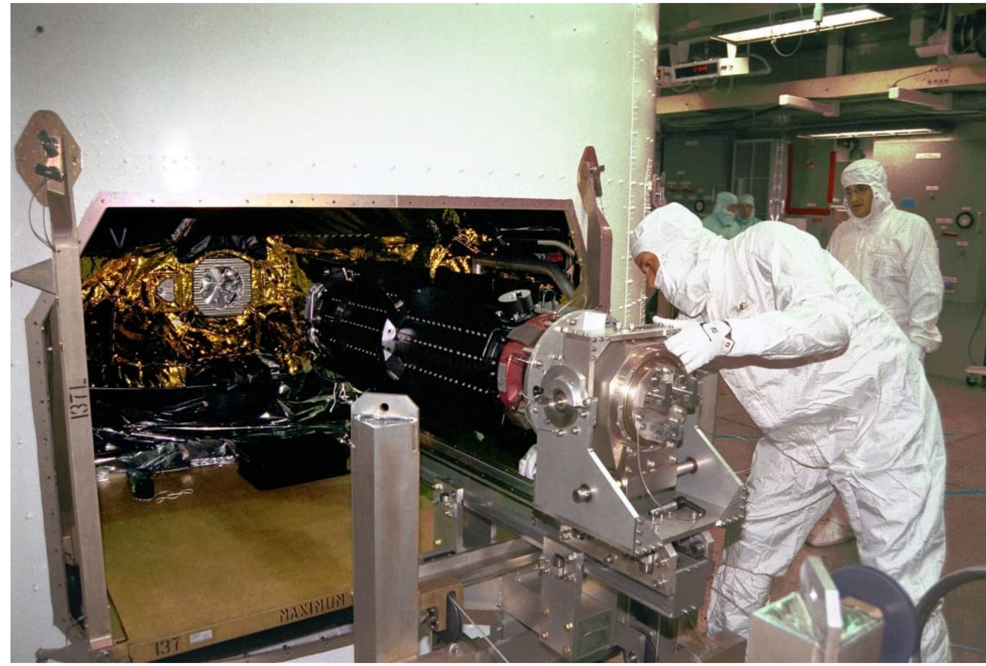
THERMOELECTRIC MODULE:

p- and n-type semiconductor legs

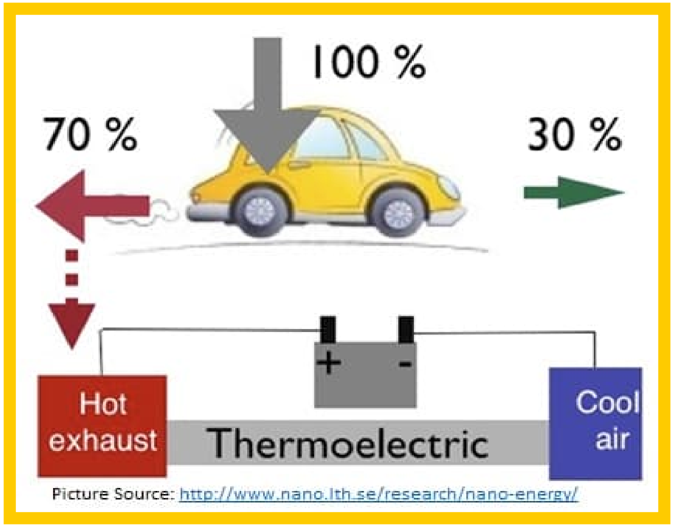


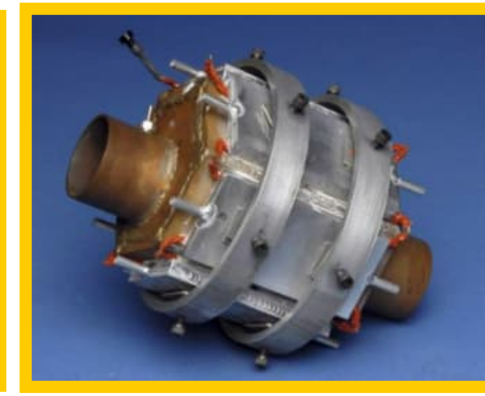
SPACE MISSIONS

- For space crafts & instruments: safe, reliable, long-lasting power systems
- Radioisotope thermoelectric generator (“nuclear battery”): electricity from heat
- Continuous heat source: ^{238}Plutonium radioactive decay
- Radioisotope power has been used by NASA over the last four decades for tens of space missions up to Mars

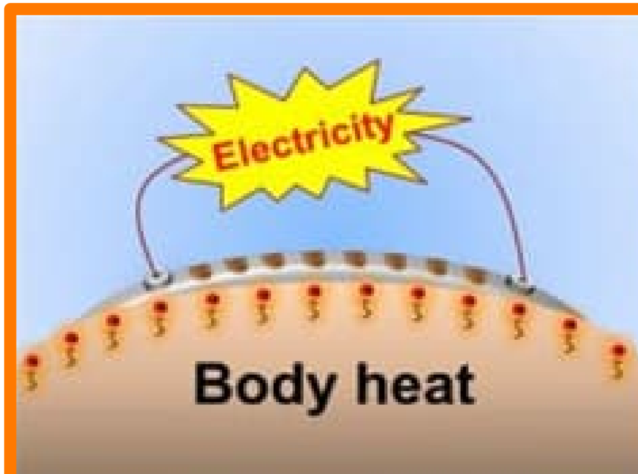


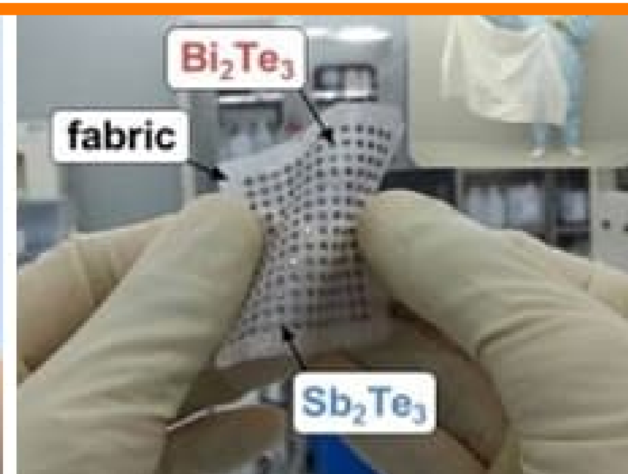
One of the three radioisotope thermoelectric generators on Cassini





THERMOELECTRICS: Examples of targeted applications





Aalto University
School of Chemical Technology

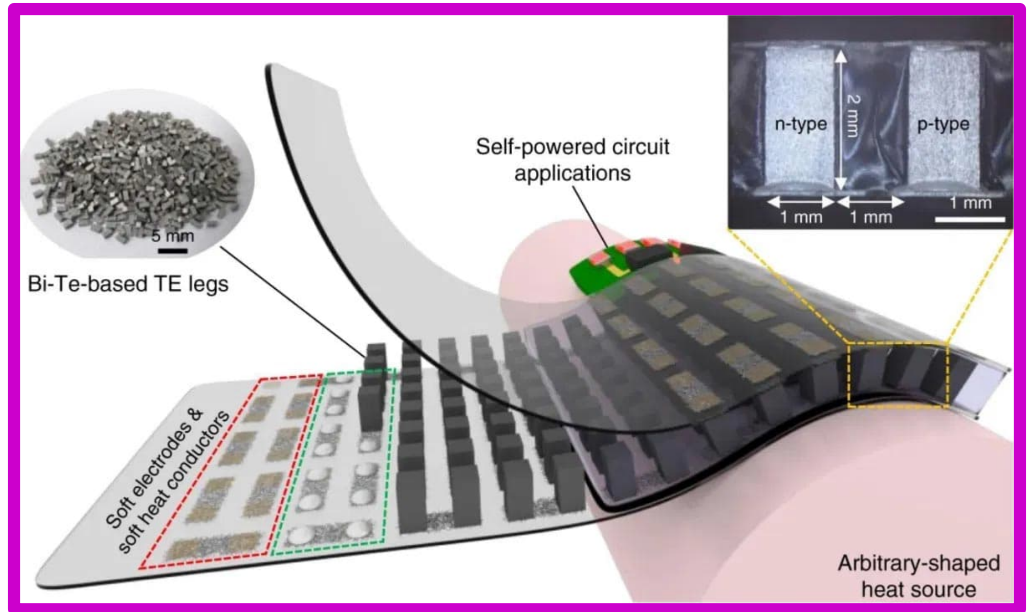
What kind of material requirements?

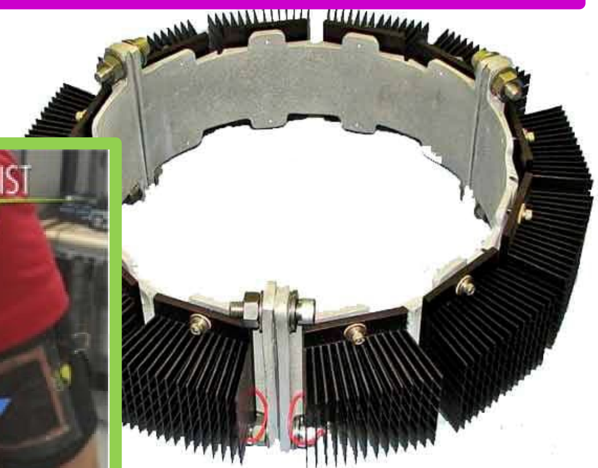
FLEXIBLE / WEARABLE THERMOELECTRICS

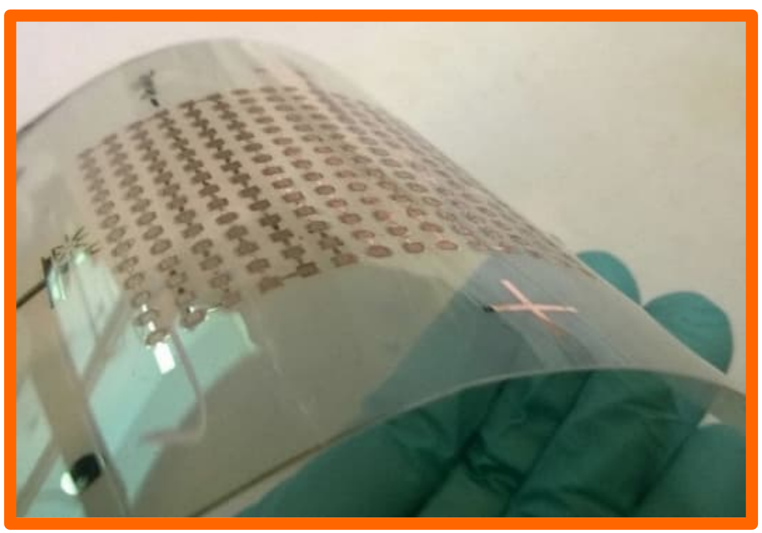
- Hot topic currently
- Flexibility needed:

