MATERIALS FOR ENERGY HARVESTING

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ENERGY HARVESTING

System at non –equilibrium → **EH** → System at equilibrium

EH ↓ (Electric) Energy

Water mill

Automatic watch

SOURCES

- **Thermal gradient**
  - Thermoelectric materials (semiconductors, clathrates, skutterudite)

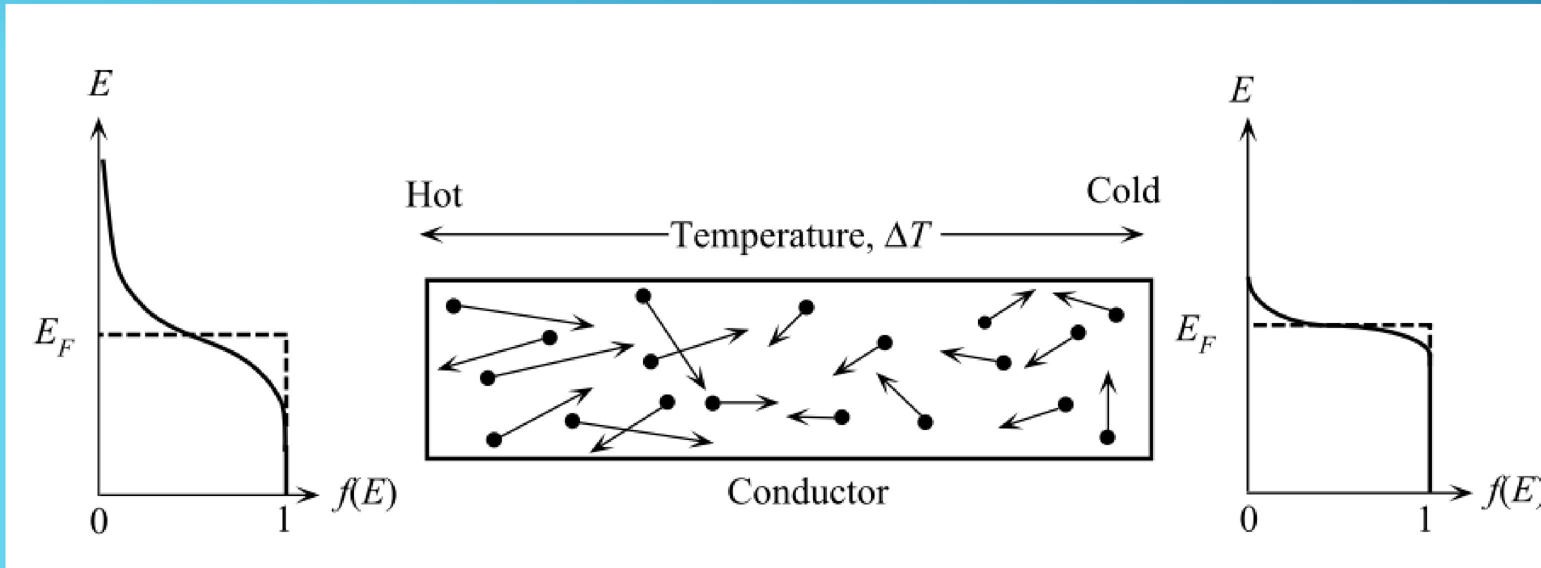
- **Motion/mechanical vibrations**
  - Piezoelectrics, magnets, electrets, magnetostrictive

- **Photovoltaics/EM background “noise”**
  - Si PV cell, rectenna, chem. harvester

