LECTURE SCHEDULE

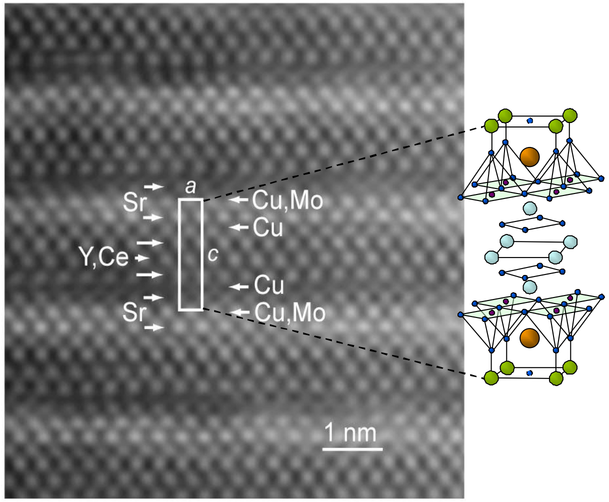
Date Topic

1.	**Wed**	**28.10.**	**Course Introduction & Short Review of the Elements**
2.	**Fri**	**30.10.**	**Periodic Properties & Periodic Table & Main Group Elements (starts)**
3.	**Fri**	**06.11.**	**Short Survey of the Chemistry of Main Group Elements (continues)**
4.	**Wed**	**11.11.**	**Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)**
5.	**Fri**	**13.11.**	**Redox Chemistry**
6.	**Mon**	**16.11.**	**Transition Metals: General Aspects & Crystal Field Theory**
7.	**Wed**	**18.11.**	**Zn, Ti, Zr, Hf & Atomic Layer Deposition (ALD)**
8.	**Fri**	**20.11.**	**V, Nb, Ta & Metal Complexes and MOFs**
9.	**Mon**	**23.11.**	**Cr, Mo, W & 2D materials**
10	**Wed**	**25.11.**	**Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity**
11.	**Fri**	**27.11.**	**Resources of Elements & Rare/Critical Elements & Element Substitutions**
12.	**Mon**	**30.11.**	**Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion**
13.	**Wed**	**02.12.**	**Inorganic Materials Chemistry Research**

EXAM: Thu Dec 10, 9:00-12:00 (IN MyCourses)

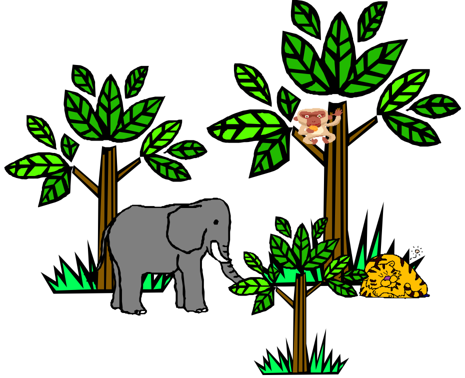
QUESTIONS: Lecture 13

1. Give the abbreviated name for $HgBa_2Ca_2Cu_3O_8$.
2. Oxidation state of Cu in La_2CuO_4, $La_2CuO_{4.1}$ and $(La_{0.9}Ba_{0.1})_2CuO_4$?
3. Are the above copper oxides superconducting ?
4. Why multilayered structure is important for high-T_c superconductors ?
5. Why multilayered structure is useful for thermoelectric materials ?



INORGANC CHEMISTRY

Aalto University
Department of Chemistry & Materials Science

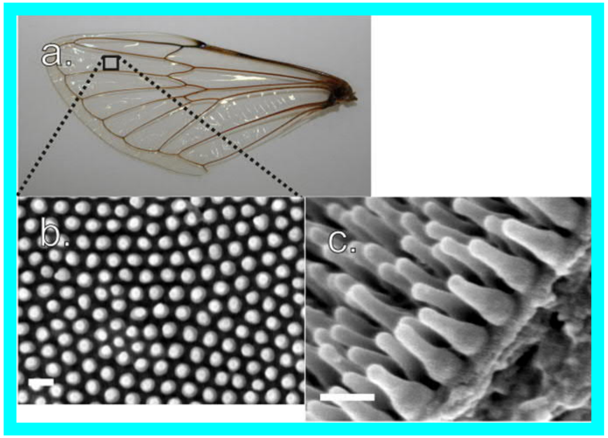


Sustainable energy materials

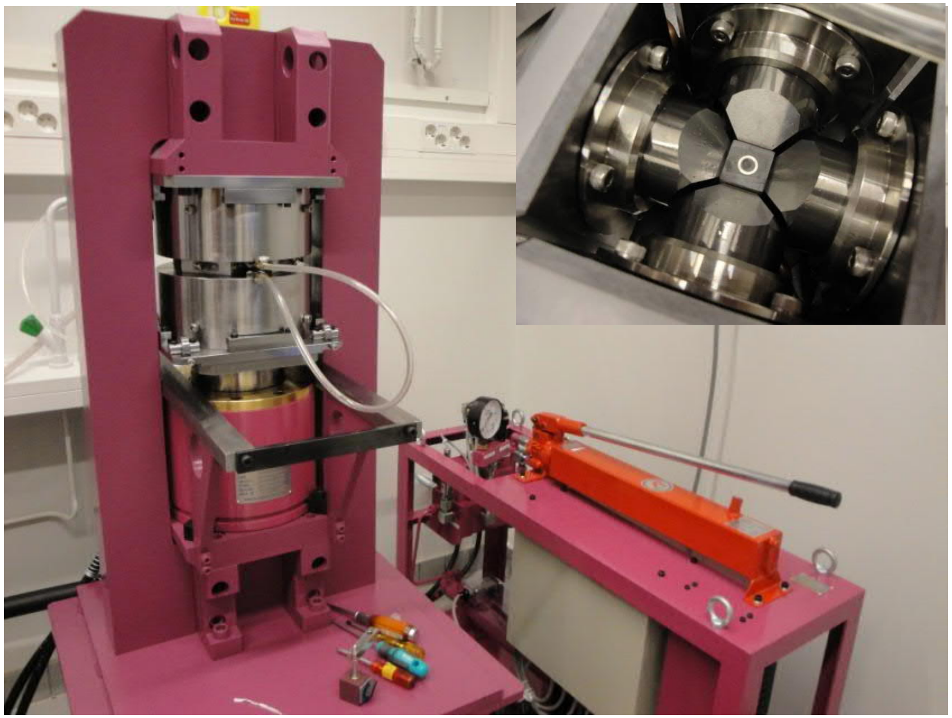
- **Novel Functional (bulk) Oxide Materials**
  - **high-T_c superconductors**
  - **thermoelectric materials**
  - **exotic magnetic materials (halfmetals, ferroelectrics)**
  - **ionic conductors (fuel cell, battery, oxygen storage)**

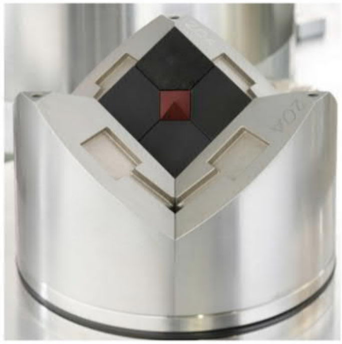
- **ALD (Atomic Layer Deposition) Thin Films**
  - **complex (ternary & quaternary) oxides**
  - **oxide coatings on novel/exciting surfaces (polymers, biomaterials, textiles, steel, etc.)**
  - **inorganic/organic hybrid materials**