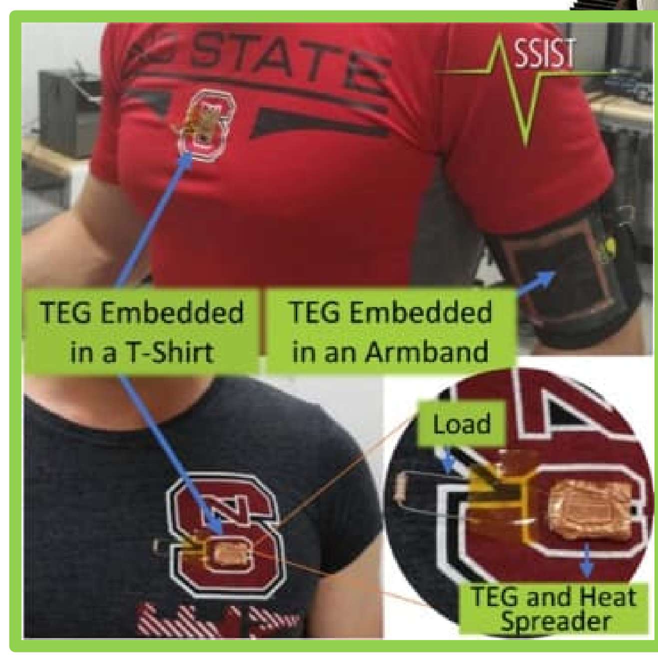
  (i) better fit with round heat sources

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







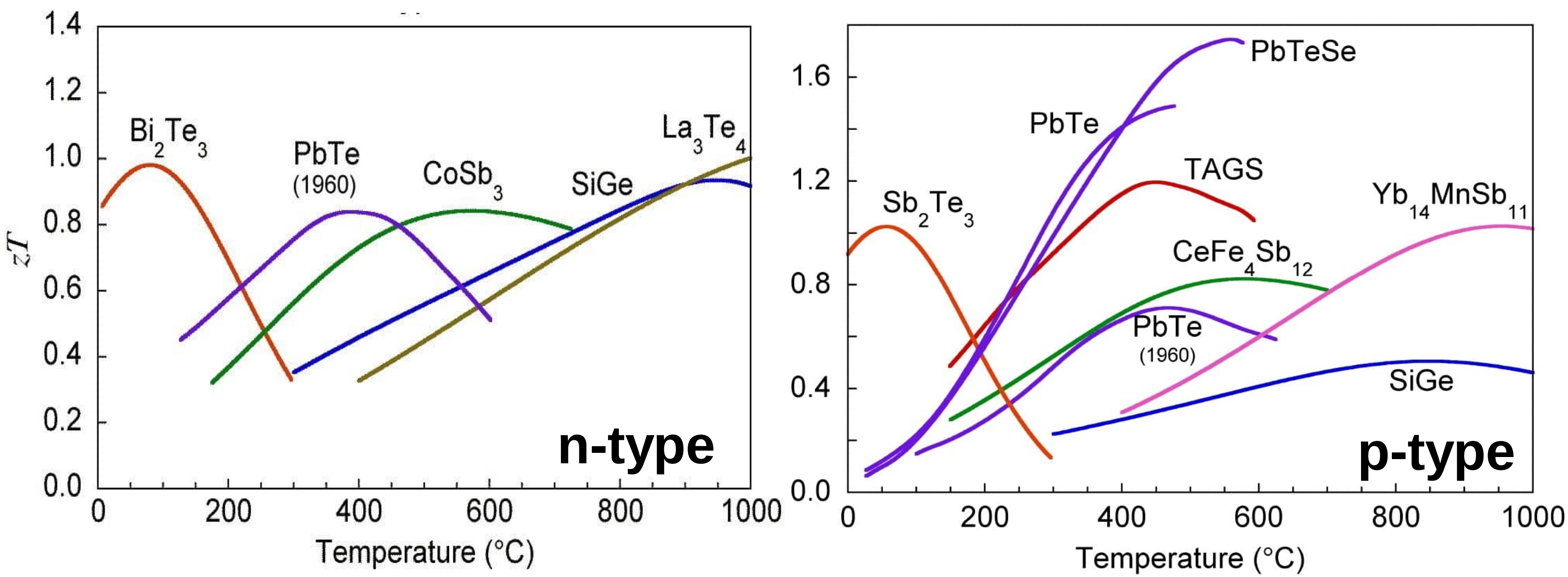


THERMOELECTRIC MATERIALS

- **Figure-of-Merit (ZT)**
- Heat-to-Electricity Conversion Efficiency (η)
- Conversion efficiency increases by increasing ZT
- ZT increases by increasing electrical conductivity (σ) & decreasing thermal conductivity (κ) → **DIFFICULTY**
- Two terms for κ: electronic (κ_e) and lattice (κ_L)
- More efficient for high-temperature application !

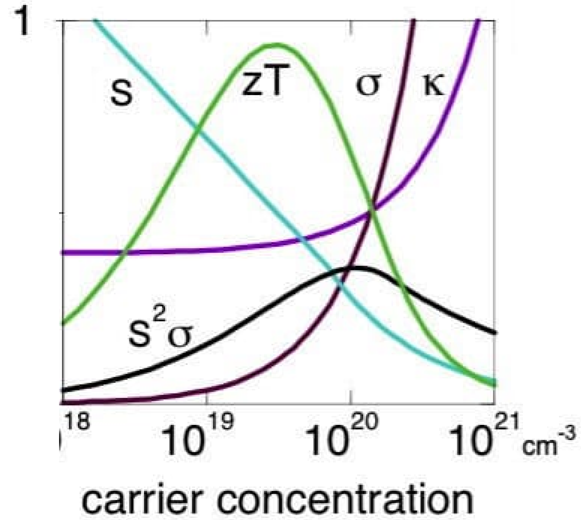
$$ZT = \frac{S^2 \sigma}{\kappa} T, \quad \kappa = \kappa_e + \kappa_L$$

$$\eta = \frac{\Delta T}{T_\mathrm{h}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_\mathrm{c} / T_\mathrm{h}}$$



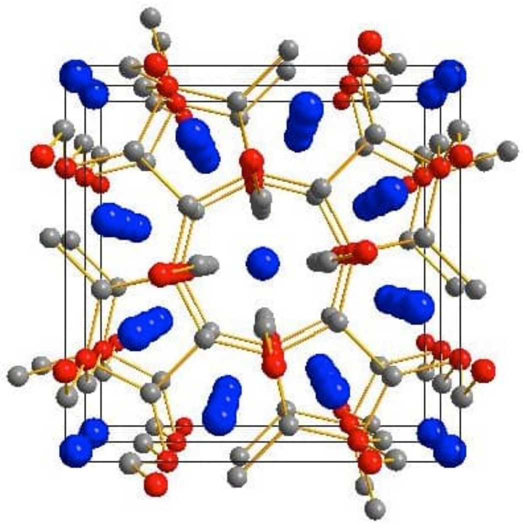
http://thermoelectrics.matsci.northwestern.edu/graphics/thermoelectrics/n-zT.jpg

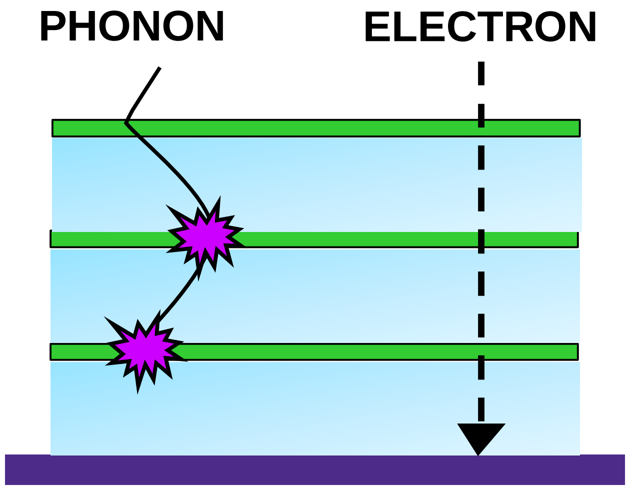
$$ZT = \frac{S^2\sigma}{\kappa}T, \ \kappa = \kappa_e + \kappa_L$$

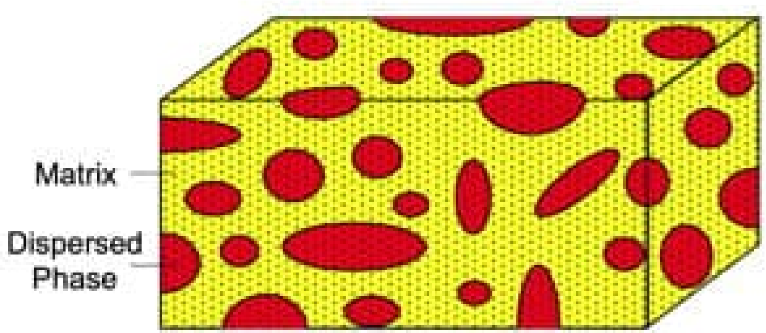


WELL-KNOWN WAYS TO ENHANCE ZT

- Carrier concentration tuning:
  - In particular for optimized combination of σ and S (Seebeck coefficient)
- For reducing thermal conductivity (lattice κ_L):
  - Heavy elements (often the rarest !)
  - Complex crystal structures
  - Defects / Nanostructures / Superlattices