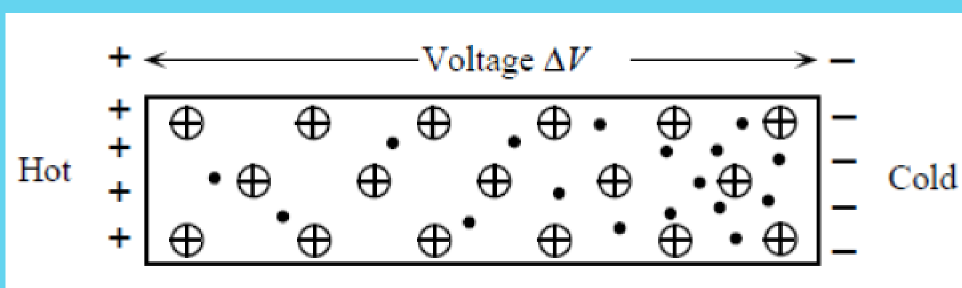
SUMMARY

- Introduction
  - Materials and devices
- Thermoelectrics
  - Physical properties
  - Phononic crystals
- Piezoelectrics
  - Physical properties/fabrication
  - ZnO microrods
- Electrets
  - Physical properties/fabrication
  - SiO_2 micro particles as electrets

THERMOELECTRIC EFFECT



A temperature difference between two points in a conductor gives rise to a voltage difference

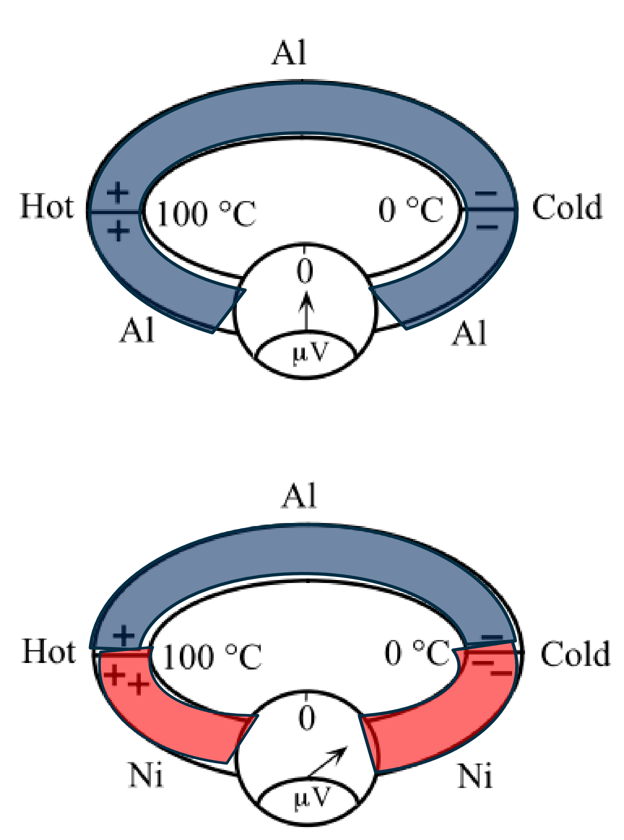


Seebeck coefficient

$$S = \frac{\Delta V}{\Delta T}$$

“Thermoelectric effects in metals: Thermocouples” S.O. Kasap (2001).

THERMOCOUPLES



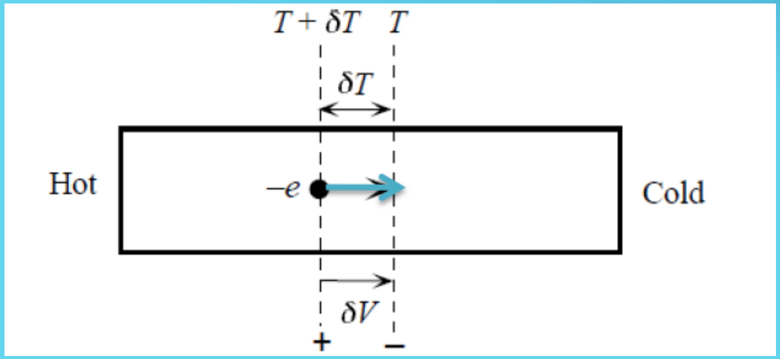
Thjs effect is exploited in thermocouples.

In a circuit made by a single wire with cold and hot regions no voltage difference is observed.

However if we have the junction between different metals , as the Seebeck effect is different in different a net voltage can be observed.