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

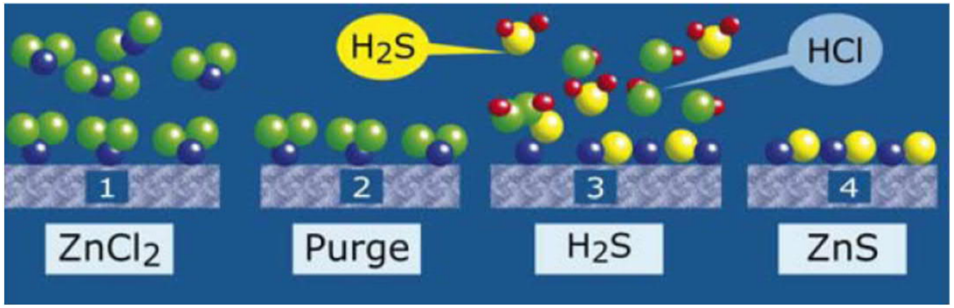


Ultra High-Pressure (HP) synthesis



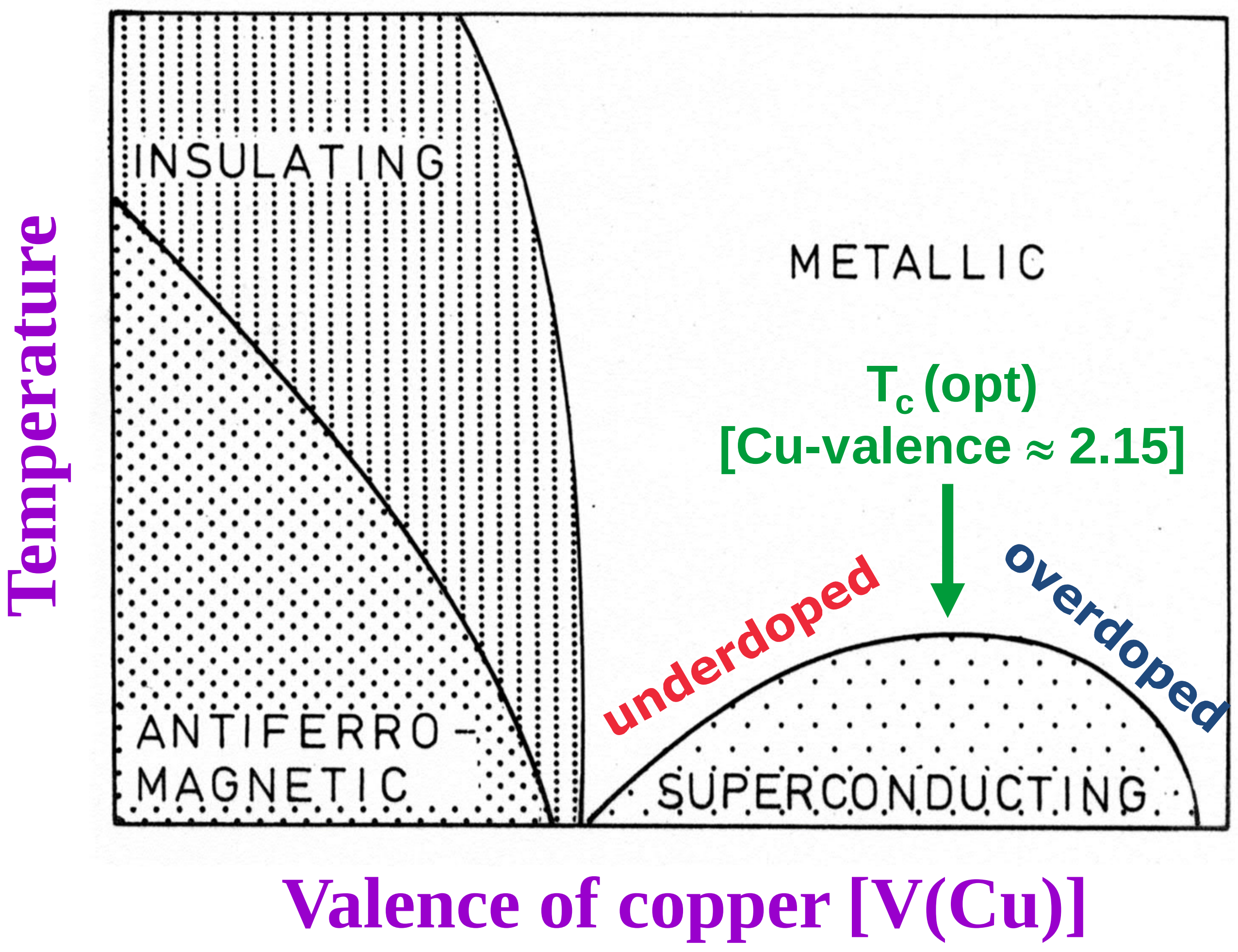


Atomic Layer Deposition (ALD) thin-film technology

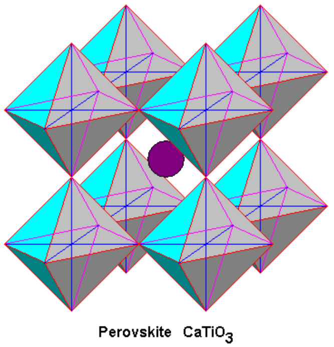


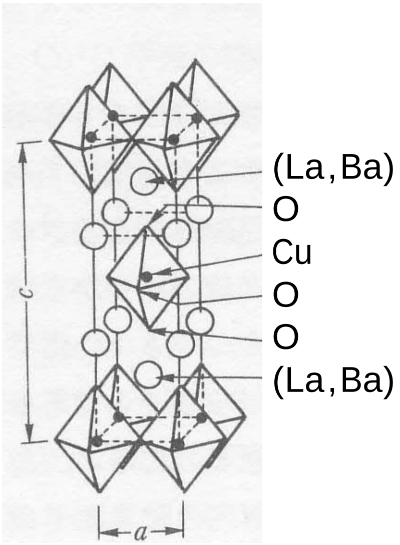
SYNTHESIS TECHNIQUES

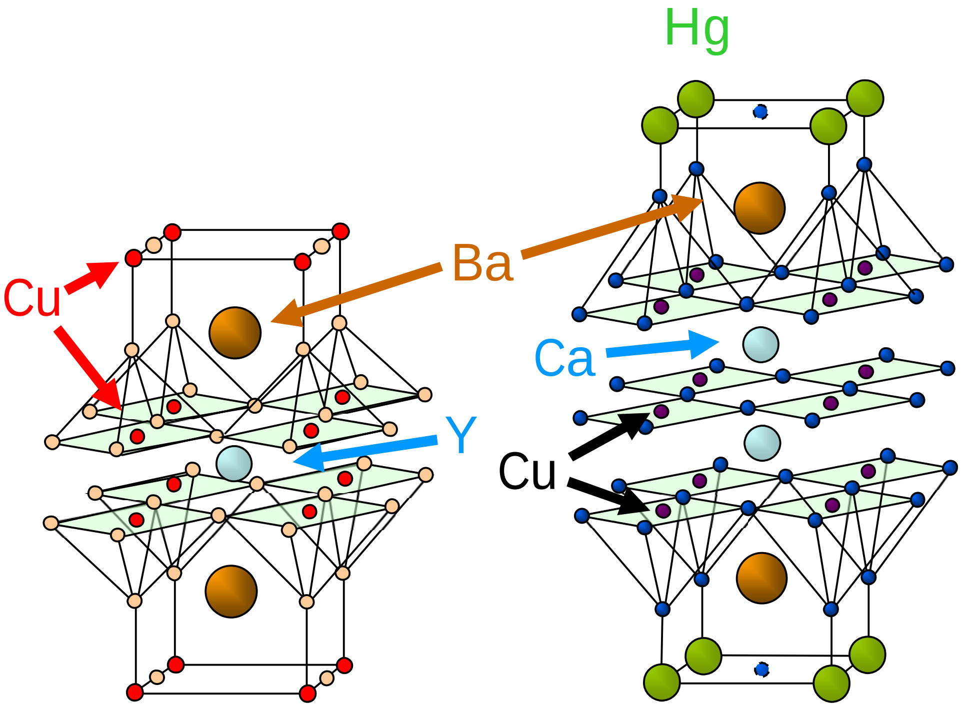
Phase Diagram of HTSCs



Crystal Structures of Representative High-T_c Superconductive Copper Oxides







$(La,Ba)_2CuO_{4+\delta}$

$T_c \approx 35$ K

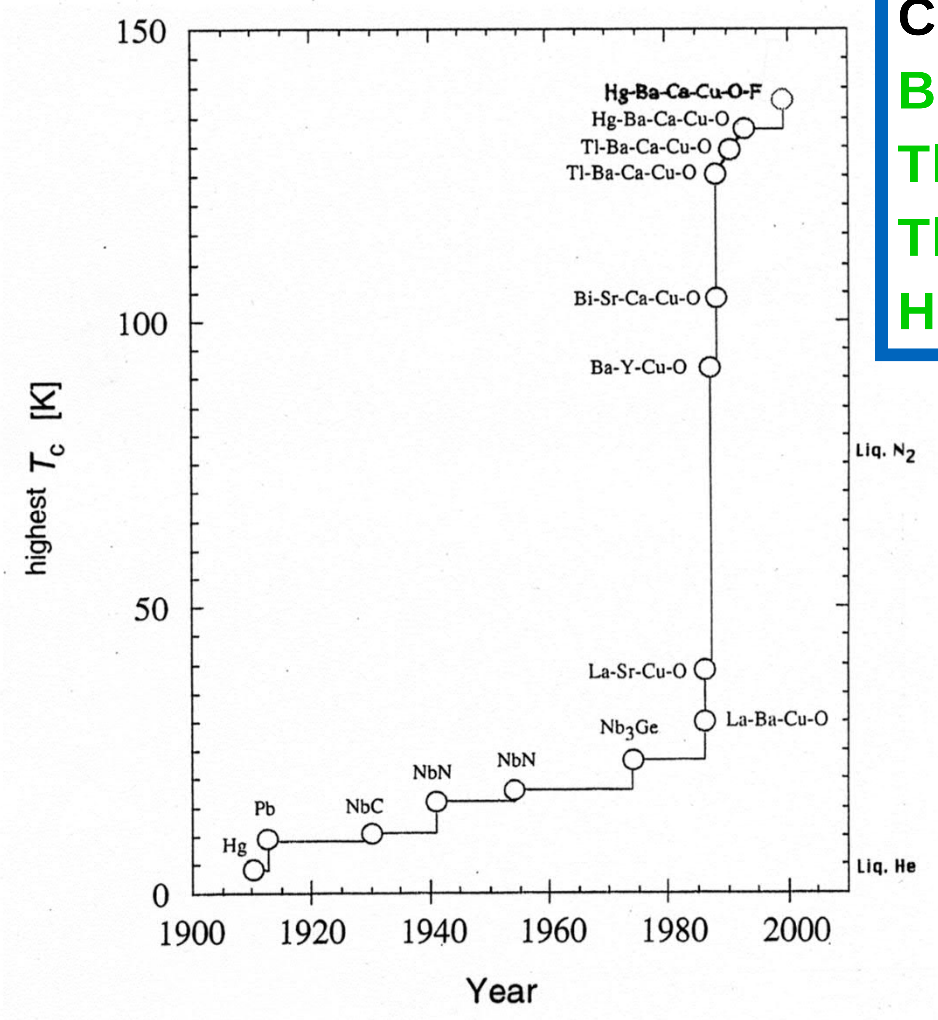
$YBa_2Cu_3O_{7-\delta}$

$T_c \approx 90$ K

$HgBa_2Ca_2Cu_3O_{9-\delta}$

$T_c \approx 135$ K

Search for new high-*Tc* superconductors



$(La_{0.92}Ba_{0.08})CuO_4$

$(La_{0.92}Sr_{0.08})_2CuO_4$

$CuBa_2YCu_2O_7$

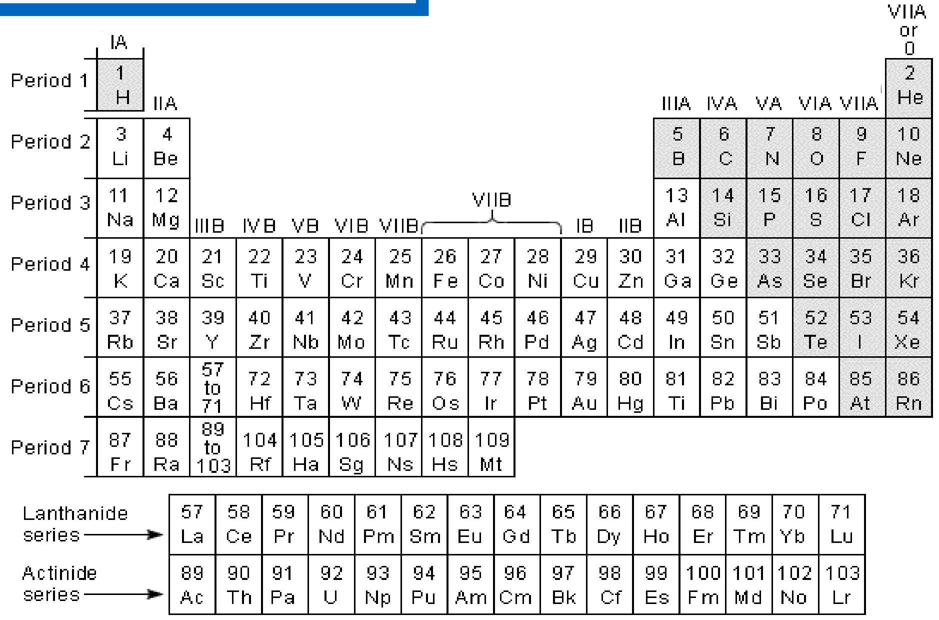
$Bi_2Sr_2Ca_2Cu_3O_{10}$

$Tl_2Ba_2Ca_2Cu_3O_{10}$

$TlBa_2Ca_2Cu_3O_9$

$HgBa_2Ca_2Cu_3O_9$

- ➢ **Chemical pressure**
- ➢ **No. of CuO_2 planes**
- ➢ **Inert-pair effect**

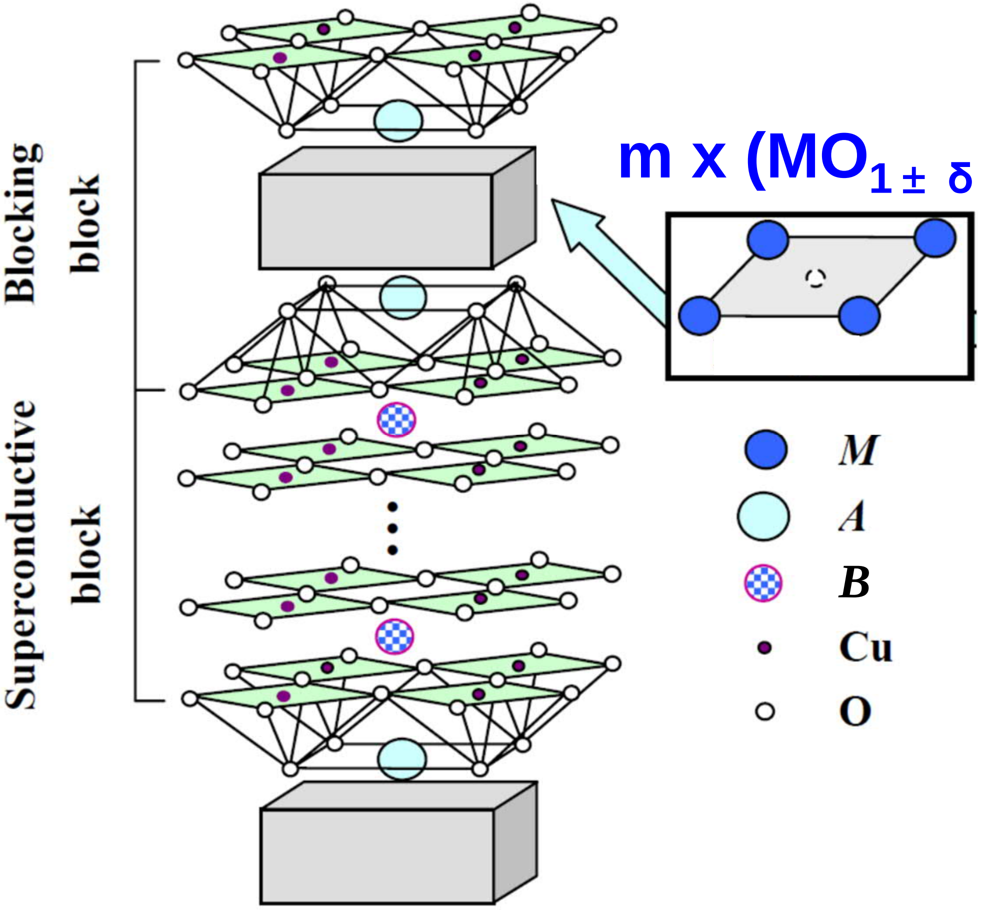


	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIA or 0
Period 1	1 H																	2 He
Period 2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
Period 3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
Period 4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
Period 5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
Period 6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
Period 7	87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

Lanthanide series →	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide series →	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

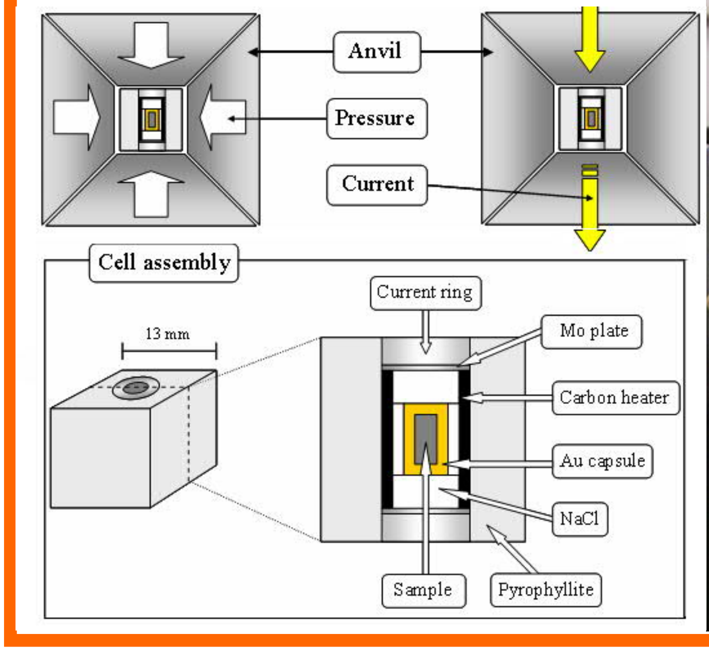
GENERAL FORMULA of High-T_c Superconductors

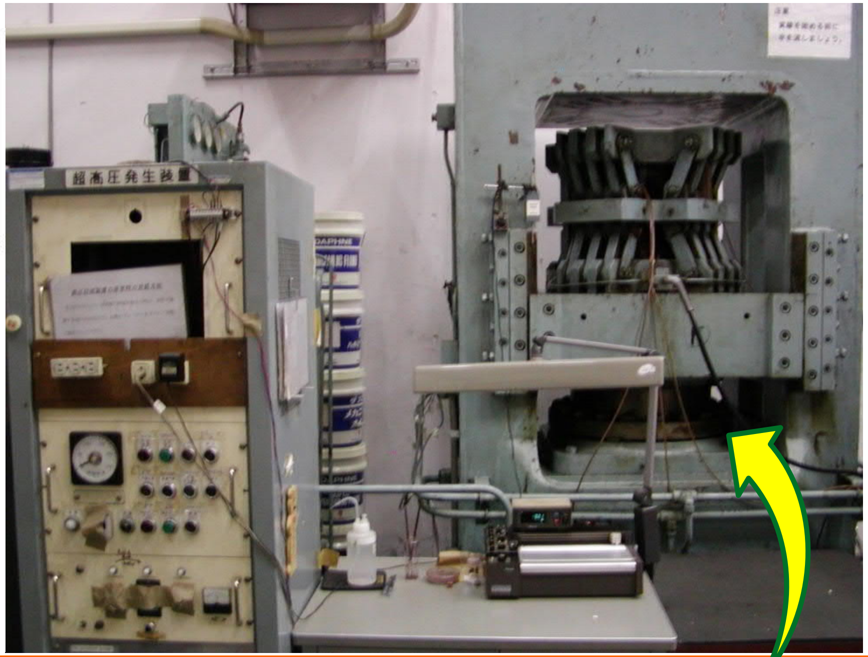
- $M_mA_2B_{n-1}Cu_nO_{m+2+2n\pm\delta}$
- M-m2(n-1)n
- HOMOLOGOUS SERIES: M, m, A and B fixed, n varies



m x ($MO_{1\pm\delta}$ layers)

M. Karppinen & H. Yamauchi,
Control of the charge inhomogeneity and high-*Tc* superconducting properties in homologous series of multi-layered copper oxides, *Mater. Sci. Eng. R* **26**, 51-96 (1999).





HIGH-PRESSURE SYNTHESIS

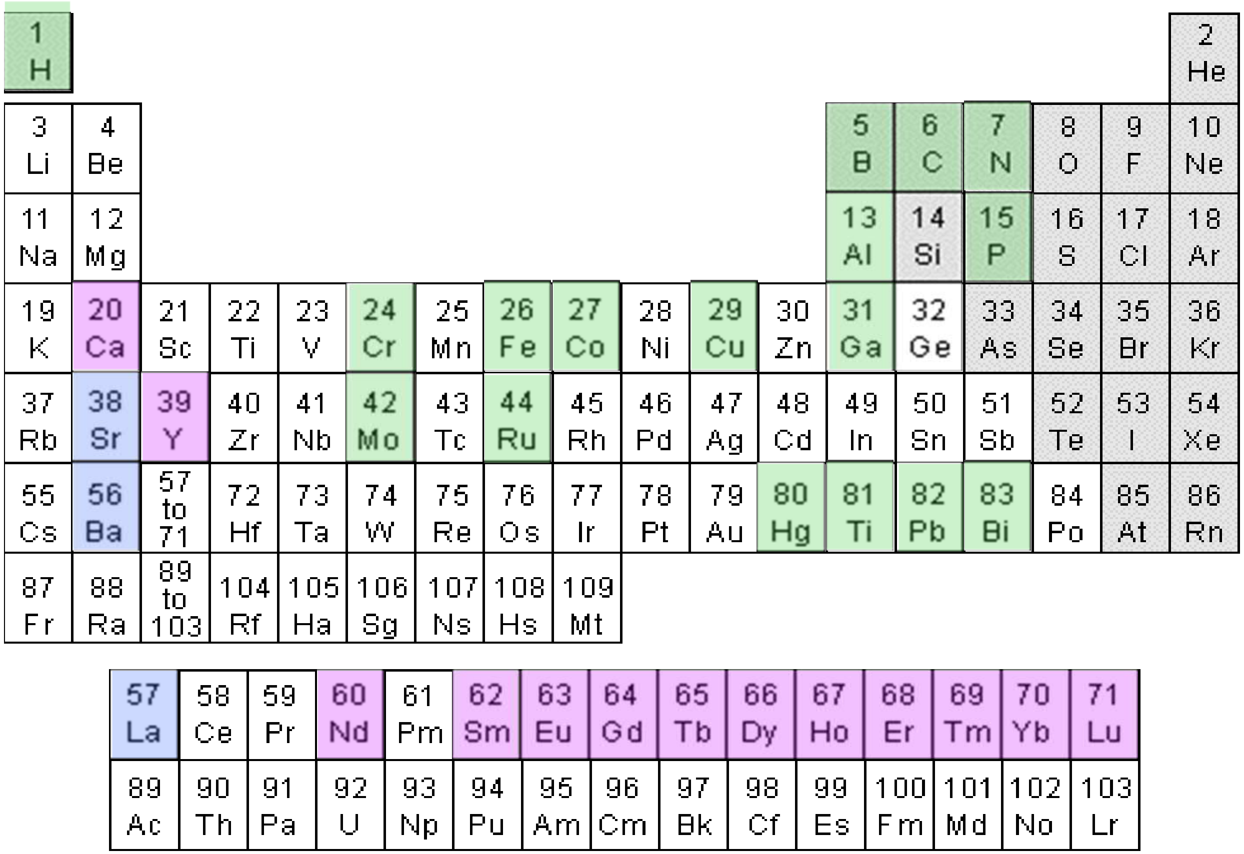
- **5 GPa = 50 000 atm**
- **400 – 1200 °C**
- **10 – 120 min**
- **50 – 100 mg**

HP equipment
at Tokyo Tech

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

$M_mA_2Q_{n-1}Cu_nO_{m+2+2n+\delta}$

M-m2(n-1)n

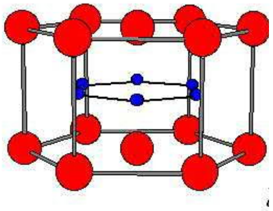


1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 to 103	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt									

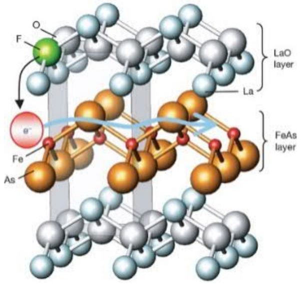
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