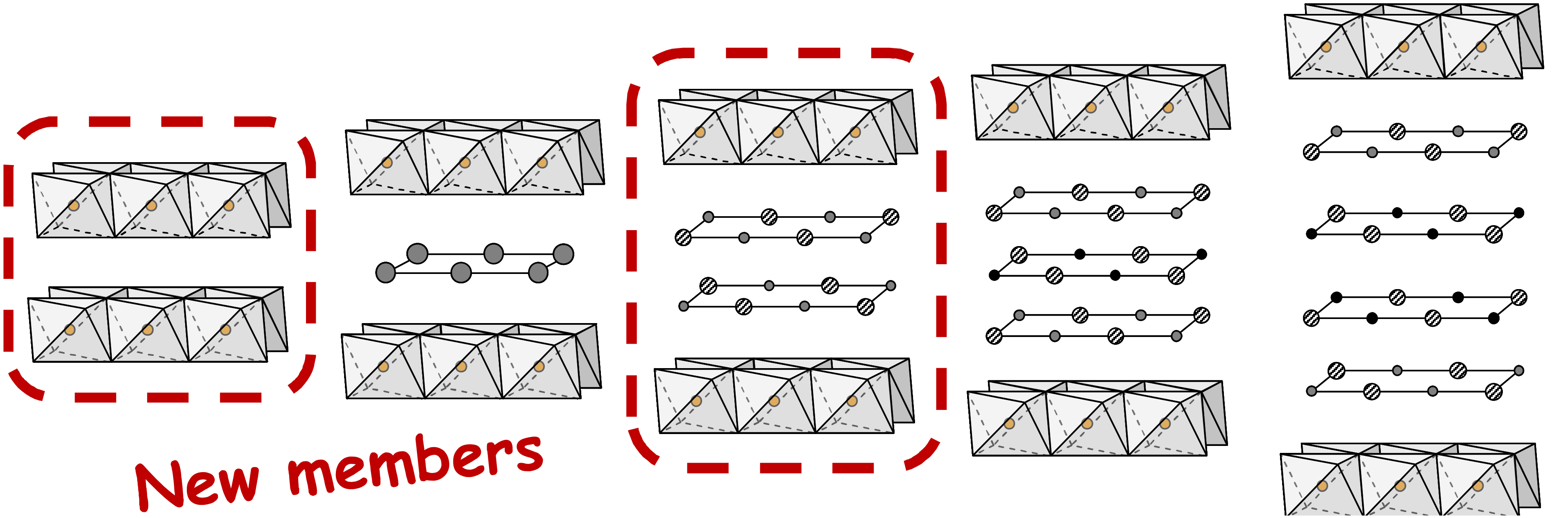


THERMOELECTRICS SUMMARY

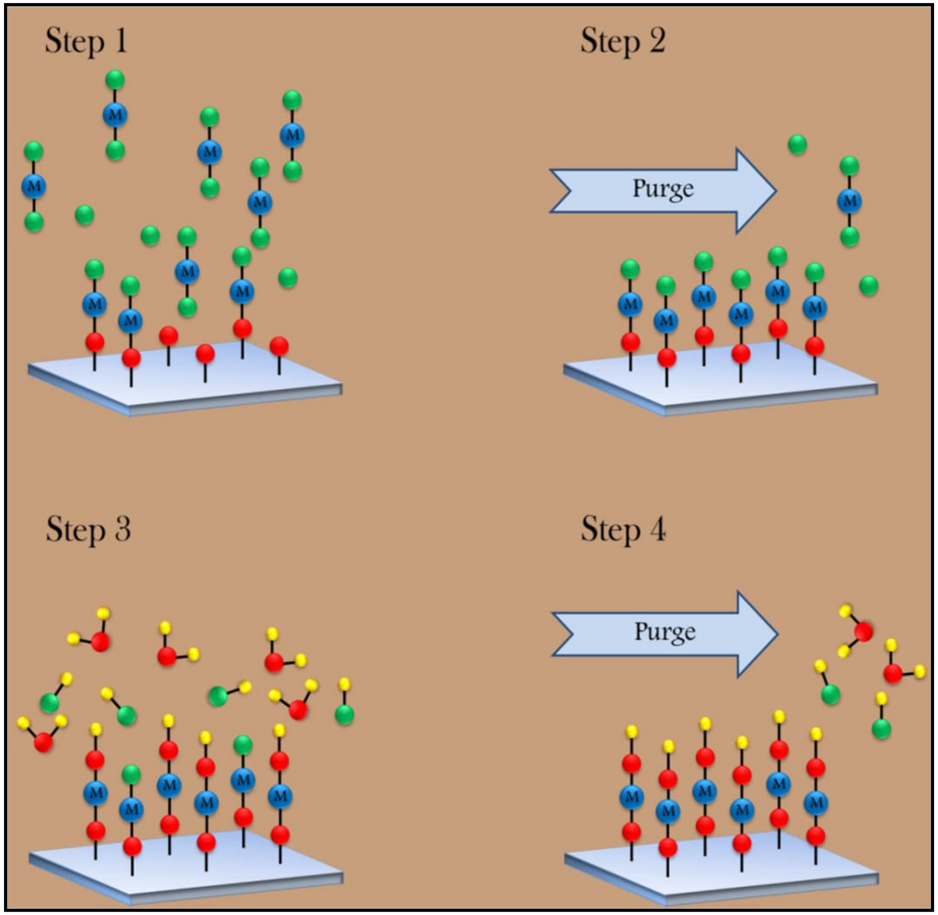
- **Over 65% of all energy produced is lost as waste heat**
- Thermoelectric power generators, which are semiconductor-based electronic devices, can turn this heat into electricity via the **Seebeck effect**
- These devices are **simple** to construct (just two different solid materials), easy to **scale-up** & 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 ≈ 2
  Dream-of-the-Dream: ZT > 4

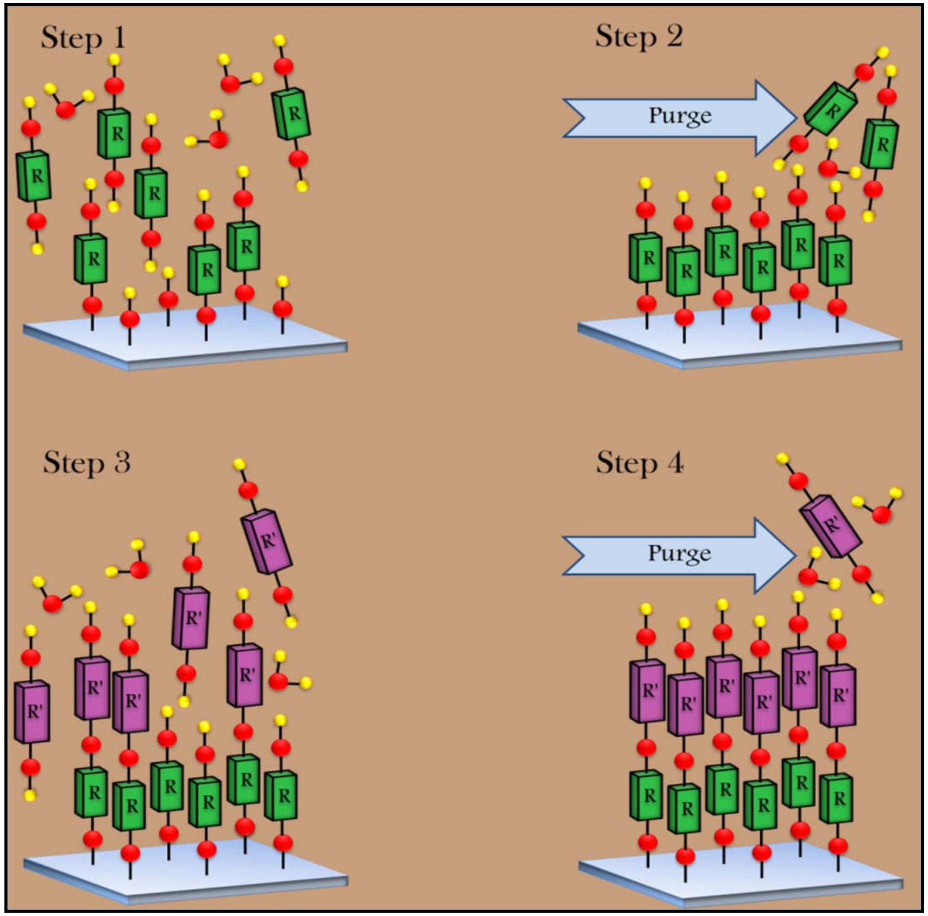
Thermoelectric Misfit Oxides: $[(MO)_m(AO)_k]_qCoO_2$

- 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 were discovered later
- CoO_2 layers with mixed-valent cobalt → electrical conductivity
- ”Misfitting” intermediate (metal or metal oxide) layers → low thermal conductivity



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)

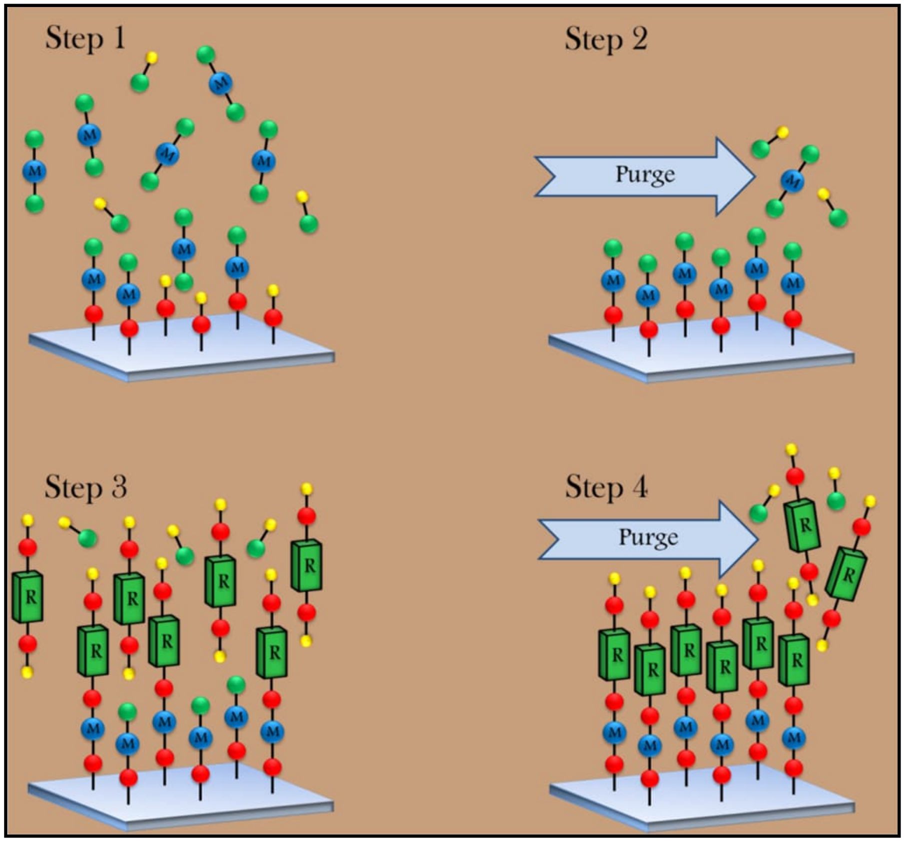
MLD (Molecular Layer Deposition)