As for a fixed couple of metal, the value depends only on the temperature difference, this device can be used as a sensor

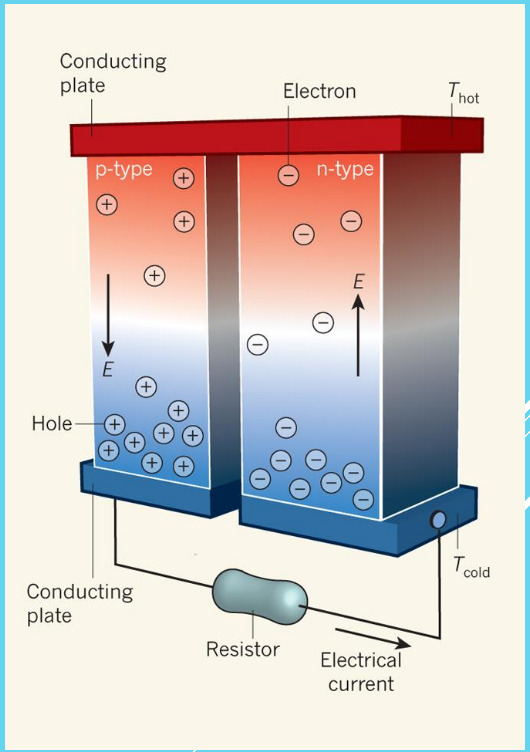
THERMOELECTRIC GENERATOR



The «hot» electrons, faster, have higher possibility to move toward the cold region than the «cold» electrons in the opposite direction.

This leads to an increase of the electric potential energy which can be exploited

Just like for the thermocouple, we need to close the circuit maintaining the asymmetry in the charge carrier behavior



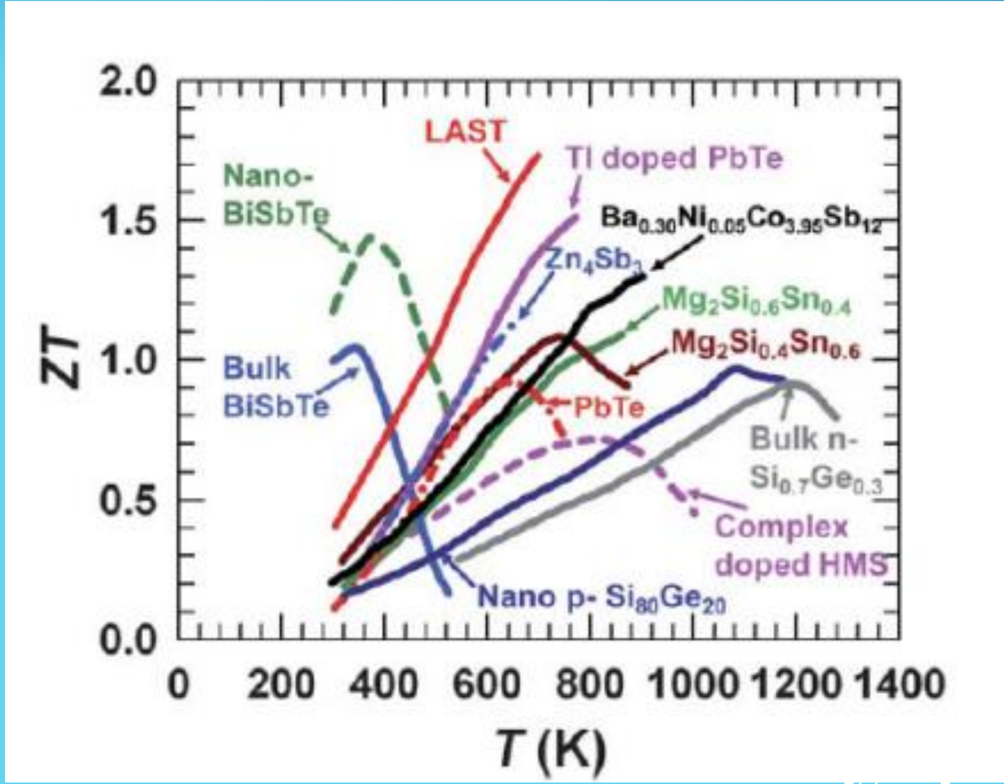
JOSEPH P. HEREMANS, The ugly duckling, Nature 508(2014)327