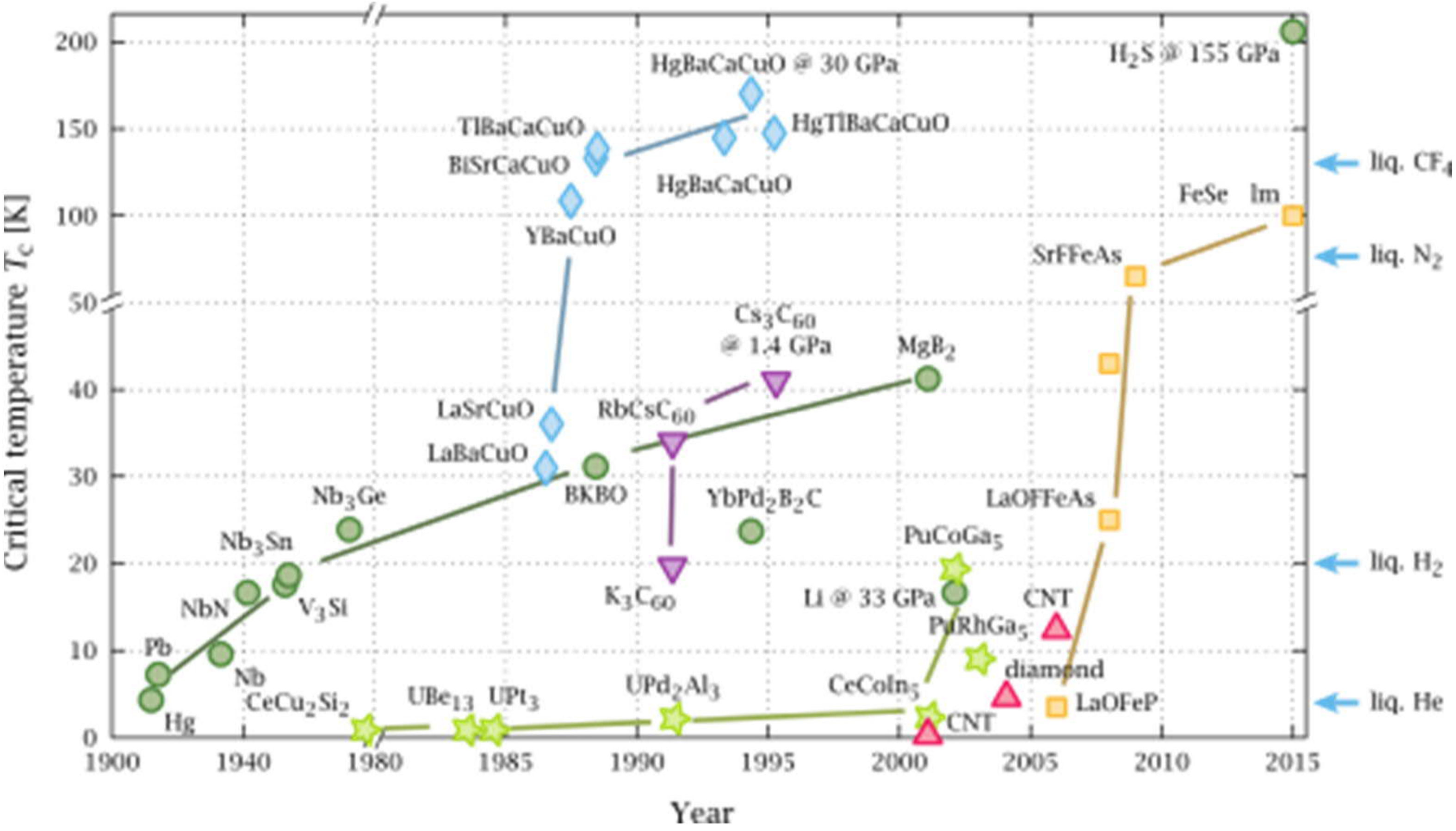
Akimitsu_fig2

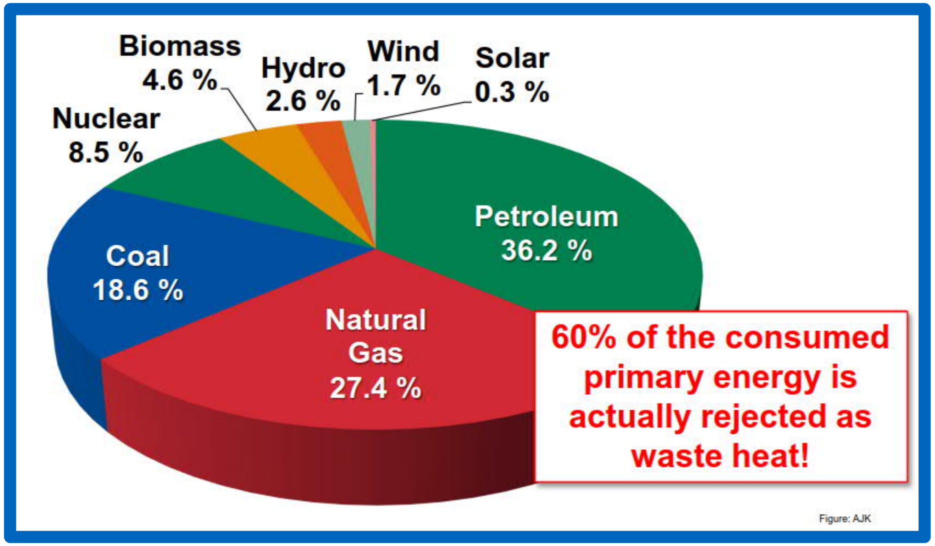
Akimitsu 2001:
MgB2



Hosono 2001:
[La(O,F)][FeAs]

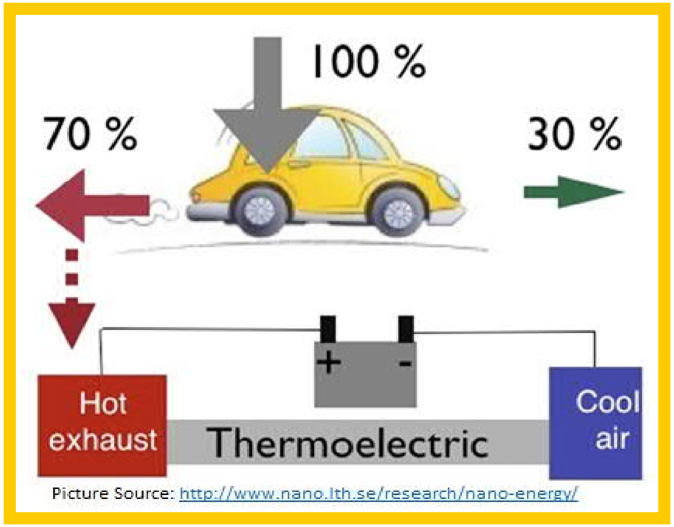




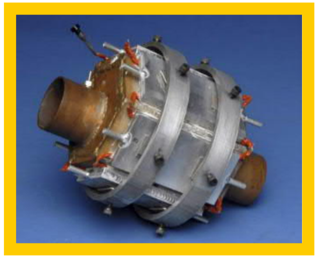


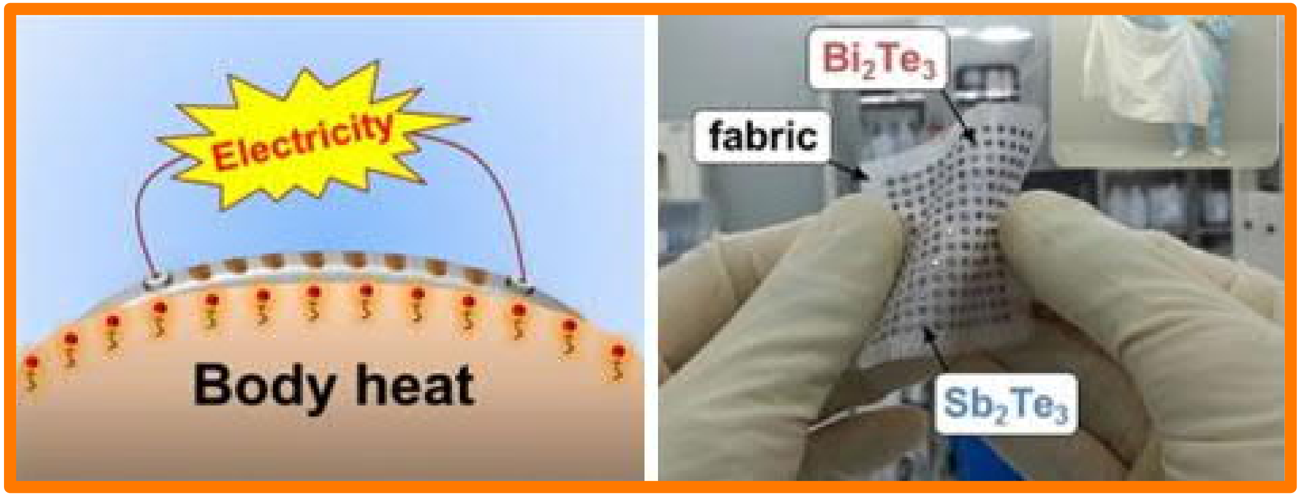
60% of the consumed primary energy is actually rejected as waste heat!

PRIMARY ENERGY SOURCES



Picture Source: http://www.nano.lth.se/research/nano-energy/





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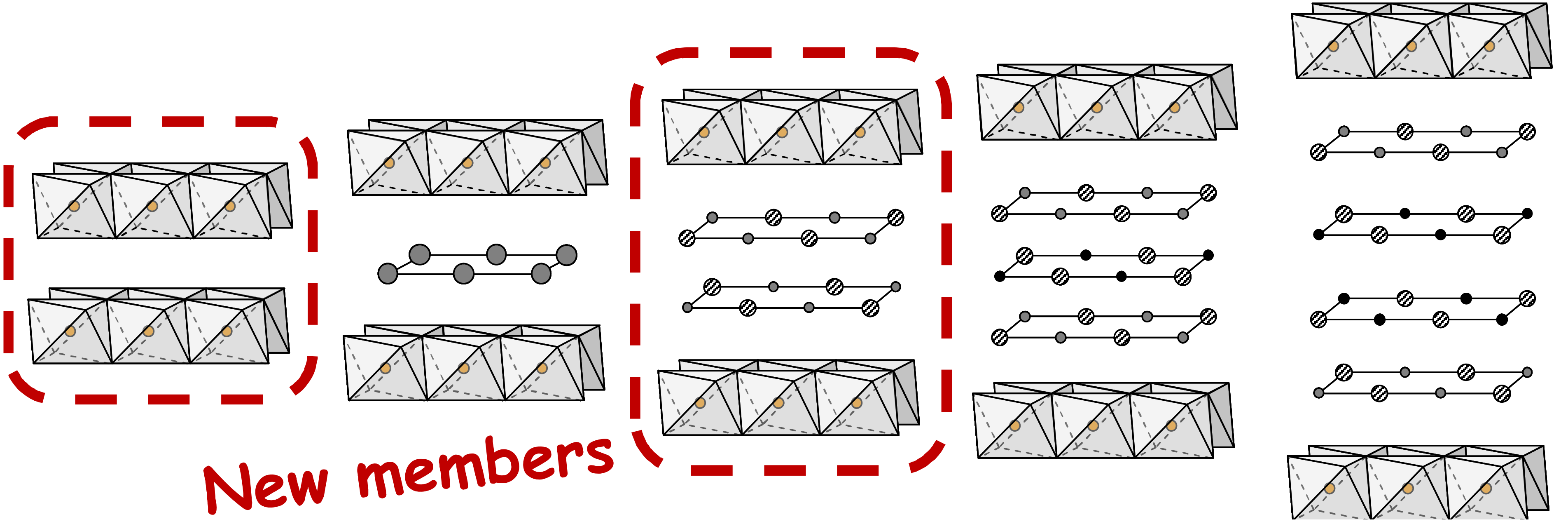
School of Chemical
Technology

THERMOELECTRICS: Electricity from (waste) Heat

HOMOLOGOUS SERIES of Thermoelectric Misfit Oxides

$[(MO)_m(AO)_k]_qCoO_2$

- Thermoelectric material: high electrical conductivity & ultralow thermal conductivity
- First oxide thermoelectric material: Na_xCoO_2 (viz. 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 (viz. HTSCs)
- ”Misfitting” metal oxide layers → structural complexity → low thermal conductivity
- Homologous series: understanding the general trends in the properties



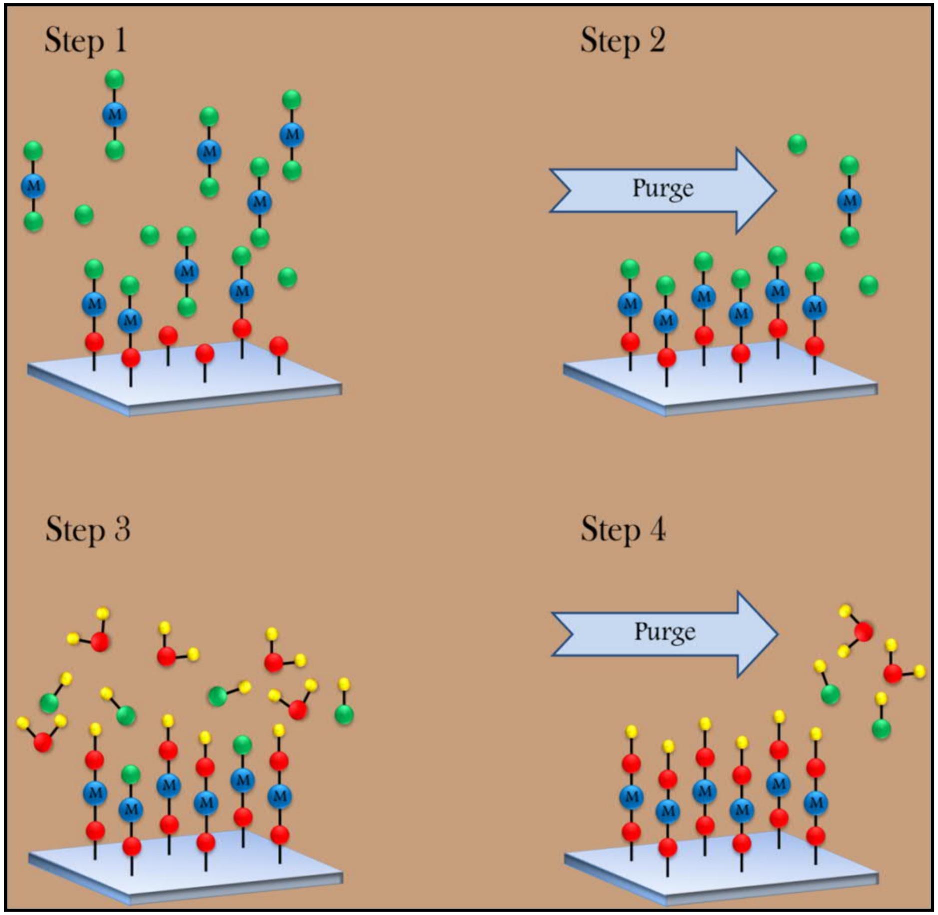
CoO_2
k=0, m=0

Na_xCoO_2
k=1, m=0

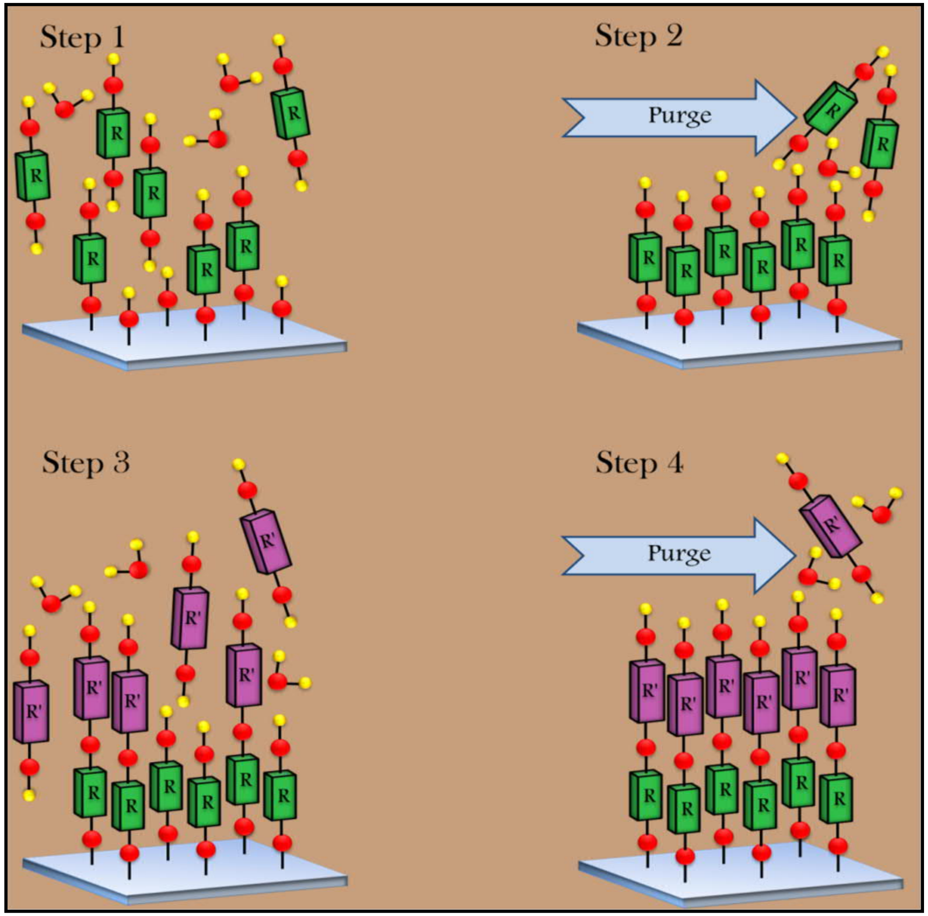
$[Sr_2O_2]_{0.5}CoO_2$
k=2, m=0

$[CoCa_2O_3]_qCoO_2$
k=2, m=1

$[Bi_2Sr_2O_4]_qCoO_2$
k=2, m=2



ALD (Atomic Layer Deposition)