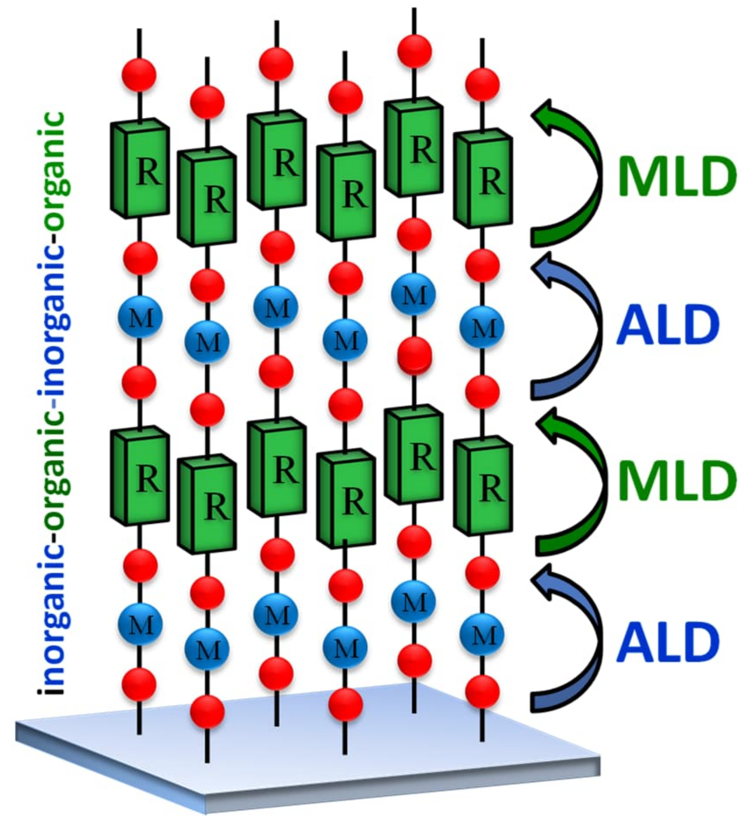
High-quality INORGANIC thin films with atomic level control for microelectronics and beyond

ORGANICS !

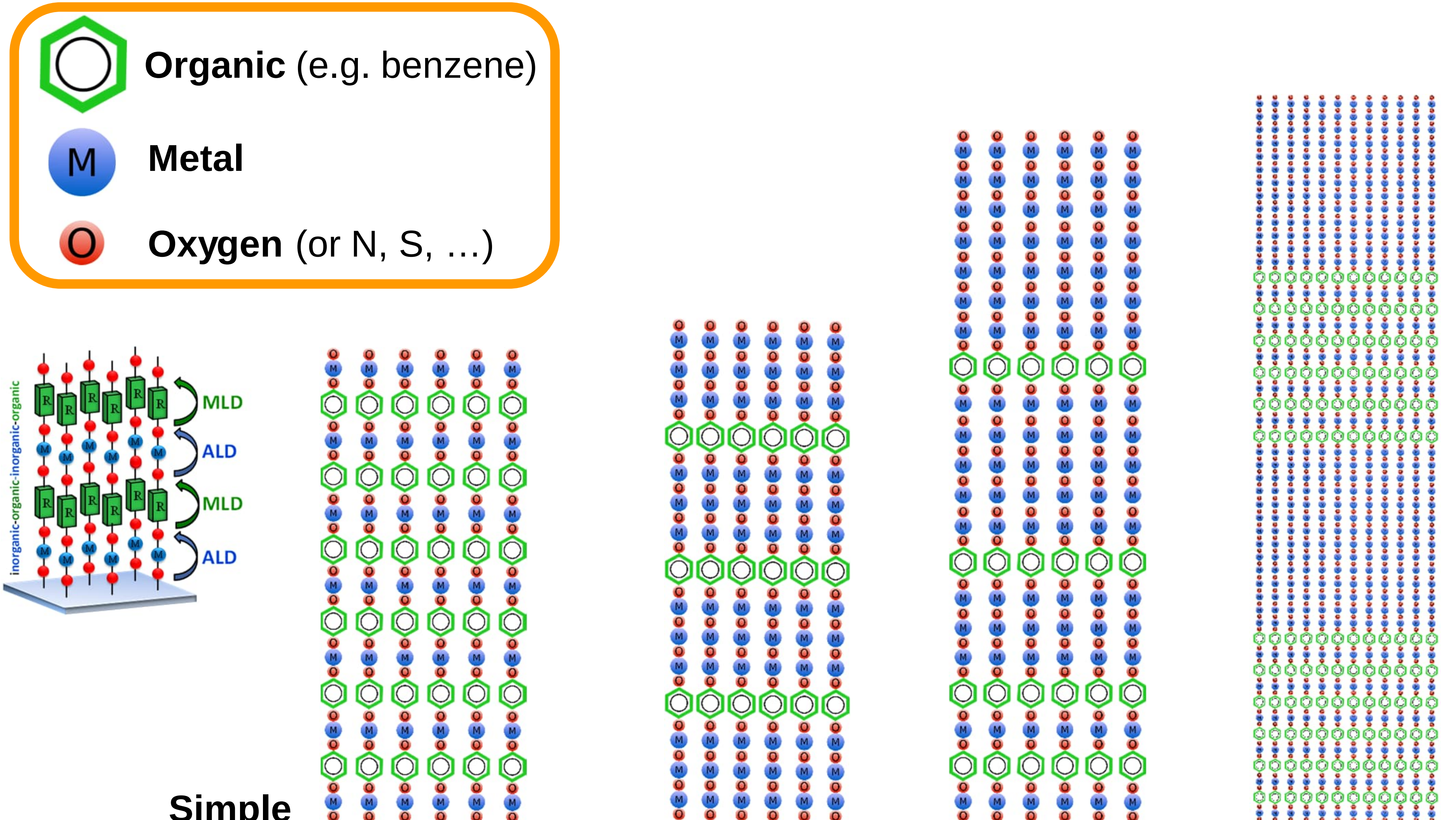
T. Yoshimura, S. Tatsuura & W. Sotoyama,
Polymer films formed with monolayer growth steps by molecular layer deposition,
Appl. Phys. Lett. 59, 482 (1991).

Inorganic-Organic (Metal-Organic) Thin Films by Combined ALD/MLD





NOVEL FLEXIBLE MULTIFUNCTIONAL HYBRID MATERIALS



Simple Metal-Organic Network (amorphous or crystalline)

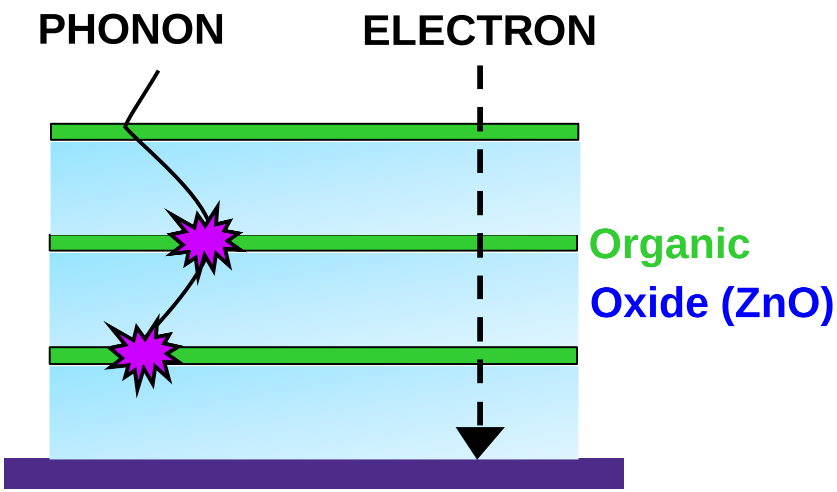
Superlattice

Gradient

Nanolaminate

DIFFERENT LAYER SEQUENCES BY DESIGN

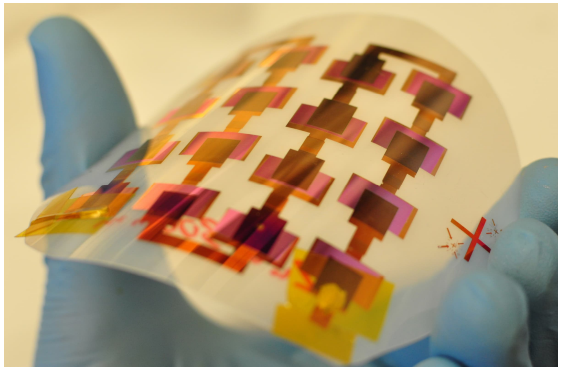
TEXTILE THERMOELECTRICS: ALD/MLD ZnO:organic