COMPARISON OF THERMOELECTRIC MATERIALS

Electric conductivity

$$ZT = \frac{\sigma_e S^2}{\kappa_L} T$$

Thermal conductivity

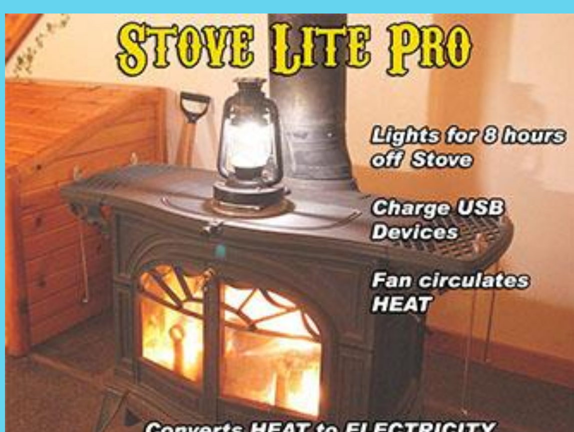


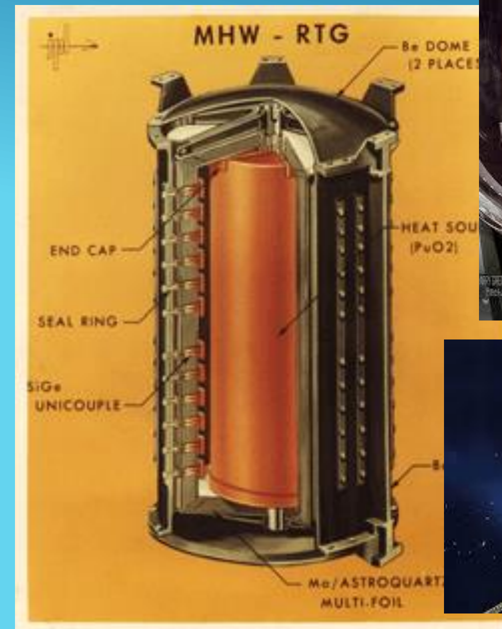
Phonon glass and electron crystal

H.B. Radousky, H. Liang, LLNL JRNL,526171, 2012

SOME DEVICES

GENTHERM
GLOBAL POWER TECHNOLOGIES



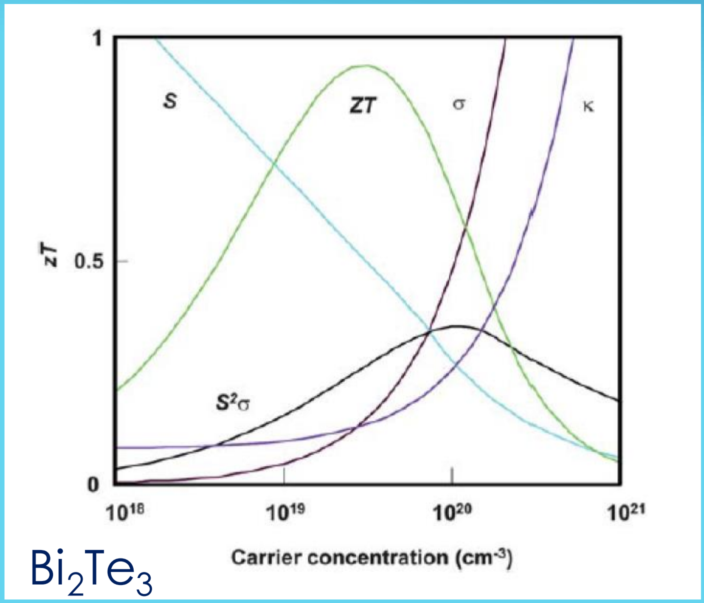


Radioisotope thermoelectric generator

Low efficiency, (3-4%, for ZT =1-2)

but highly reliable (No moving parts)