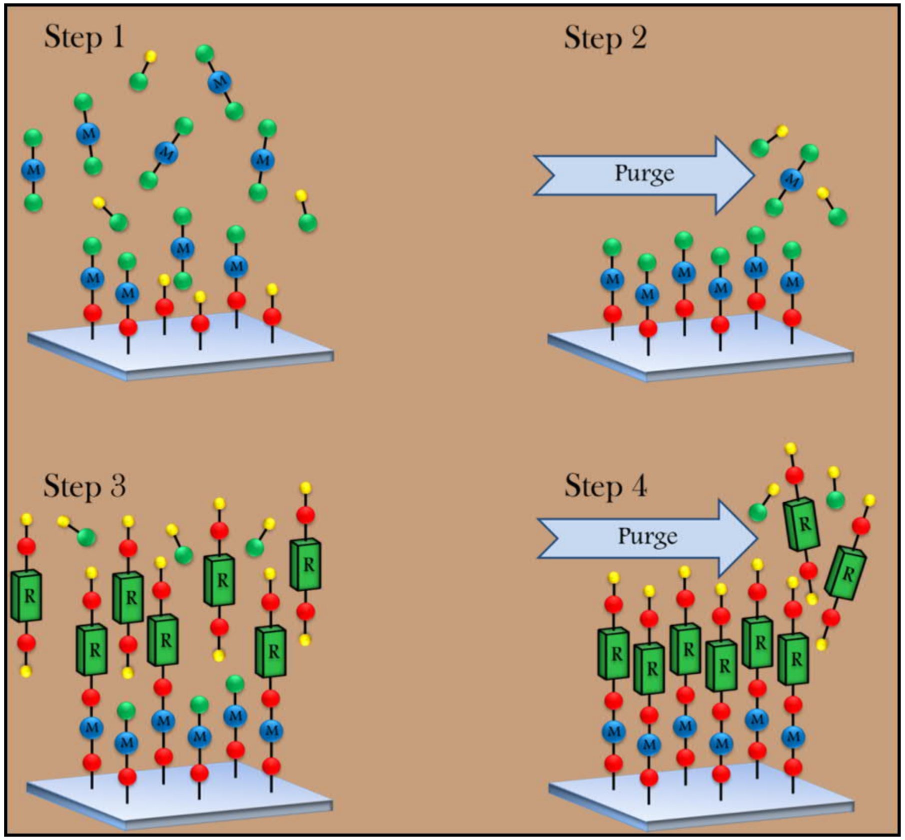


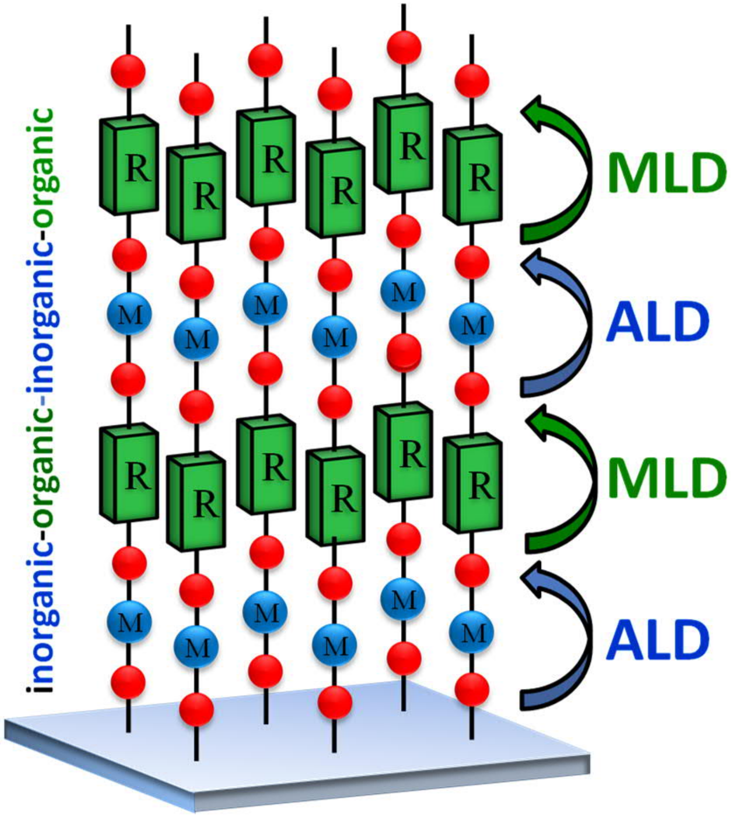
MLD (Molecular Layer Deposition)

High-quality
INORGANIC thin films
with atomic level control

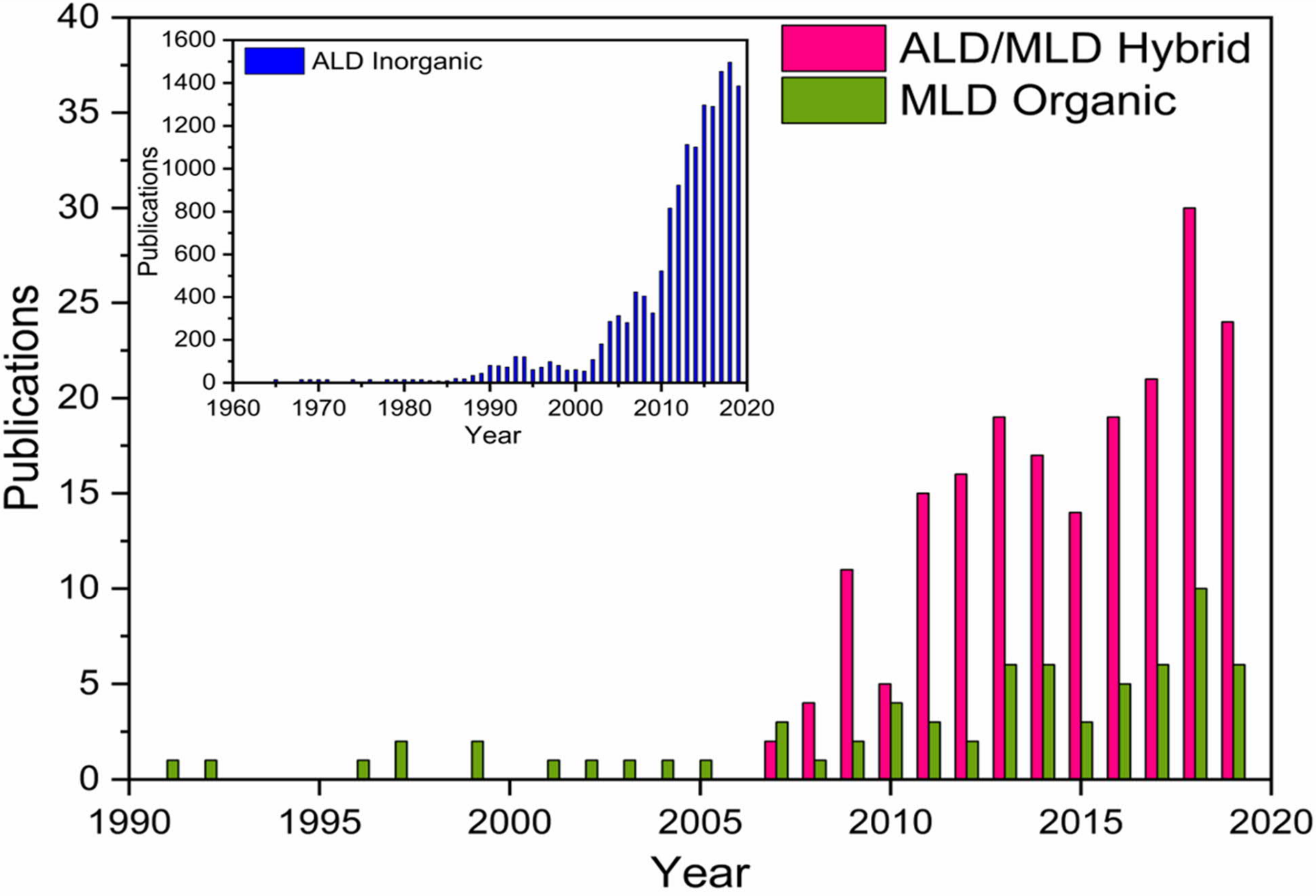
ORGANICS !
(in 1990s)

Inorganic-Organic Hybrid Thin Films
by Combined ALD/MLD

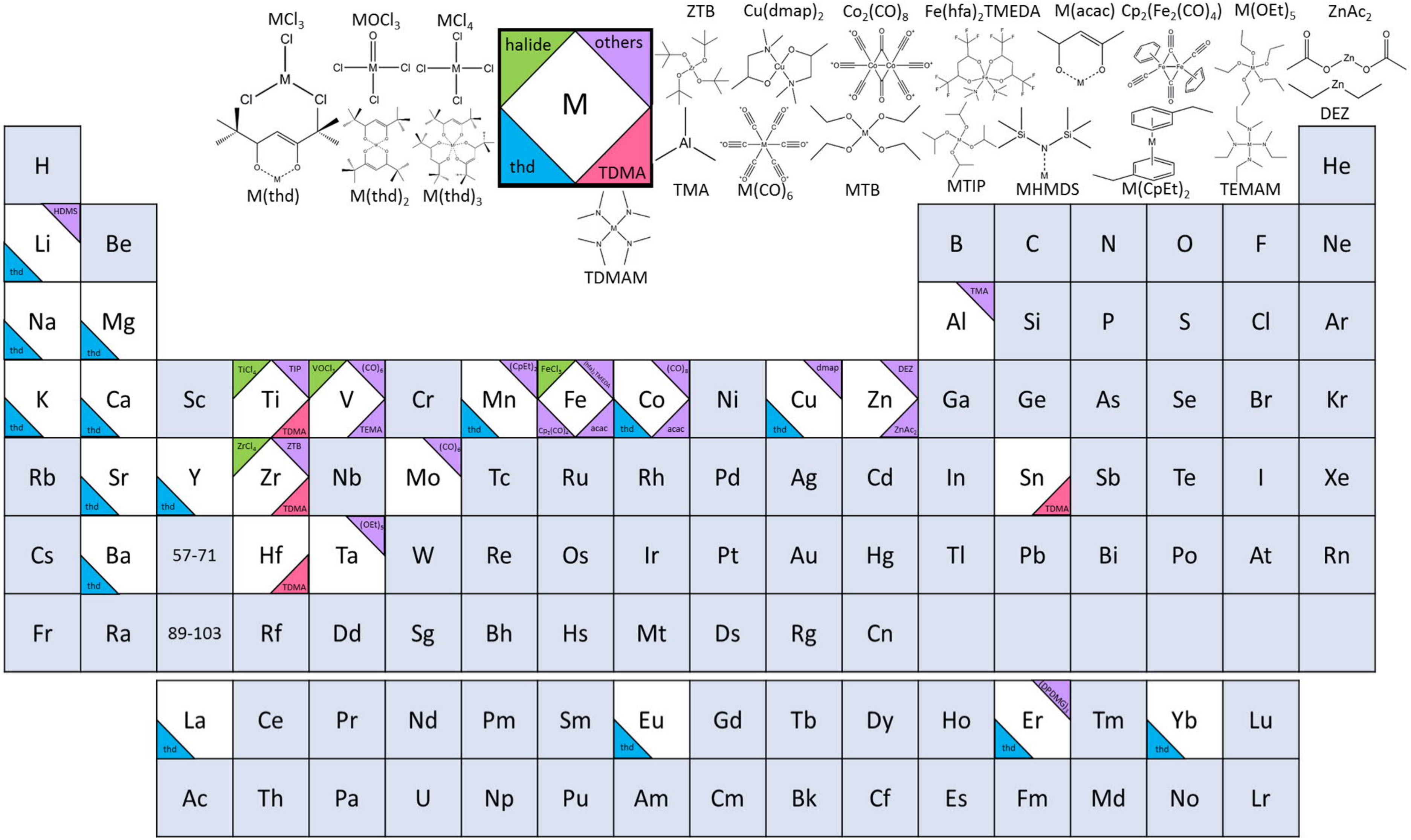




MULTIFUNCTIONAL SINGLE-PHASE HYBRID (compound) MATERIALS !!!