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

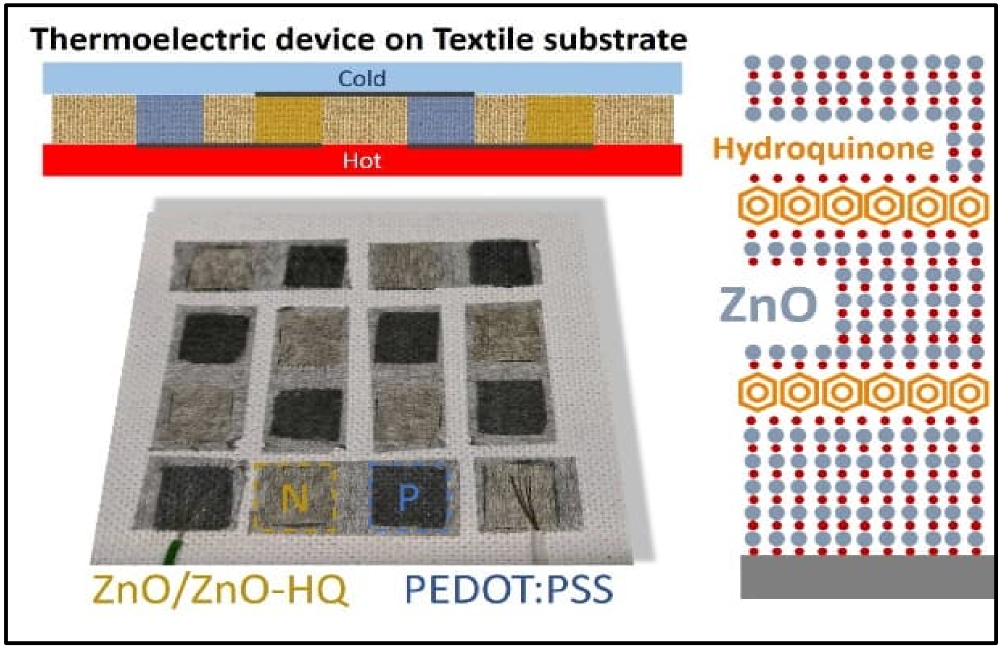
T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, *J. Mater. Chem. A* 2, 12150 (2014).

Flexible TE "device" on plastics

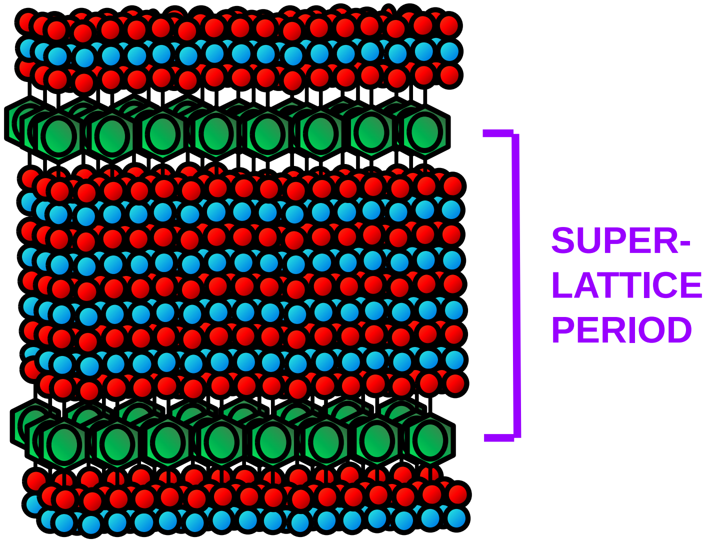


Textile-integrated thermoelectrics

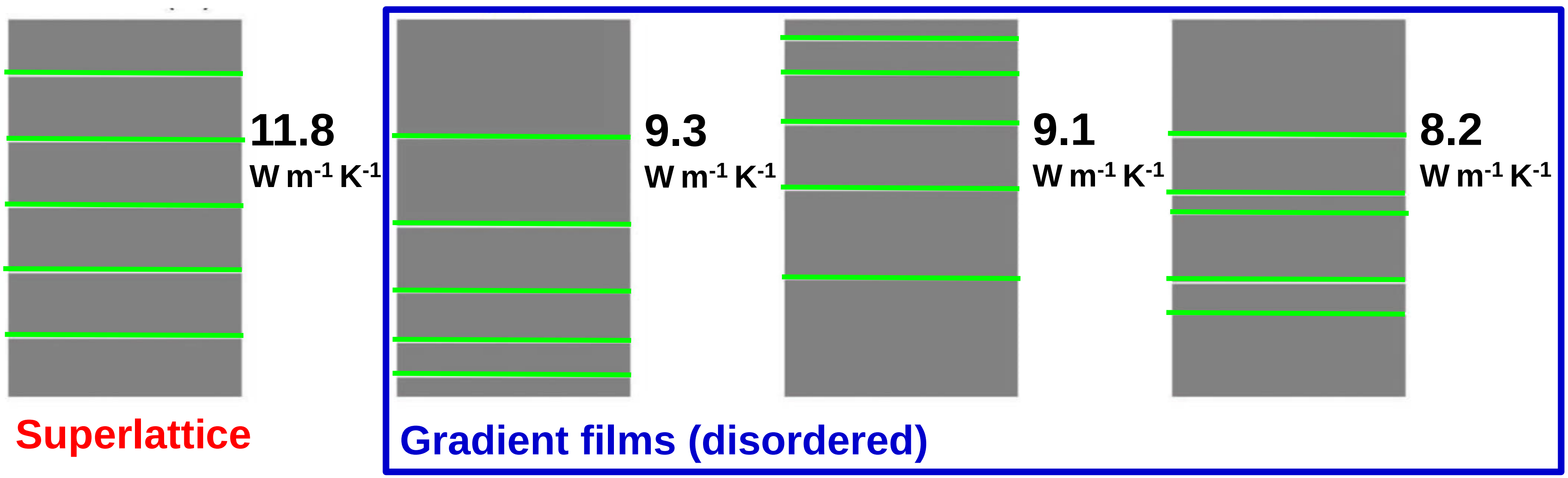
ZnO:org film grows in a conformal manner on textile fibers so that the entire textile piece becomes an active part of the device



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



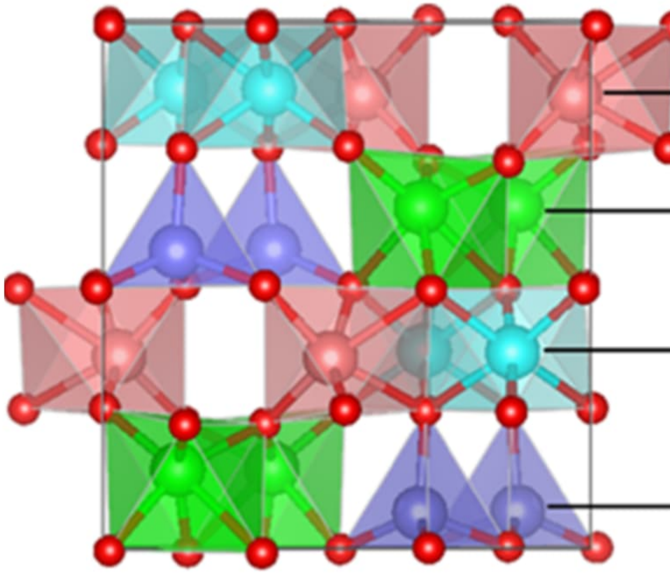
Thermal conductivity [W m^{-1} K^{-1}]	
ZnO (~100 nm)	~43
5 org. layers	11.8
6 org. layers	7.1
12 org. layers	4.1
20 org. layers	3.1
40 org. layers	1.3
80 org. layers	0.7



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)

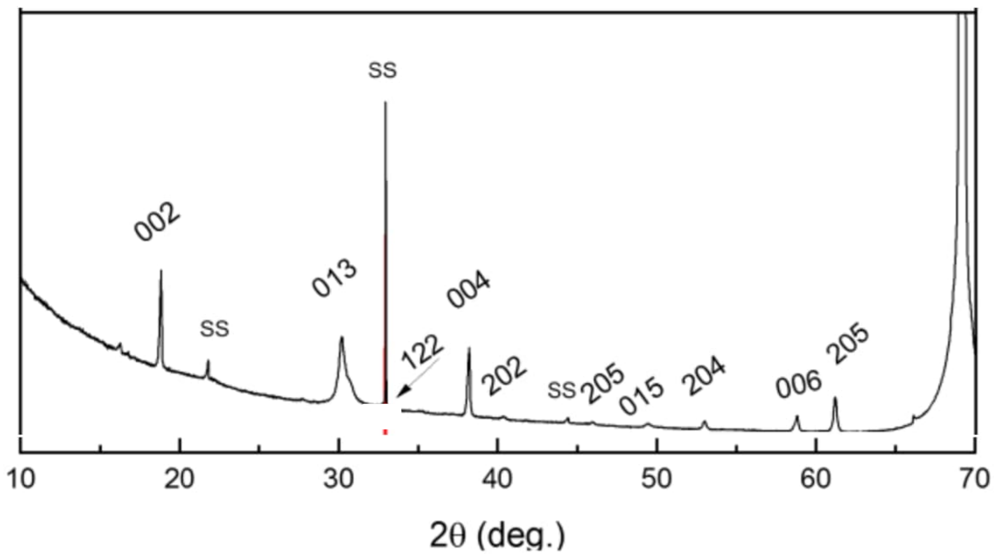
State-of-the-art: Synthesized in nano-scale/trace amounts only
- J. Tuček, R. Zbořil, A. Namai & S.I. Ohkoshi, Chem. Mater. 22, 6483 (2010)