MATERIAL OPTIMIZATION



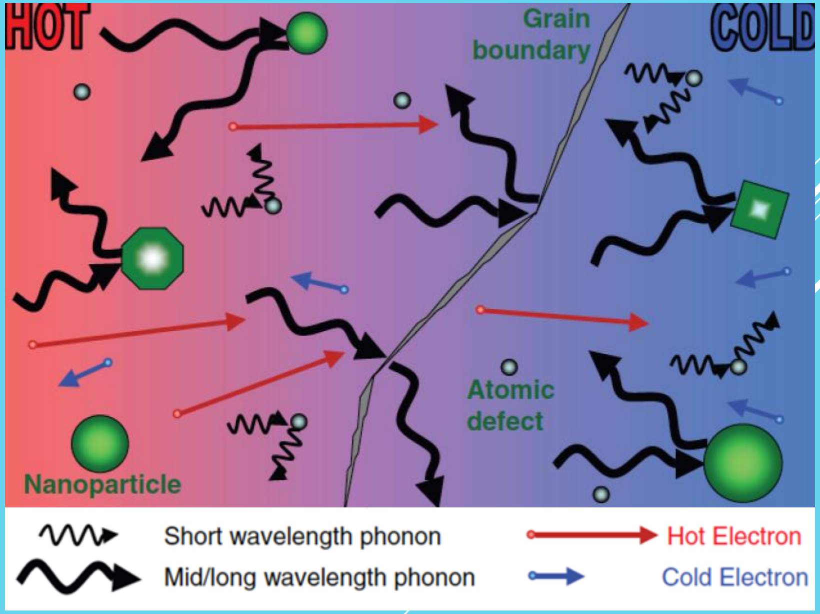
Bi_2Te_3

$$ZT = \frac{\sigma_e S^2}{\kappa_L} T$$

$$\kappa_L = \kappa_e + \kappa_p$$

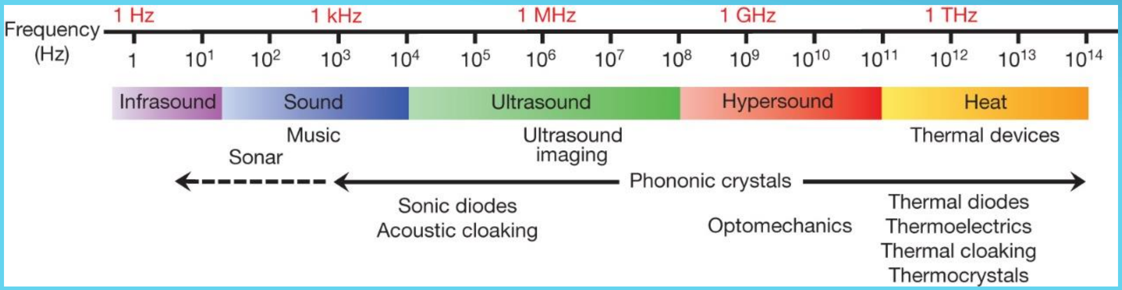
Electric conductivity and electronic part of the thermal conductivity are strictly related.

Phonons are more sensitive than electrons to discontinuites in the materials.
Defects and interfaces can decrease the phononic thermal conductivity



H.B. Radousky, H. Liang, LLNL JRNL,526171

SOUND AND HEAT REVOLUTIONS IN PHONONICS

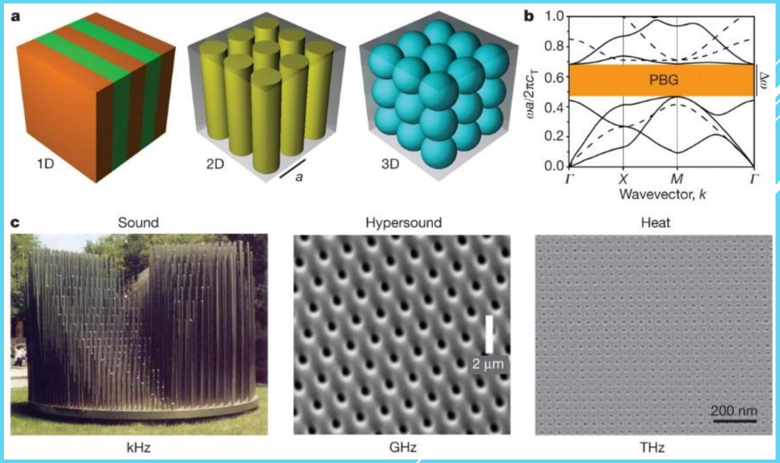


The phononic spectrum

The development of sonic and thermal devices requires the design, fabrication and characterization of composite materials ranging from the centimetre scale to the nanometre scale