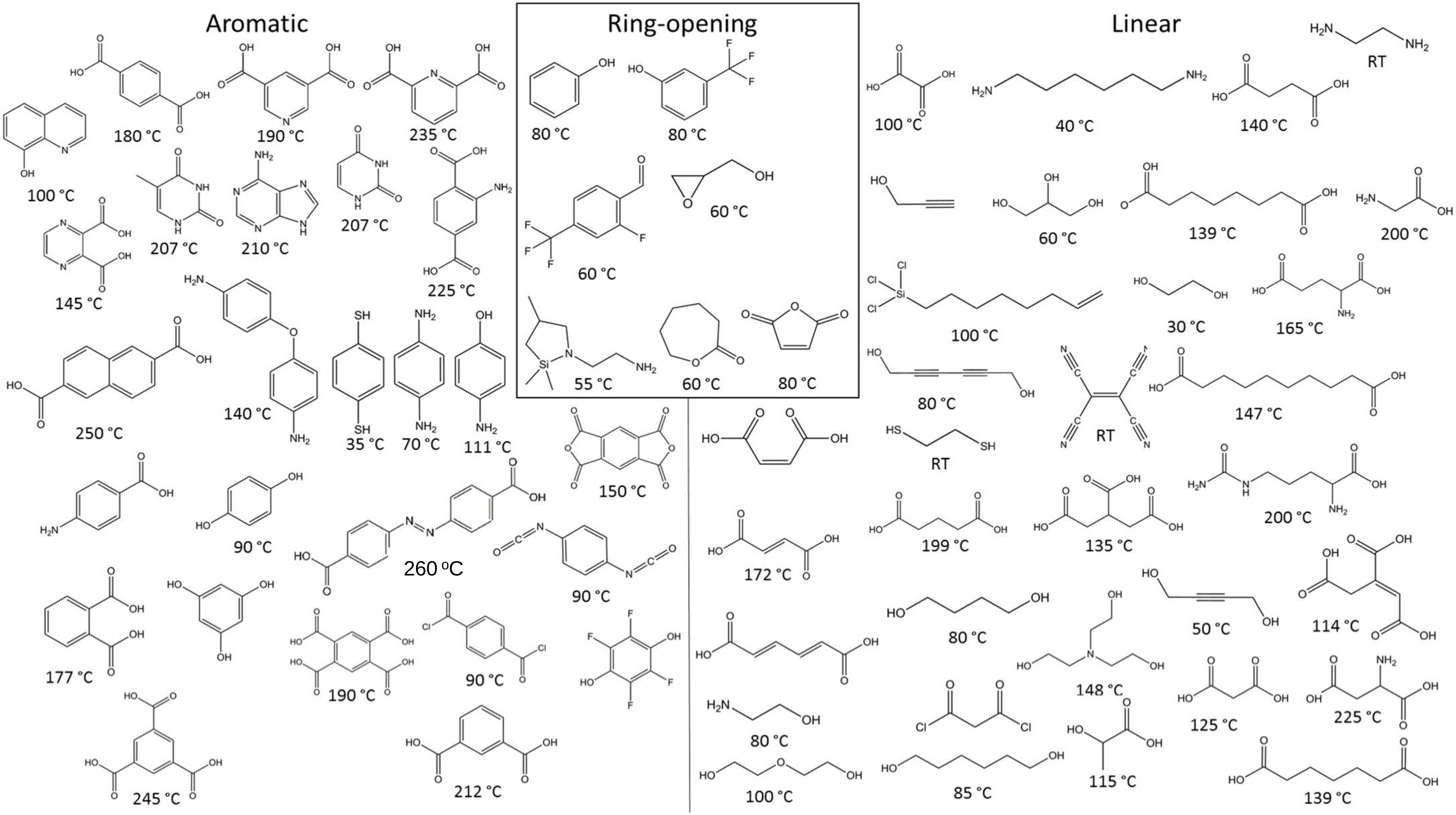
ALD/MLD Hybrid
MLD Organic
Publications
Year
0
5
10
15
20
25
30
35
40
1990
1995
2000
2005
2010
2015
2020
ALD Inorganic
0
200
400
600
800
1000
1200
1400
1600
1960
1970
1980
1990
2000
2010
2020



H																	He
Li HDMS thd	Be											B	C	N	O	F	Ne
Na thd	Mg thd											Al TMA	Si	P	S	Cl	Ar
K thd	Ca thd	Sc	Ti $TiCl_4$ TIP TDMA	V $VOCl_3$ $(CO)_6$ TEMA	Cr	Mn $(CpEt)_2$ thd	Fe $FeCl_3$ $(hfa)_2TMEDA$ $Cp_2(CO)_4$ acac	Co $(CO)_8$ thd acac	Ni	Cu dmap thd	Zn DEZ $ZnAc_2$	Ga	Ge	As	Se	Br	Kr
Rb	Sr thd	Y thd	Zr $ZrCl_4$ ZTB TDMA	Nb	Mo $(CO)_6$	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn TDMA	Sb	Te	I	Xe
Cs	Ba thd	57-71	Hf TDMA	Ta $(OEt)_5$	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-103	Rf	Dd	Sg	Bh	Hs	Mt	Ds	Rg	Cn						
		La thd	Ce	Pr	Nd	Pm	Sm	Eu thd	Gd	Tb	Dy	Ho	Er thd $(DPDMG)_3$	Tm	Yb thd	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Aalto University
School of Chemical Technology

ALD/MLD Processes: Metal Precursors



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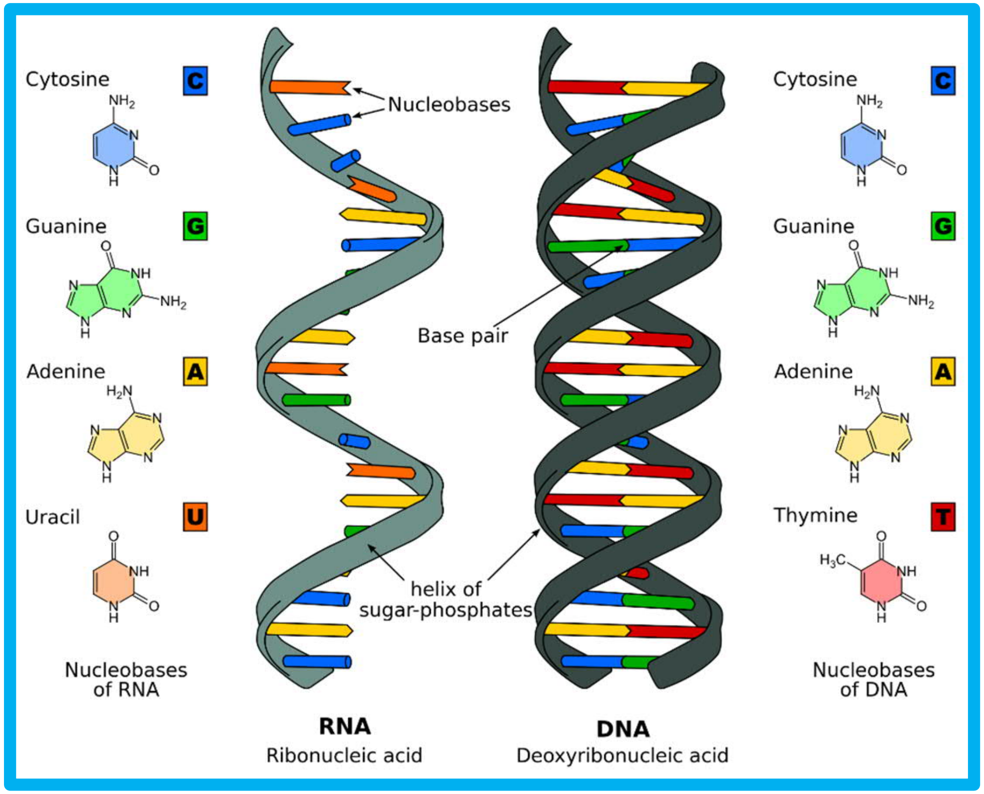
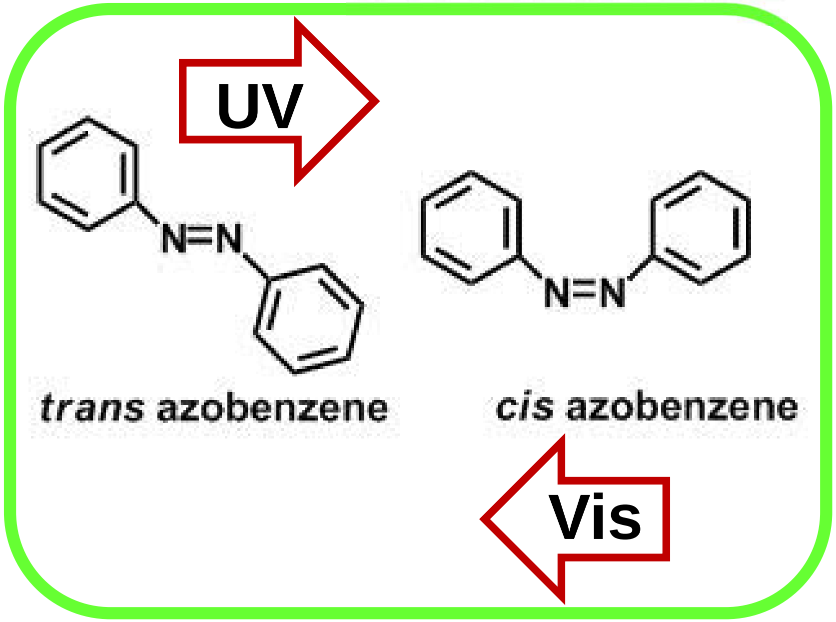
ALD/MLD Processes: Organic Precursors

(sublimation temperatures)



NUCLEOBASES FROM NATURE

PHOTORESPONSIVE AZOBENZENE

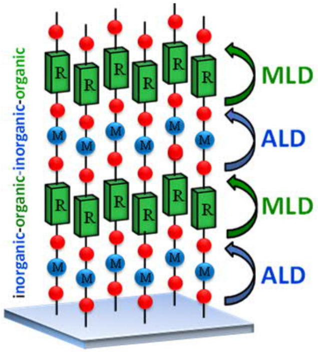


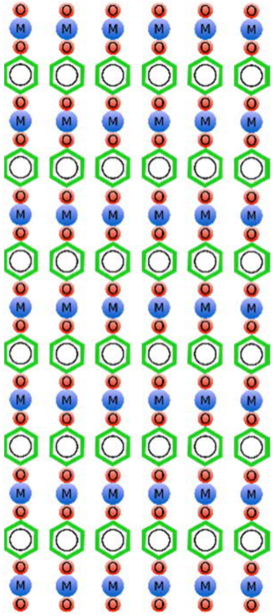
NEW EXCITING ORGANIC COMPONENTS

⬡ **Organic** (e.g. benzene)

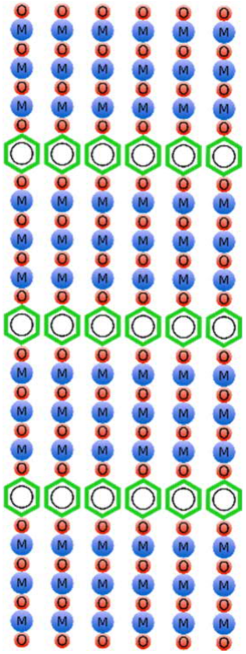
M **Metal**

O **Oxygen** (or N, S, …)

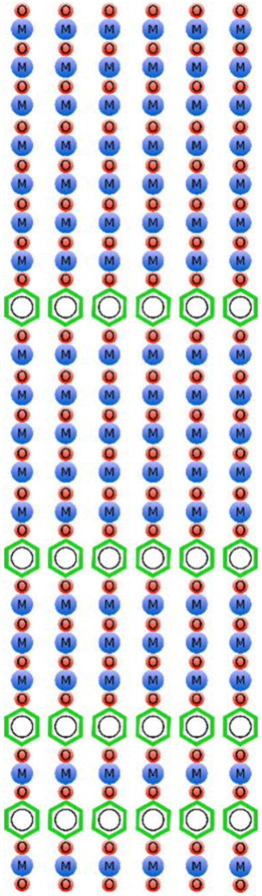




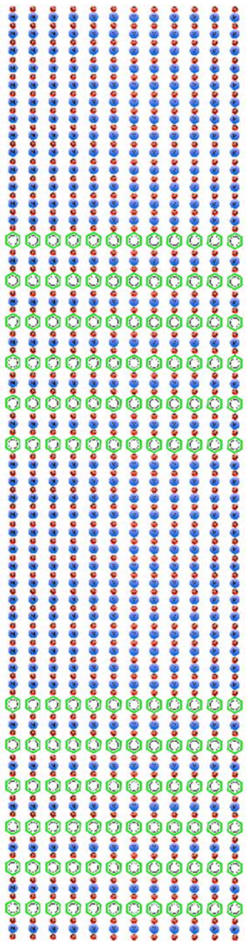
Simple
Metal-Organic Network
(amorphous or crystalline)



Superlattice



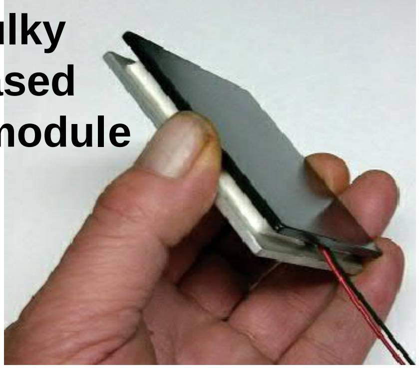
Gradient hybrid



Nanolaminate

DIFFERENT LAYER SEQUENCES BY DESIGN

Conventional bulky & rigid Bi_2Te_3-based thermoelectric module



MATERIAL DEVELOPMENT for THERMOELECTRICS

- **Higher Conversion Efficiency**

  - high electrical conductivity & low thermal conductivity

- **Sustainable Raw Materials**

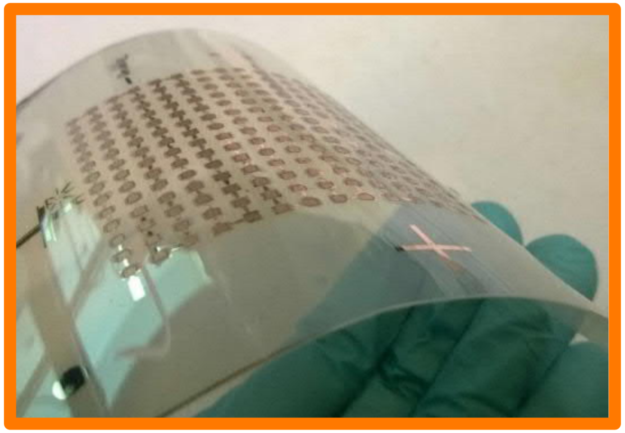
  - Earth-abundant ”noncritical” elements

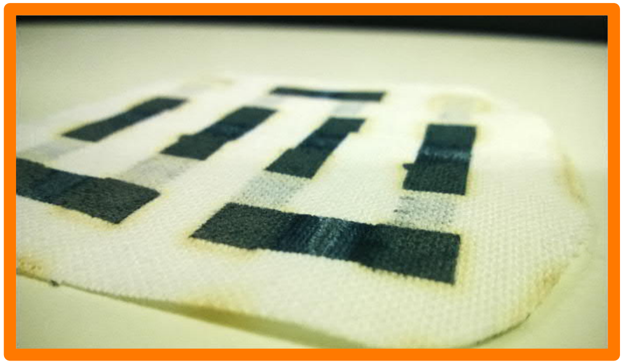
- **Mechanical flexibility**

  - organic components

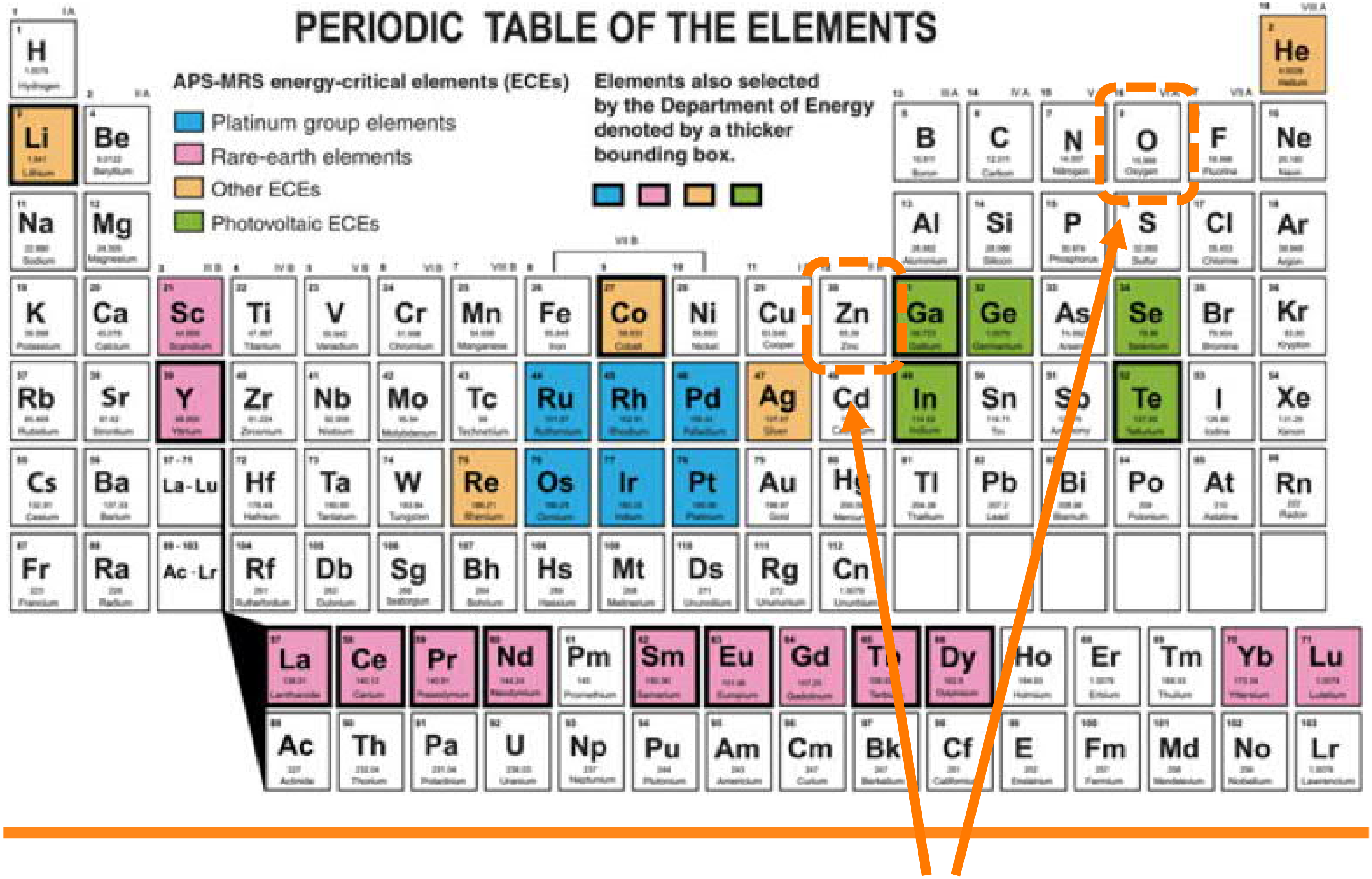
  - deposition on flexible surfaces

Examples of our efforts





Energy Critical Elements (by APS & MRS)