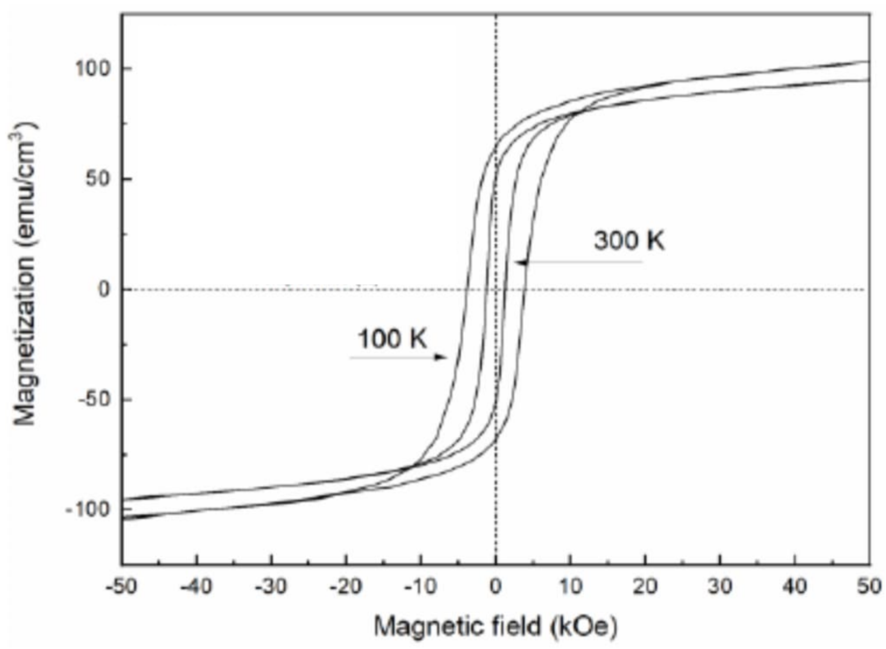
2017: ALD of ε-Fe_2O_3 thin films
- A. Tanskanen, O. Mustonen & M. Karppinen, APL Mater. 5, 056104 (2017)

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"

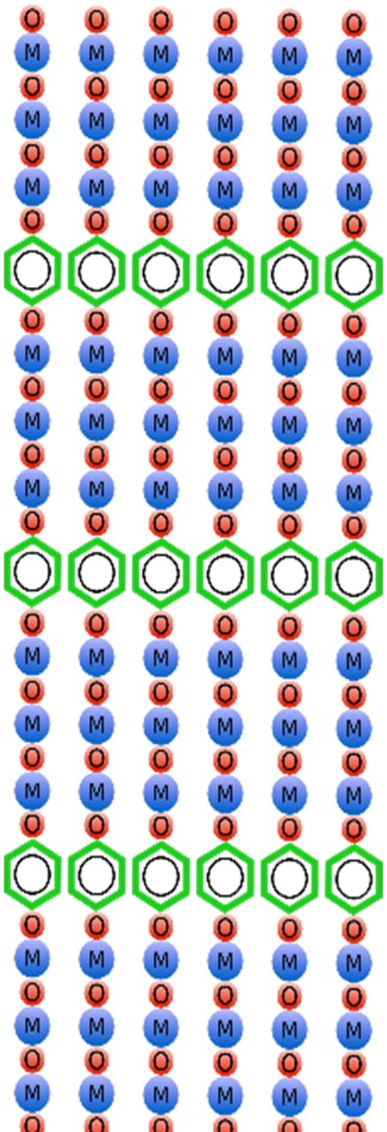




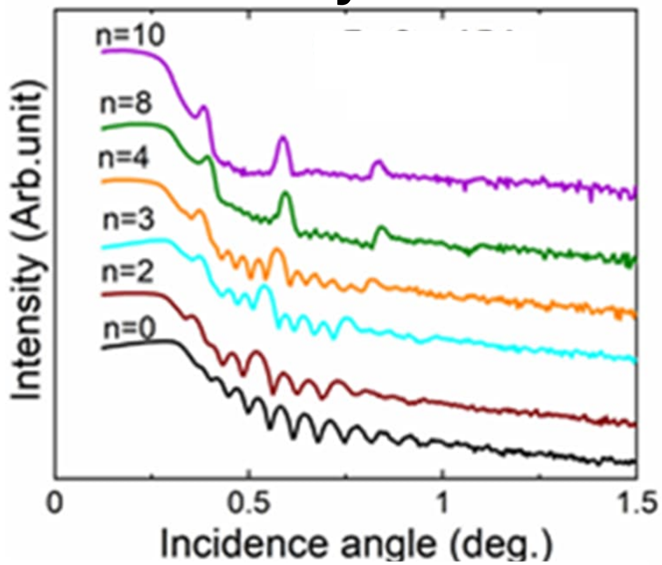
A. Tanskanen, O. Mustonen & M. Karppinen,
Simple ALD process for ε-Fe_2O_3 thin films,
APL Materials **5**, 056104 (2017).

ε-Fe_2O_3:Organic Superlattices (SL) by ALD/MLD

ORGANICS: terephthalic acid (TPA) or azobenzene (AZO)