PERIODIC TABLE OF THE ELEMENTS

APS-MRS energy-critical elements (ECEs)

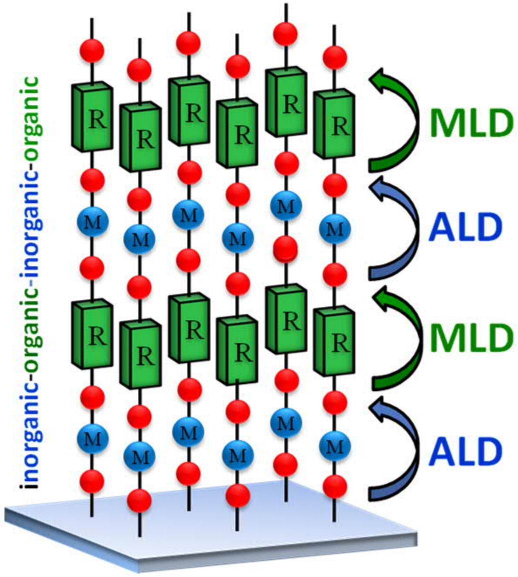
- 🟦 Platinum group elements
- 🟪 Rare-earth elements
- 🟧 Other ECEs
- 🟩 Photovoltaic ECEs

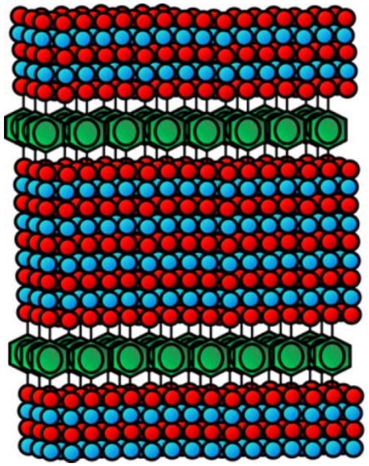
Elements also selected by the Department of Energy denoted by a thicker bounding box.

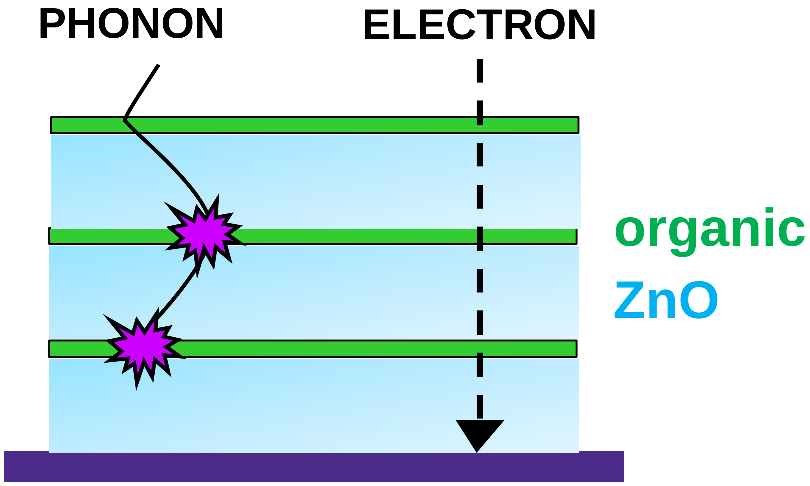
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	E	Fm	Md	No	Lr

OUR CHOICE: ZnO

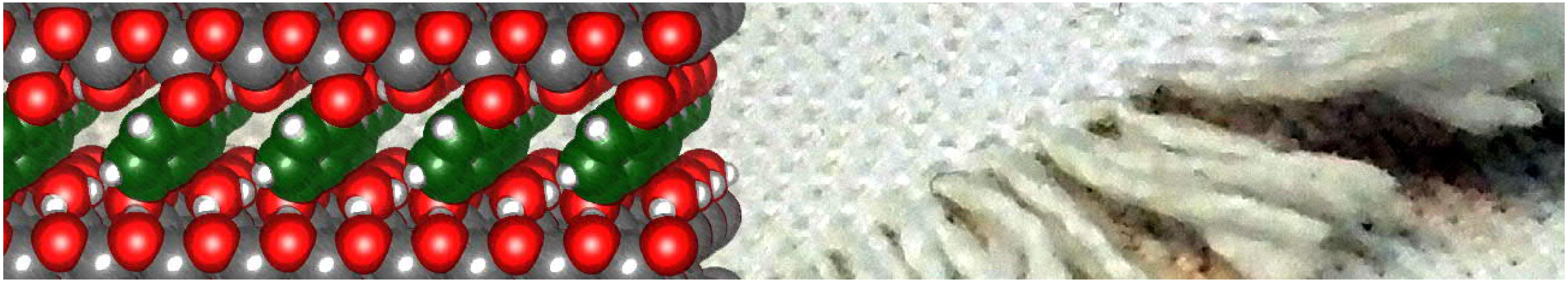






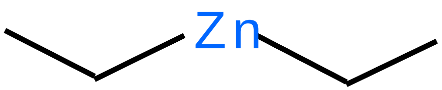
Sustainable OXIDE-ORGANIC Thermoelectric Superlattice Thin Films

- **More than 50-times improved thermoelectric properties**
- **Fabricated with industry-feasible ”Finnish” ALD/MLD technology**
- **Flexible/wearable thermoelectric coatings integrated with e.g. textiles**

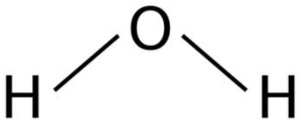


ALD/MLD for ZnO : Benzene superlattice

$Zn(CH_2CH_3)_2$



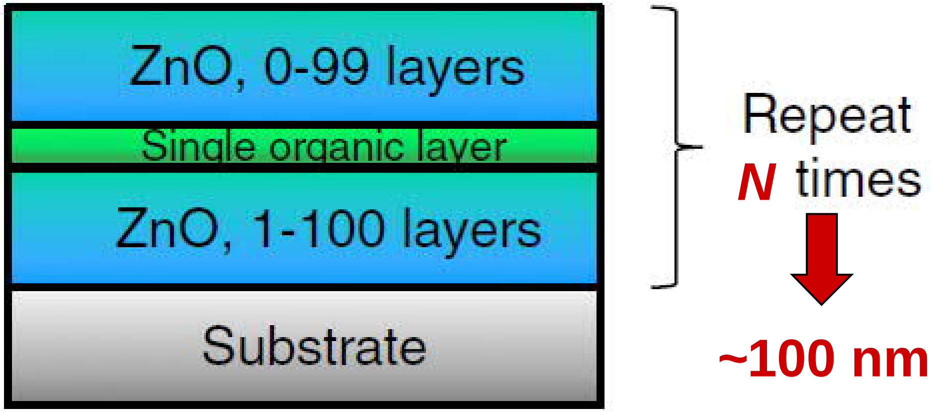
Water



HQ: Hydroquinone

DEPOSITIONS

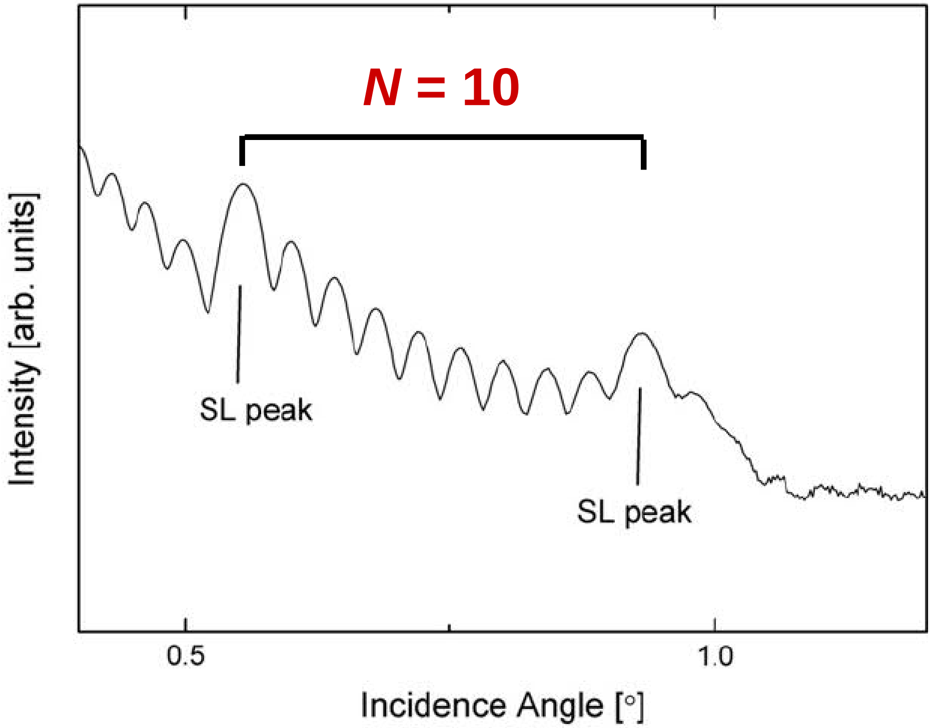
- 220 °C
- 600 ALD/MLD cycles in total



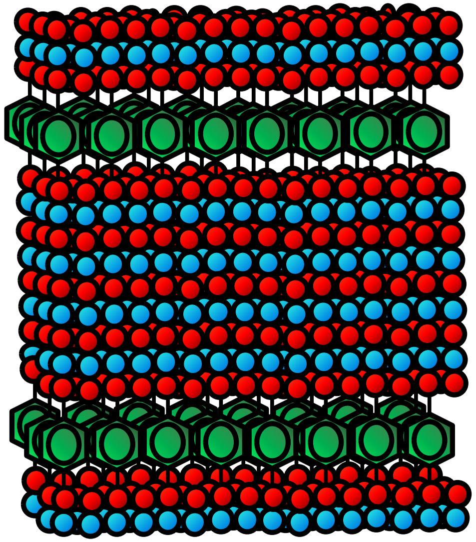
Repeat
N times

~100 nm

XRR: X-ray Reflectivity



ZnO : benzene



SUPERLATTICE PERIOD

99 : 1 → 16 nm
49 : 1 → 8 nm
29 : 1 → 5 nm
9 : 1 → 2 nm
4 : 1 → 1 nm

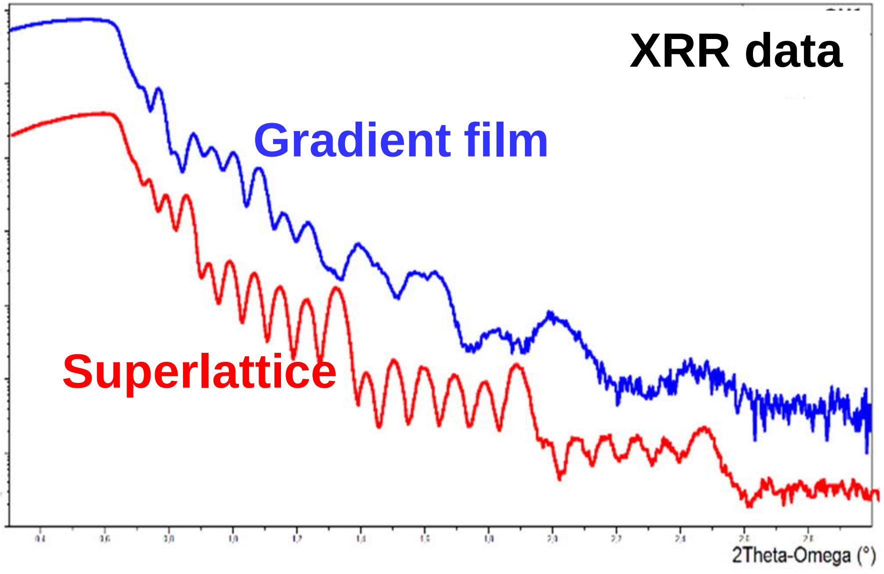
THERMAL CONDUCTIVITY (at RT)

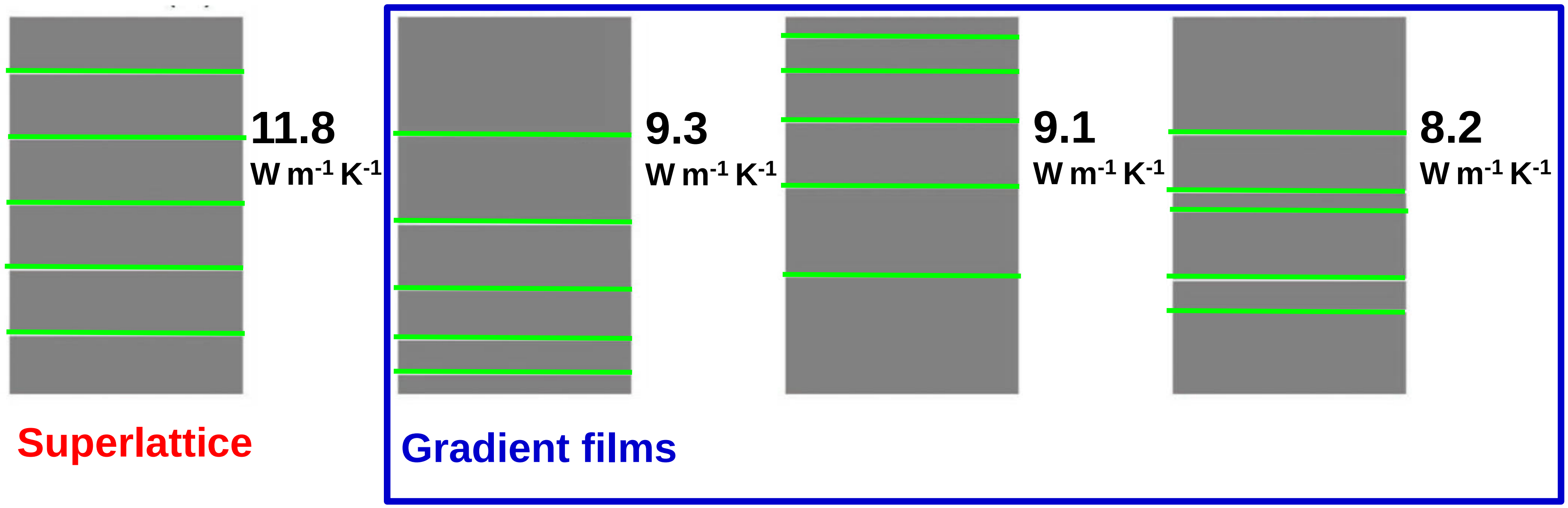
Sample	**K [W m^{-1} K^{-1}]**
ZnO	~43
ZnO : benzene **(99 : 1)**	7.1
ZnO : benzene **(49 : 1)**	4.1
ZnO : benzene **(29 : 1)**	3.1
ZnO : benzene **(9 : 1)**	1.3
ZnO : benzene **(4 : 1)**	0.7

- T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, ***J. Mater. Chem. A* 2**, 12150 (2014).
- A. Giri, J.-P. Niemelä, C.J. Szwejkowski, M. Karppinen & P.E. Hopkins, ***Phys. Rev. B* 93**, 024201 (2016).
- A. Giri, J.-P. Niemelä, T. Tynell, J. Gaskins, B.F. Donovan, M. Karppinen & P.E. Hopkins, ***Phys. Rev. B* 93**, 115310 (2016).

Total film thickness: ~105 nm
Number of organic layers: 5
Average ZnO layer thickness: ~17 nm

Superlattice: all ZnO layers ~17 nm
Gradient film: ZnO layers 9 ~ 28 nm





Aalto University
School of Chemical Technology

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).

- **Metal Coordination Complex**

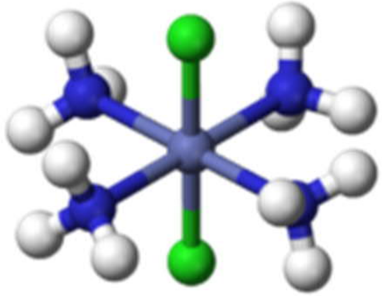
  - central metal atom + ligands

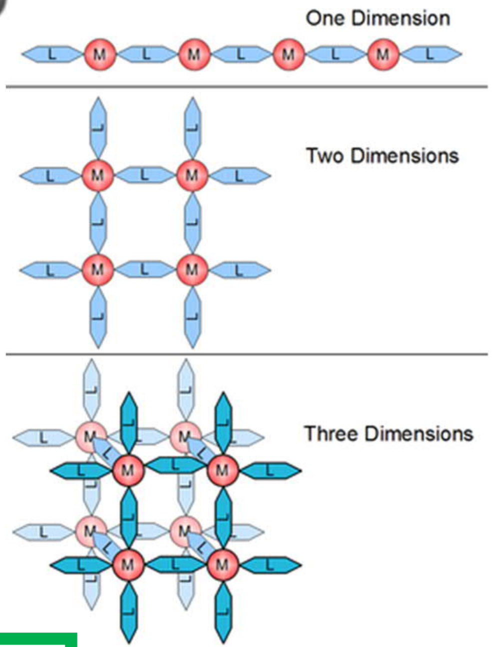
- **Coordination Network**

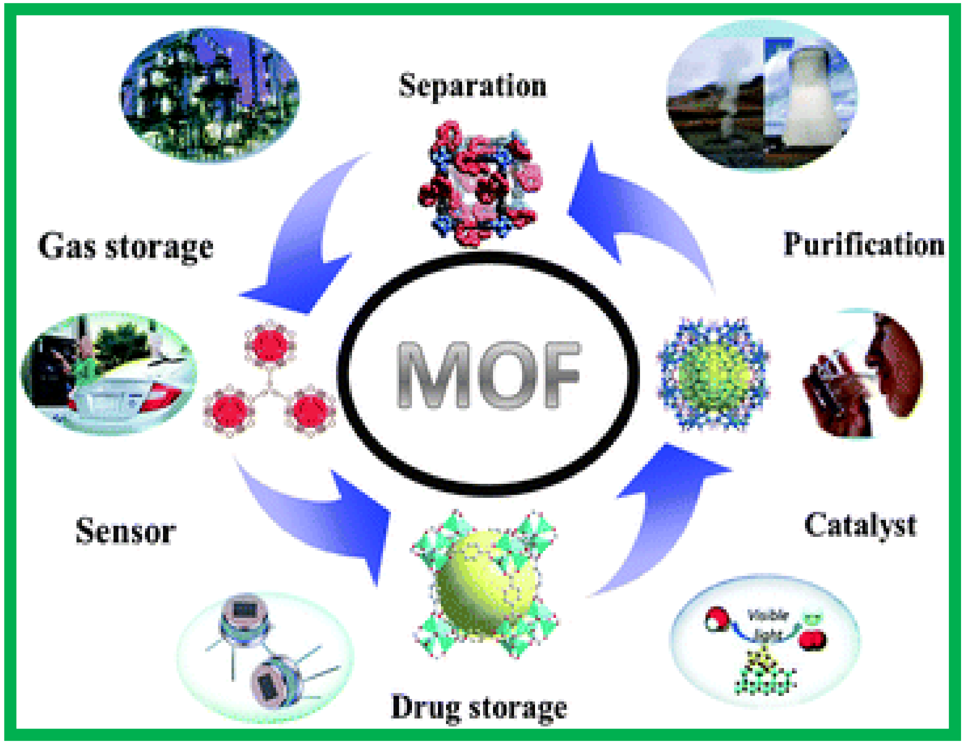
  - organic ligands act as linkers
  - 1D, 2D or 3D materials

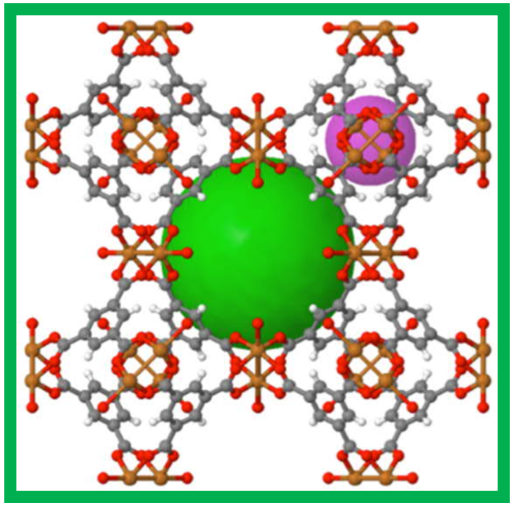
- **Metal Organic Framework (MOF)**

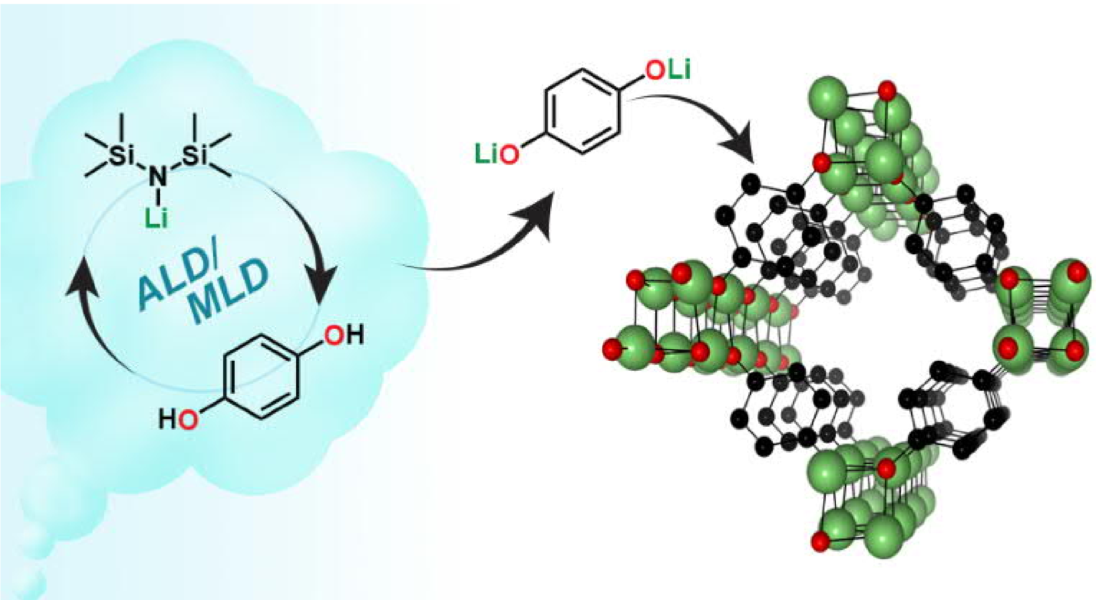
  - highly porous materials
  - attractive application possibilities

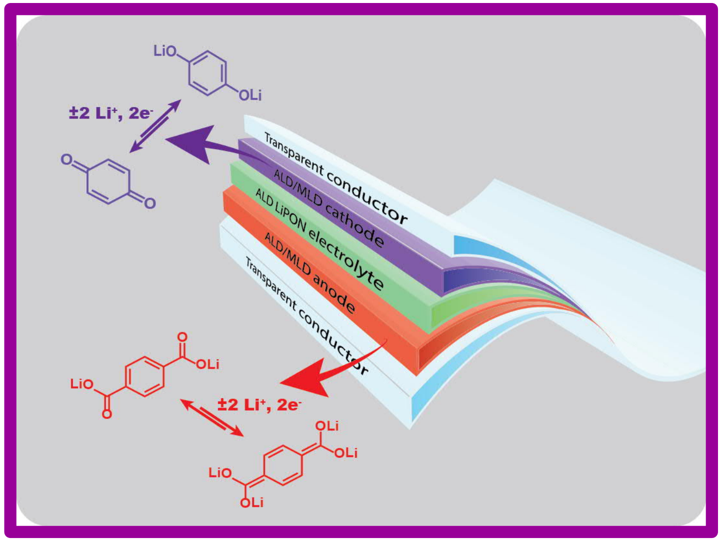












TOYOTA

ALD / MLD

Gaseous Precursors → **Crystalline Li-Organic Thin Films**

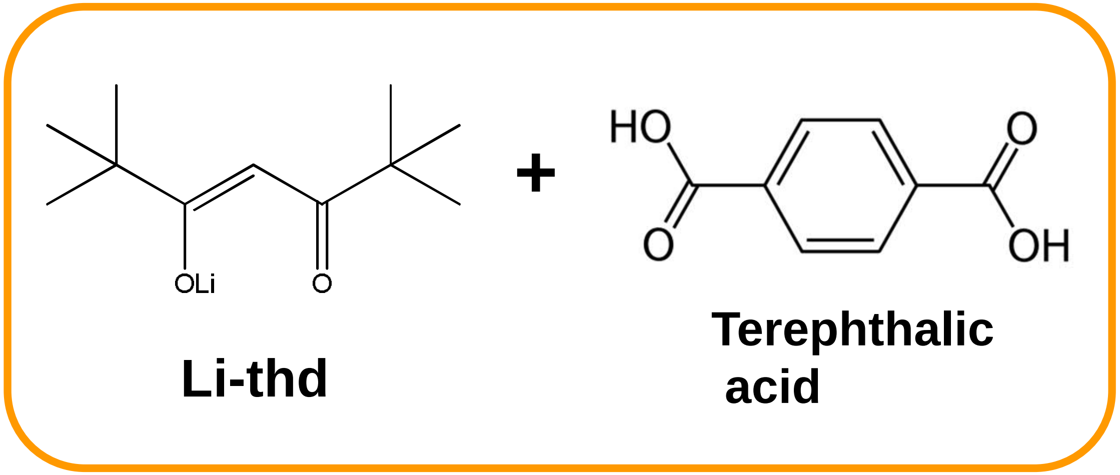
- **NOT (necessarily) made by any other technique**
- **Structure by computational modelling**
- **Promising ELECTRODES for Li-ion battery**

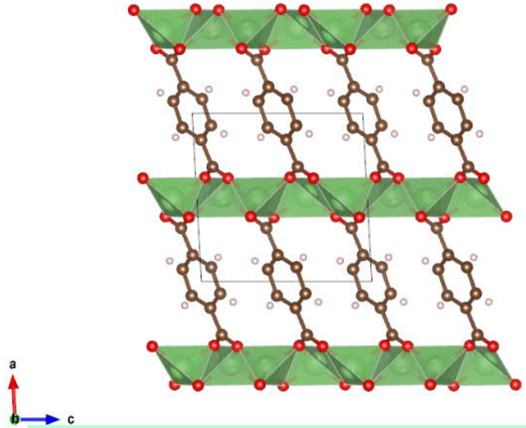
Aalto University
School of Engineering

- M. Nisula, Y. Shindo, H. Koga & M. Karppinen, *Chem. Mater.* **27**, 6987 (2015).
- M. Nisula & M. Karppinen, *Nano Letters* **16**, 1276 (2016).
- M. Nisula, J. Linnera, A.J. Karttunen & M. Karppinen, *Chem. Eur. J.* **23**, 2988 (2017).
- M. Nisula & M. Karppinen, *J. Mater. Chem. A* **6**, 7027 (2018).
- J. Heiska, M. Nisula & M. Karppinen, *J. Mater. Chem. A* **7**, 18735 (2019).

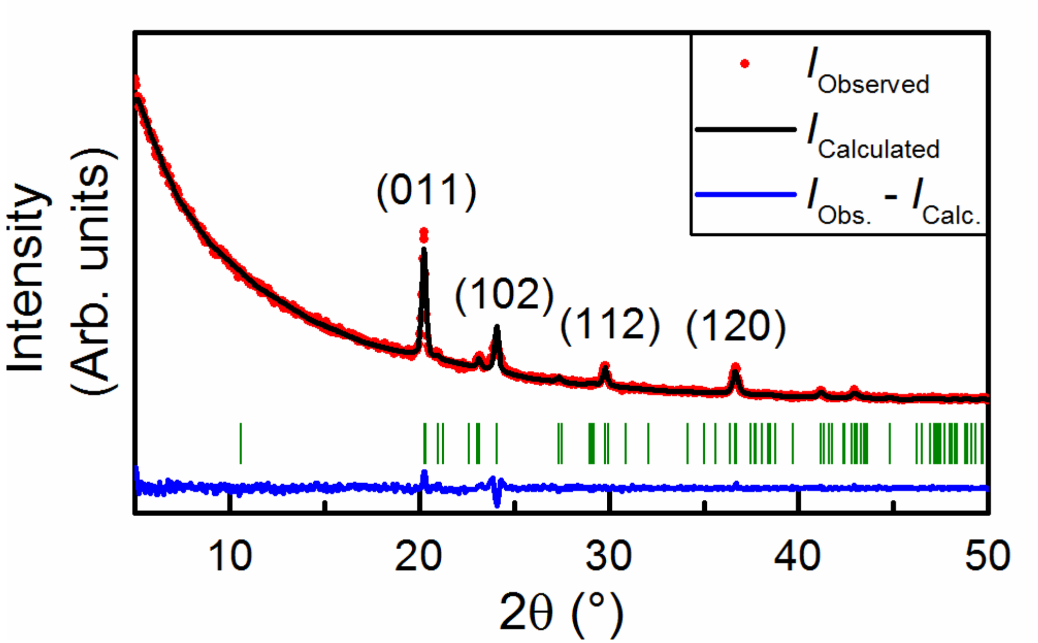
ANODE
Li-terephthalate

ALD/MLD:
Li-thd + TPA





Layered structure with alternating layers of LiO_4 tetrahedra & benzene-rings



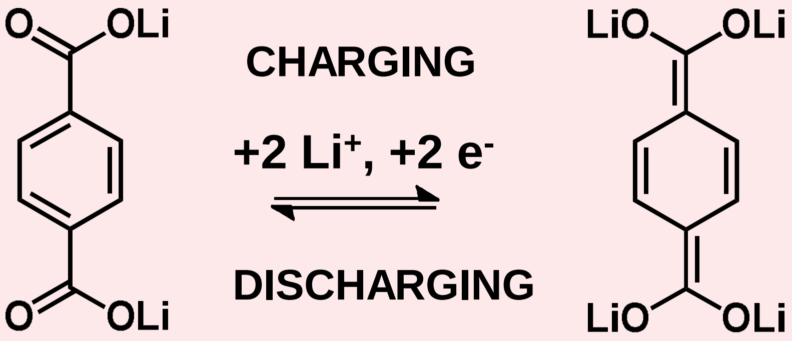
M. Nisula & M. Karppinen, Atomic/molecular layer deposition of lithium terephthalate thin films as high rate capability Li-ion battery anodes, *Nano Lett.* **16**, 1276 (2016).