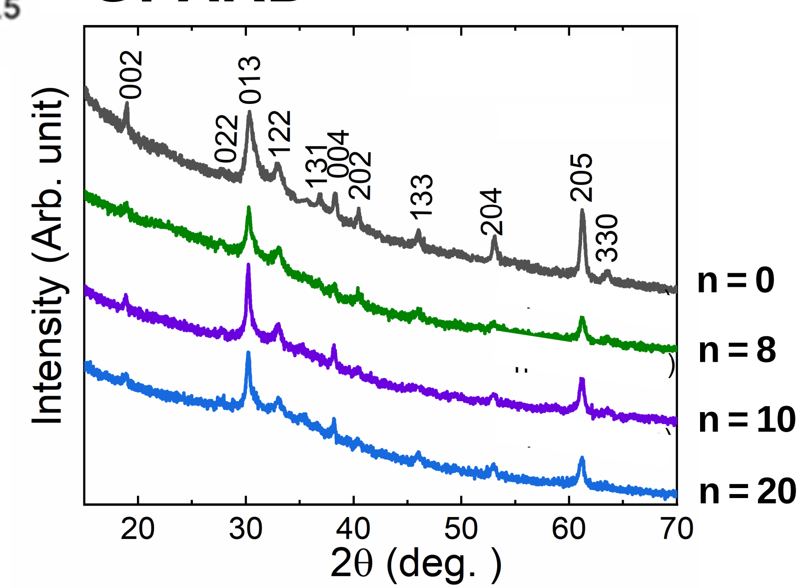


XRR: X-ray reflection

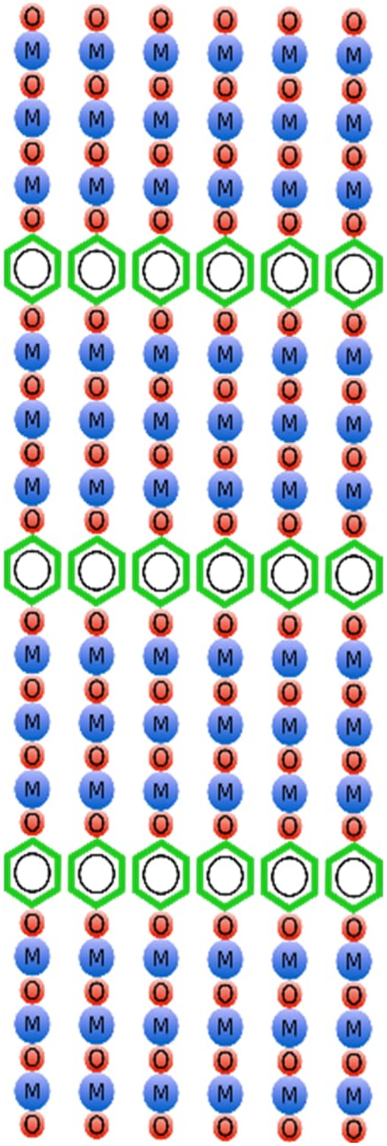


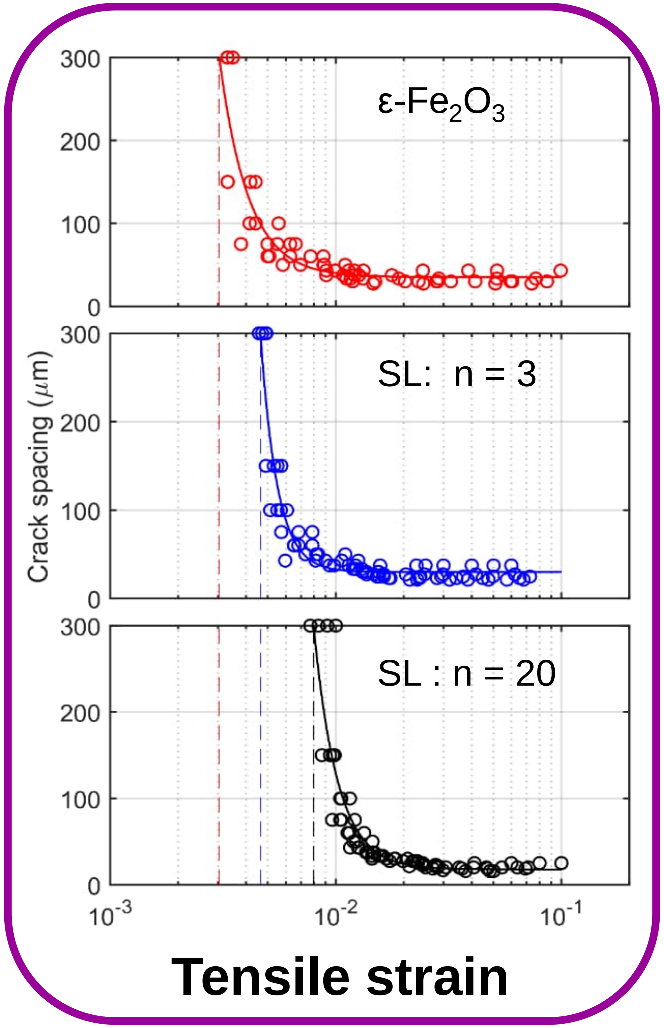
n: number of organic layers

GI-XRD



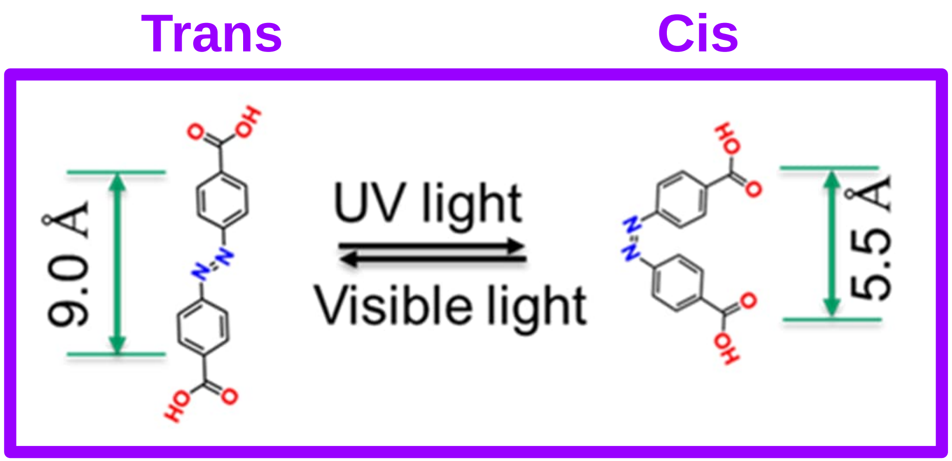
MECHANICALLY FLEXIBLE: ε-Fe_2O_3:org

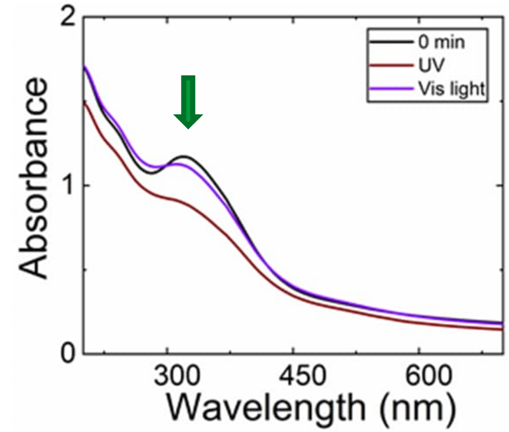




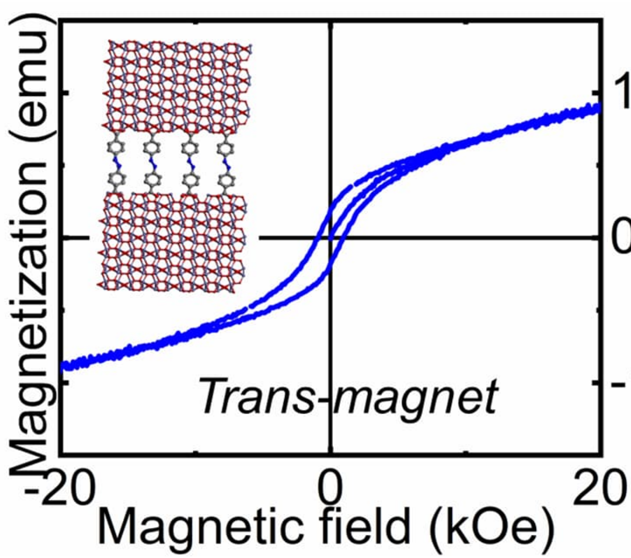
A. Philip, J.-P. Niemelä, G.C. Tewari, B. Putz, T.E.J. Edwards, M. Itoh, I. Utke & M. Karppinen, Flexible ε-Fe_2O_3-terephthalate thin-film magnets through ALD/MLD, *ACS Appl. Mater. Interfaces* 12, 21912 (2020).

PHOTOSWITCHABLE: ε-Fe_2O_3:azobenzene

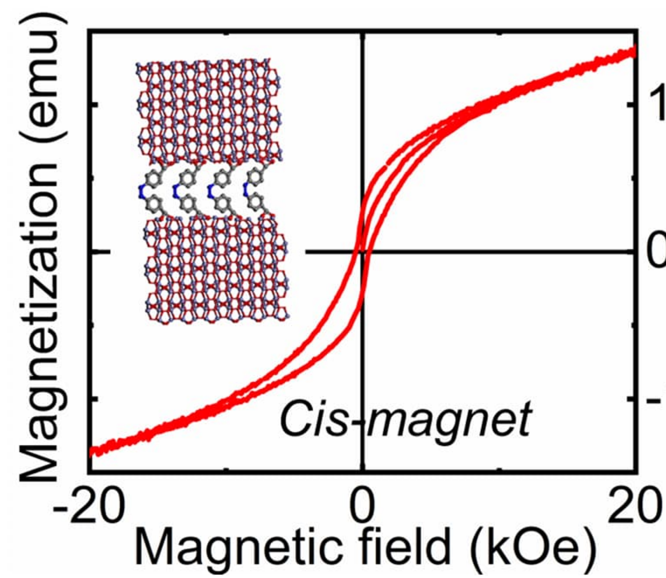




UV absorption: trans-cis transition is reversible



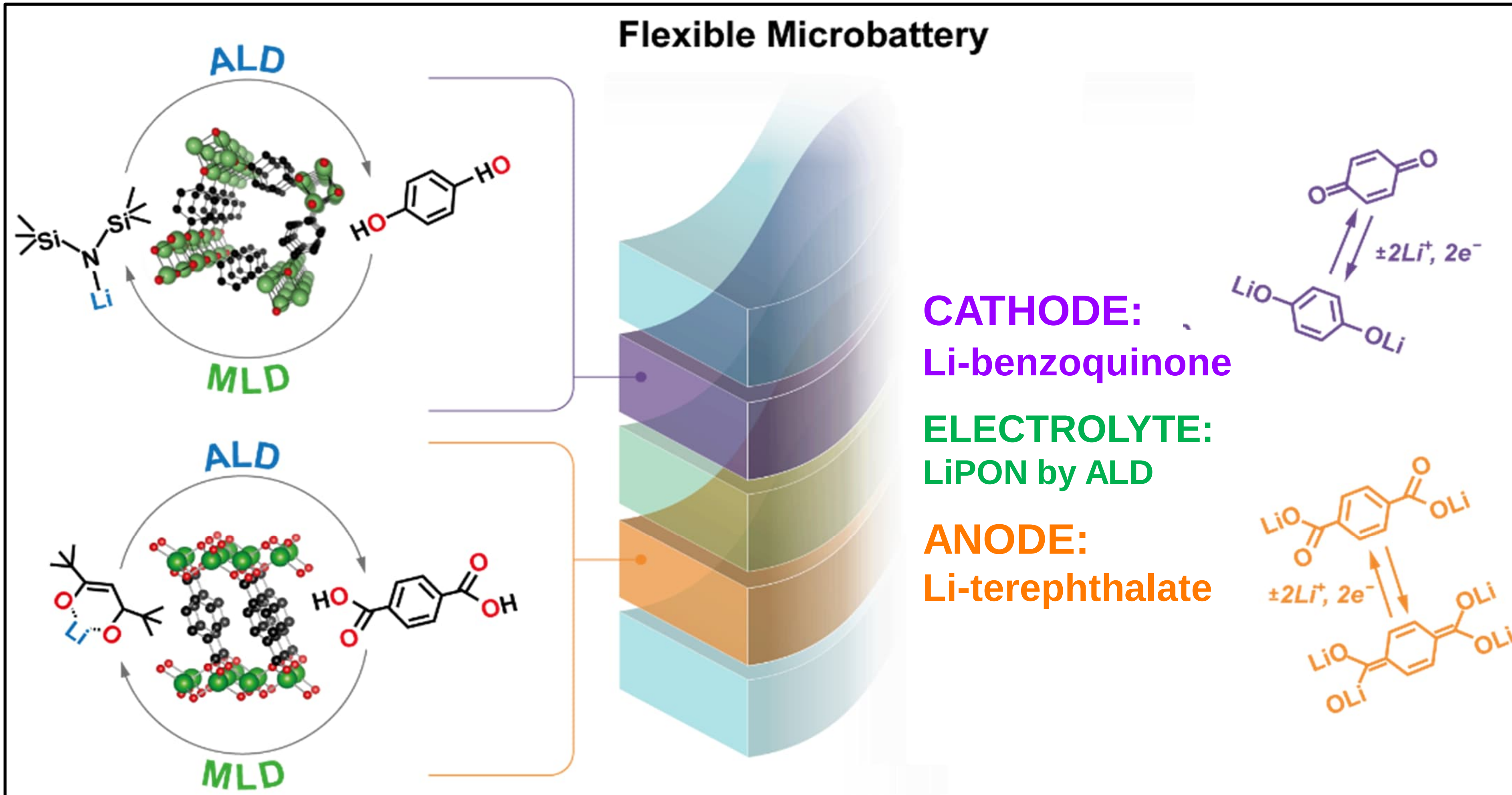
UV (365 nm)



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).

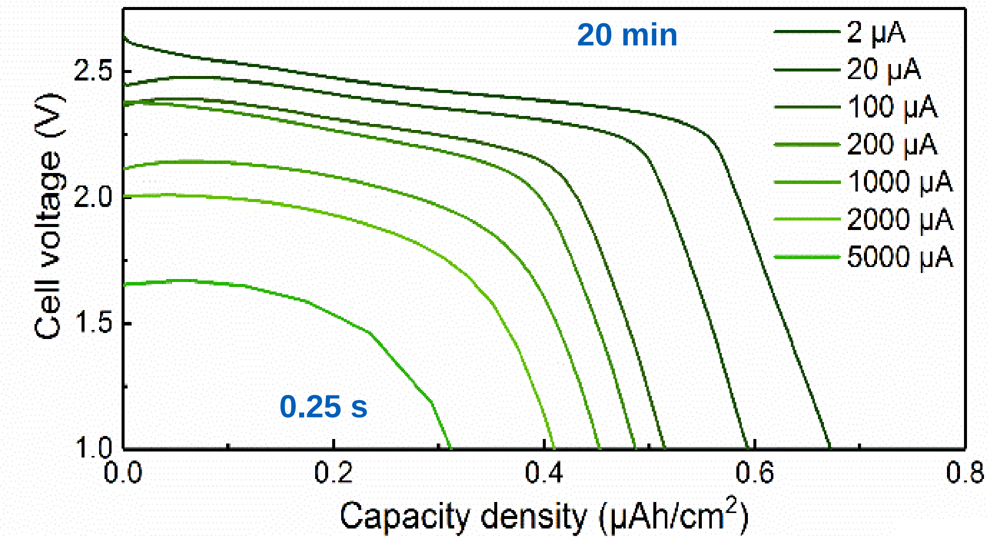
MATERIAL FUNCTION HIGHLIGHTS: Li-ion microbattery

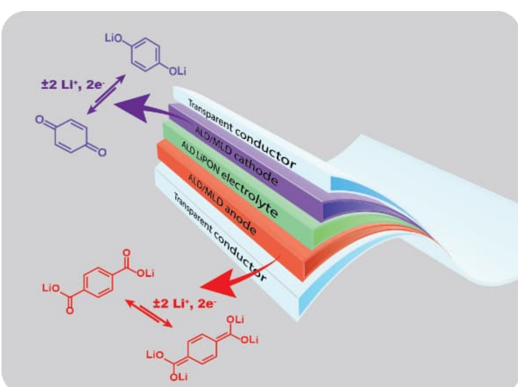


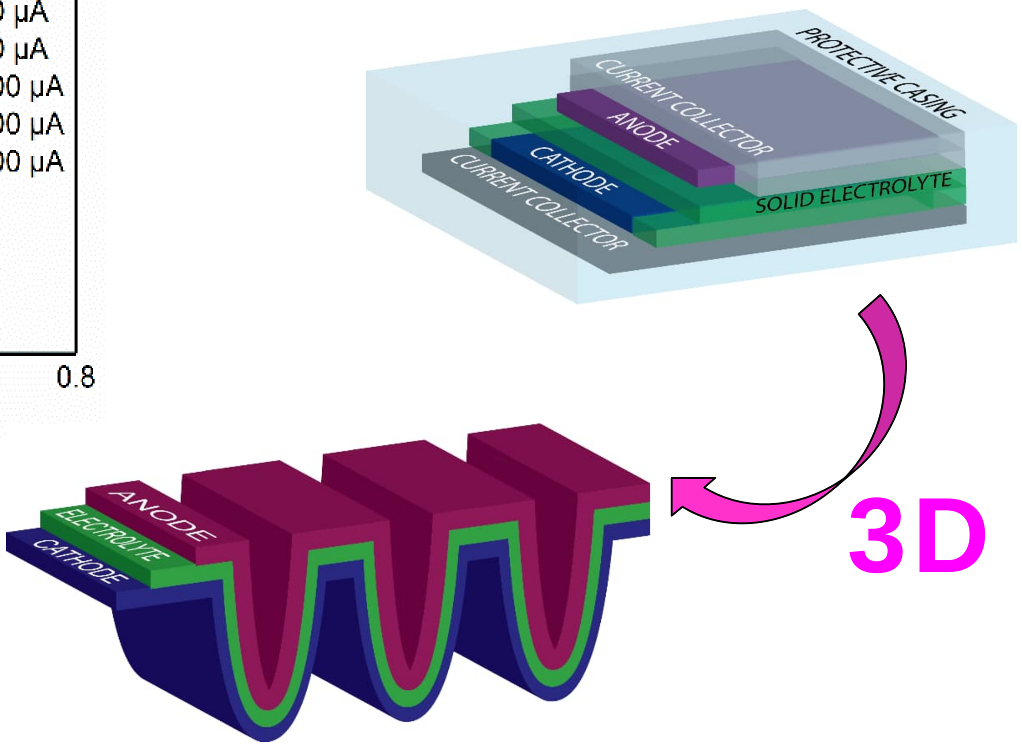
M. Nisula & M. Karppinen, In-situ lithiated quinone cathode for ALD/MLD-fabricated high-power thin-film battery, *Journal of Materials Chemistry A* 6, 7027 (2018).

TOYOTA

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







HIGH POWER & ENERGY DENSITY

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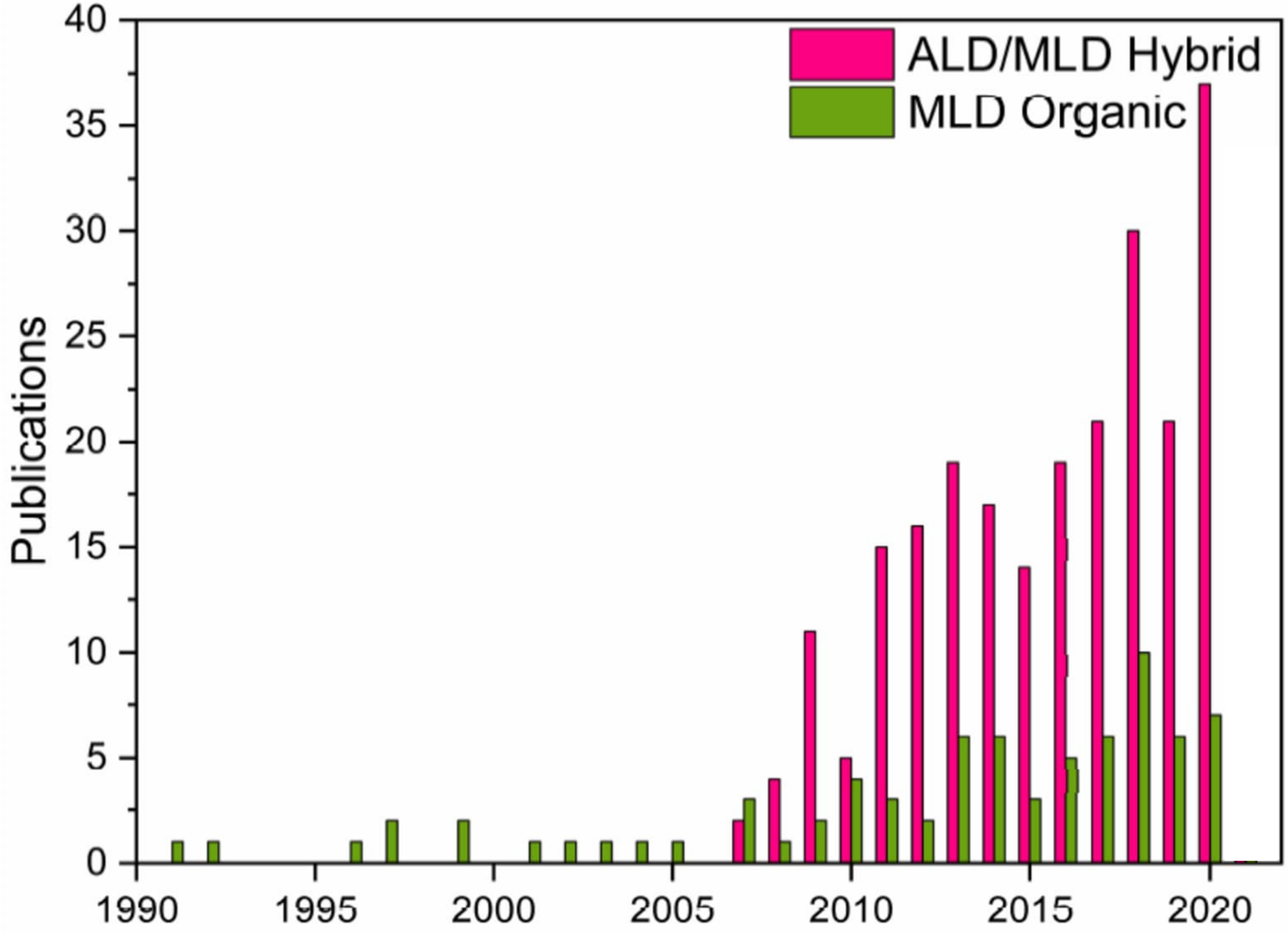

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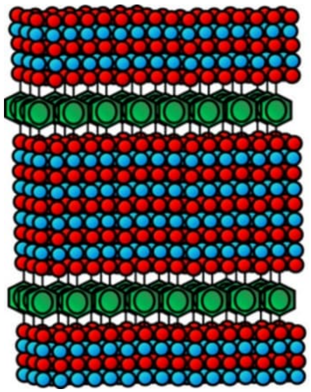

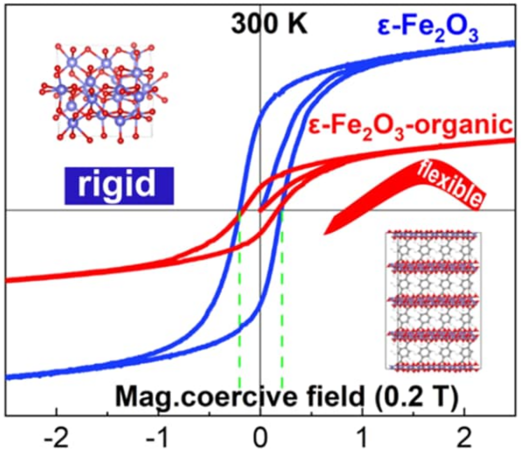

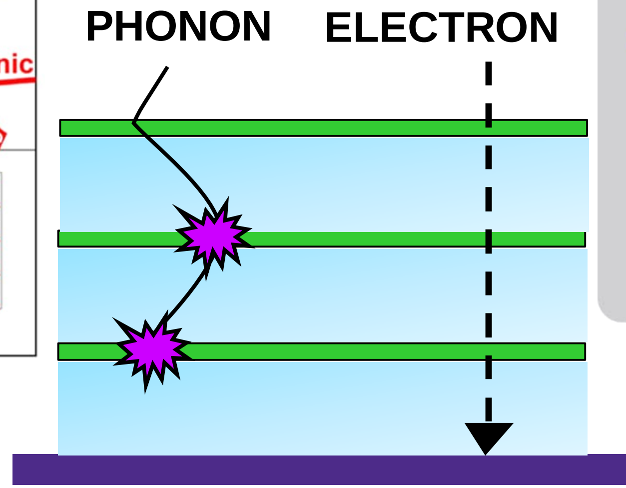

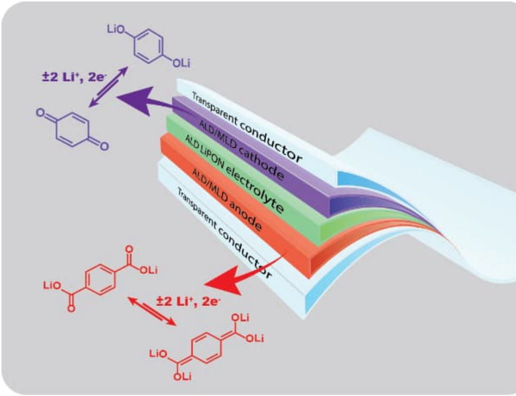

- **ALD/MLD can yield various new types of hybrid materials:**
  new MOFs & layer-engineered superlattice and gradient materials
- **Many of these new materials can NOT be made by any other technique**
- **Novel material properties have been discovered and much more expected !!!**