ORGANIC ELECTRODE MATERIALS

- **Sustainable in terms of elemental composition → Long-term dream**
- **Light elements only & Multiple electron transfer reactions**
  → High specific capacities
- **For example: Tarascon *et al.*, *Nature Mater*. 8, 120 (2009)**

Lithium terephthalate Li-TP

- Redox potential: 0.8 V vs. Li
- Specific capacity: 300 mAh/g
- Volume change: small (6%)



- **MAJOR PROBLEMS (in a conventional bulk wet-cell)**

- Dissolution in conventional liquid electrolytes → Solid electrolyte

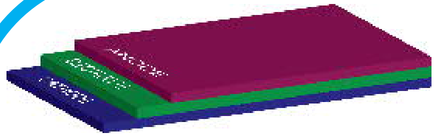
- Intrinsically extremely low electronic conductivity → Ultrathin film

→ THIN-FILM MICROBATTERY

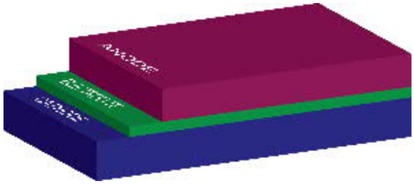
THIN-FILM MICROBATTERY

- **Trade-off: Energy density – *versus* – Power density**
- **SOLUTION: Planar → 3D structure**

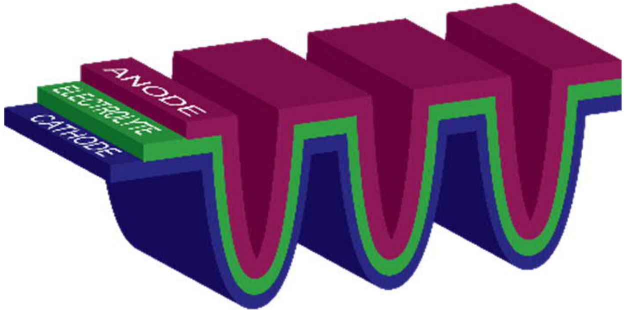
Concept of 3D Thin-Film Battery



High POWER



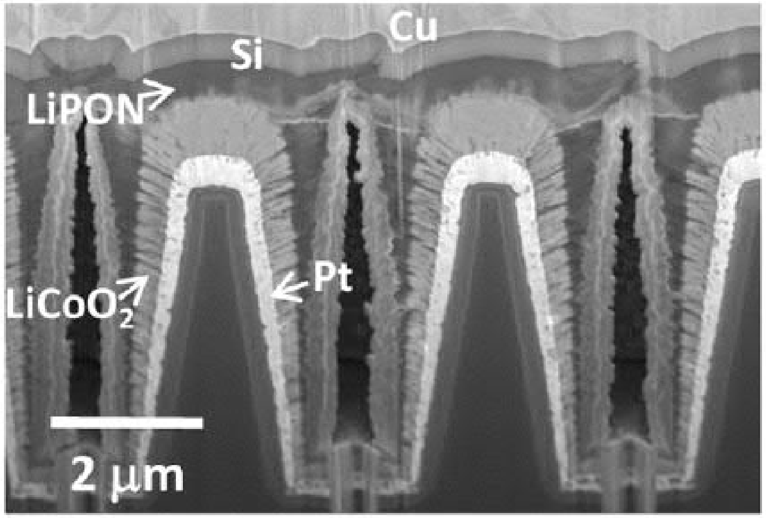
High ENERGY



Notten *et al*.,
3D integrated all-solid-state
rechargeable batteries,
***Appl. Mater.* (2007)**

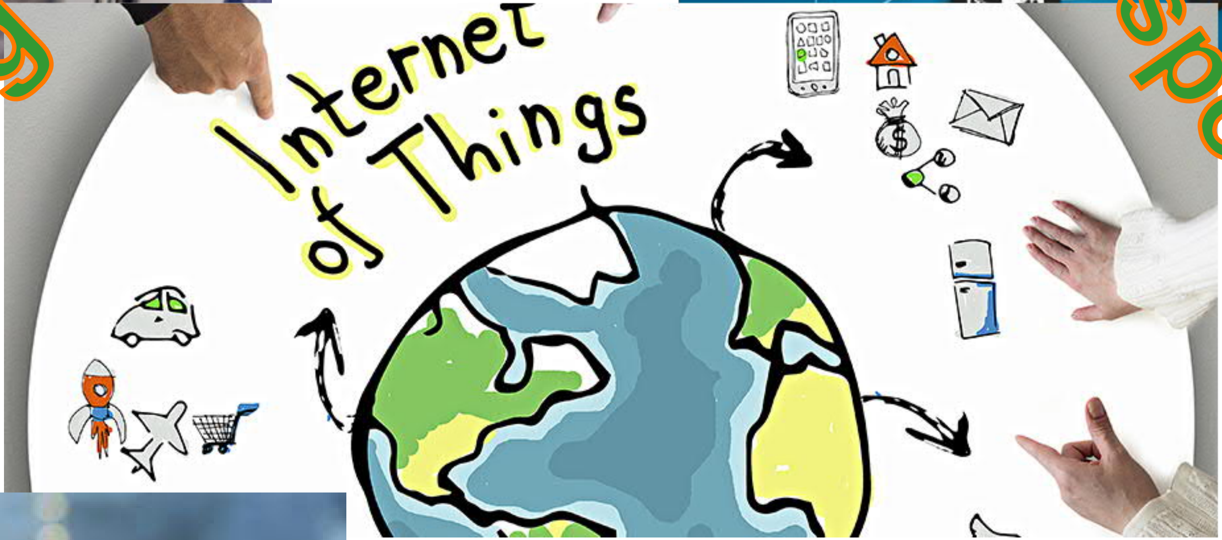
Sputtering → Low Performance

Talin et al.,
Fabrication, testing and simulation of
all-solid-state 3D Li-ion batteries,
***ACS Appl. Mater. Interfaces* (2016)**



Acting

Sensing



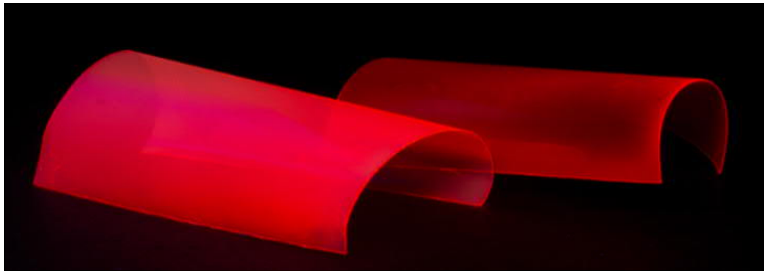
Responding

Connecting

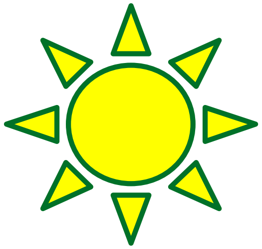
THERMOELECTRICS: electric power locally from waste (body) heat

THIN-FILM MICROBATTERY: local energy storage

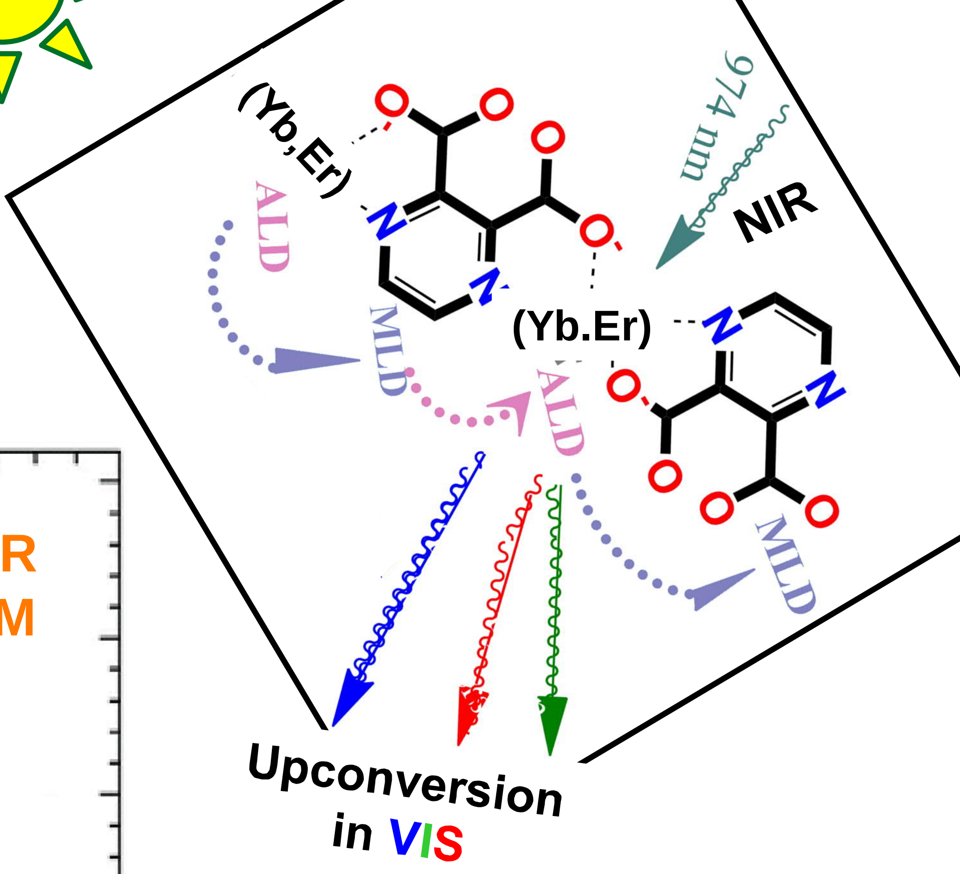
PHOTOLUMINESCENCE:
VIS from UV radiation

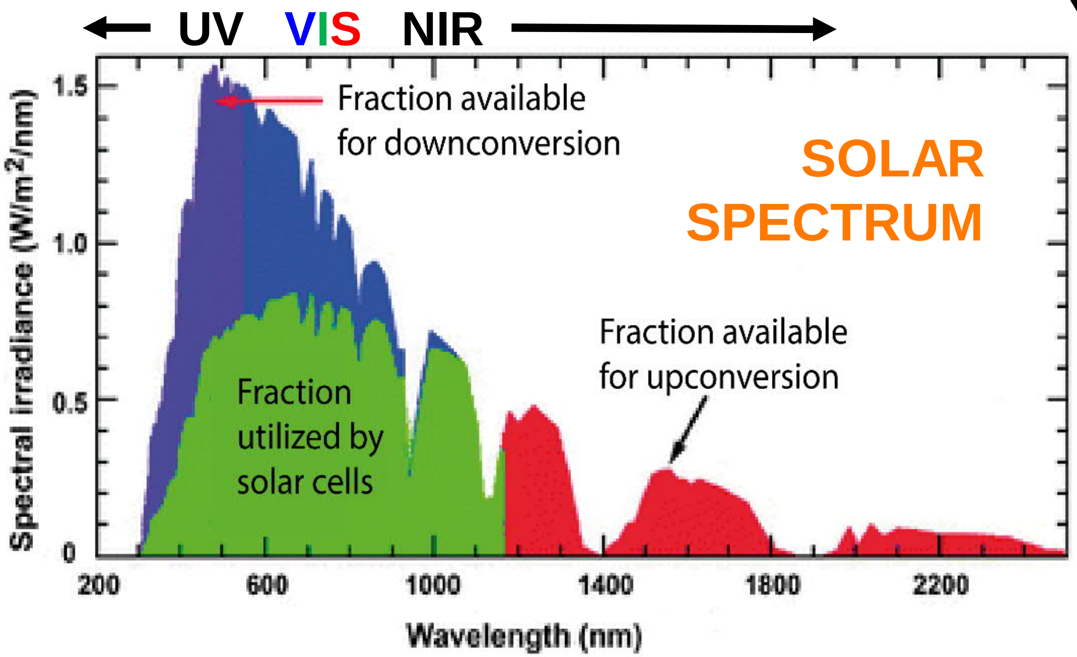


Eu-organic ALD/MLD films



UPCONVERSION:
VIS from NIR radiation



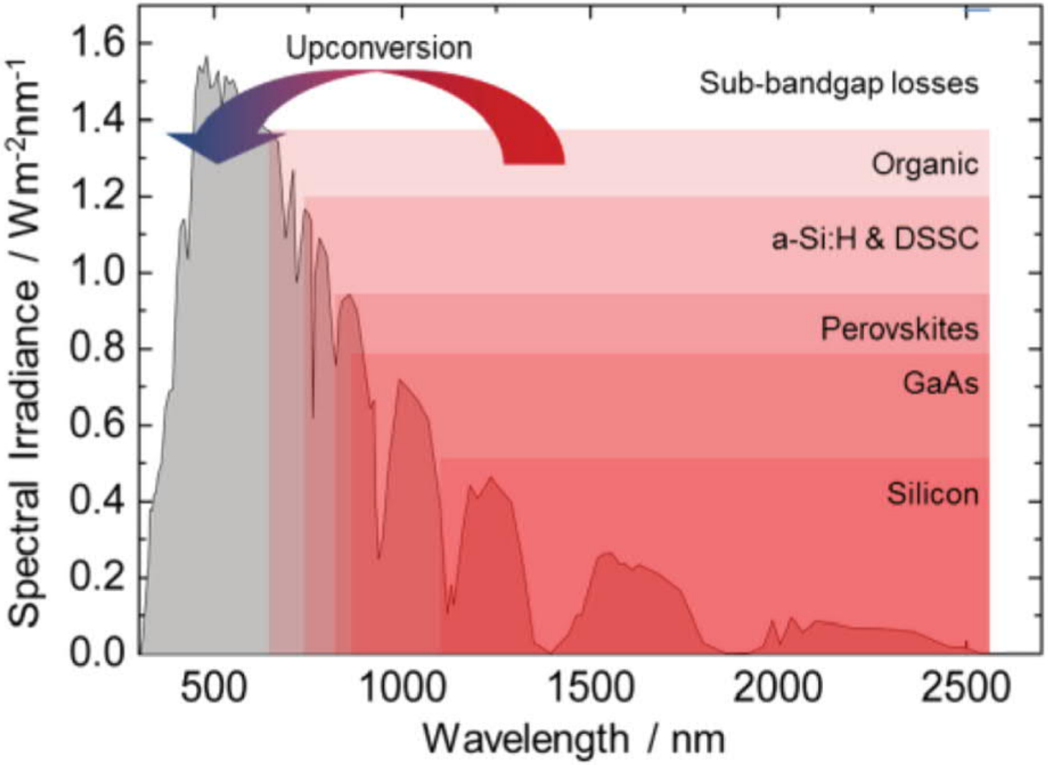


SOLAR SPECTRUM

(Yb,Er)-organic ALD/MLD films

Aalto University
School of Engineering

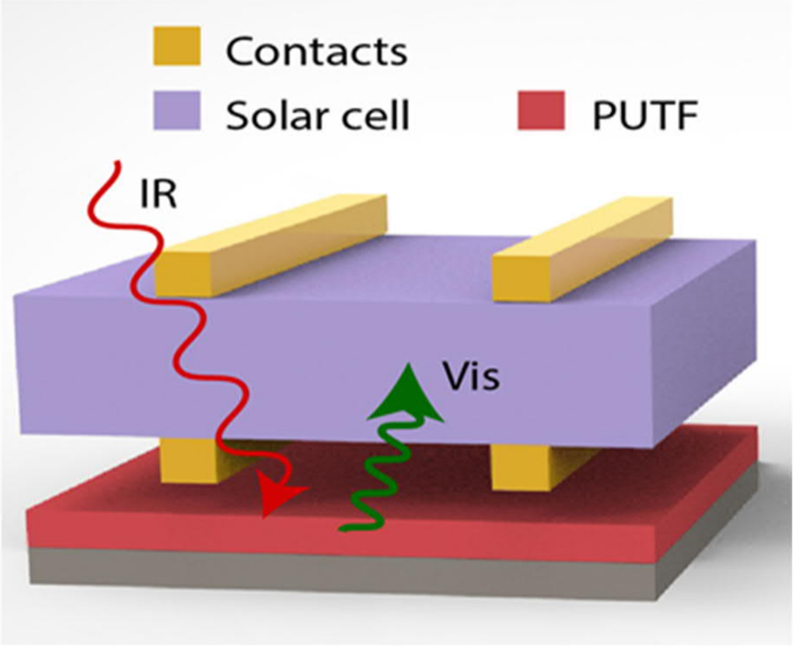
- Z. Giedraityte, P. Sundberg & M. Karppinen, *J. Mater. Chem. C* **3**, 12316 (2015).
- Z. Giedraityte, M. Tuomisto, M. Lastusaari & M. Karppinen, *ACS Appl. Mater. Interfaces* **10**, 8845 (2018).



Different PV Technologies

Red: fraction of solar spectrum not absorbed

Grey: fraction utilized



Our Experiment Setup

Bifacial Silicon Solar Cell +

Photon-Converting Thin Film (PUTF):
60 nm, based on Er^{3+}/Ho^{3+}

Aalto University
School of Chemical Technology

A. Ghazy, M. Safdar, M. Lastusaari, A. Aho, A. Tukiainen, H. Savin, M. Guina & M. Karppinen, Luminescent $(Er,Ho)_2O_3$ thin films by ALD to enhance the performance of silicon solar cells, *Solar Energy Materials & Solar Cells* **219**, 110787 (2021).