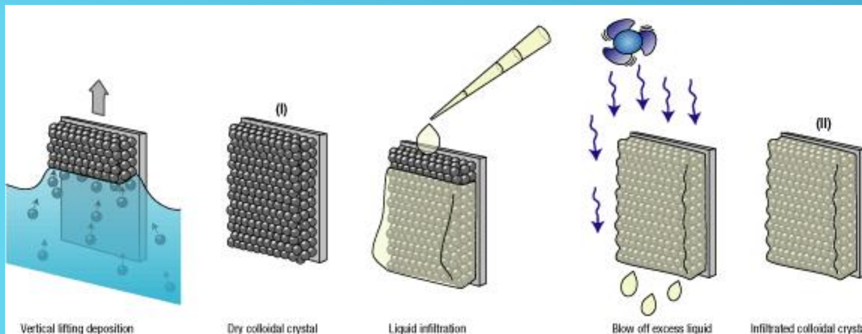
In phononic crystals, mechanical waves with frequencies within a specific range are not allowed to propagate within the periodic structure. This **'phononic bandgap'** owing to wave interference effects, occurs for phonon wavelengths that are comparable to the structure periodicity.

Phononic crystals

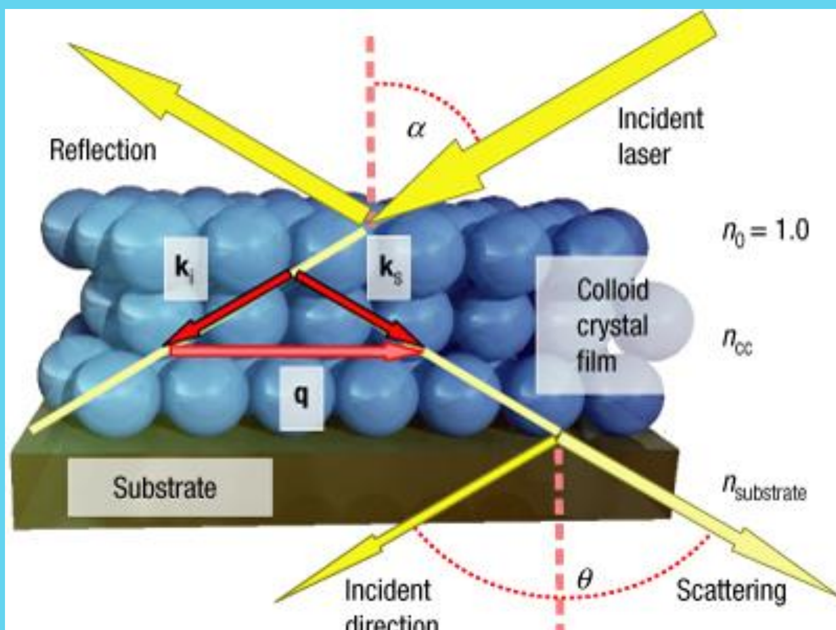


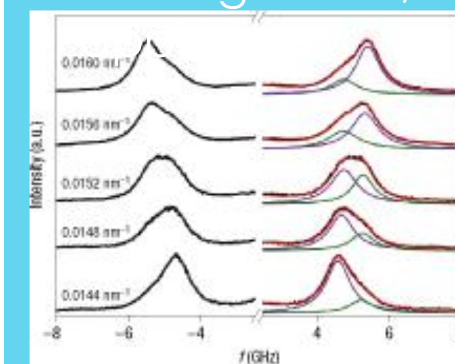
M Maldovan Nature ***503****, 209-217 (2013)*

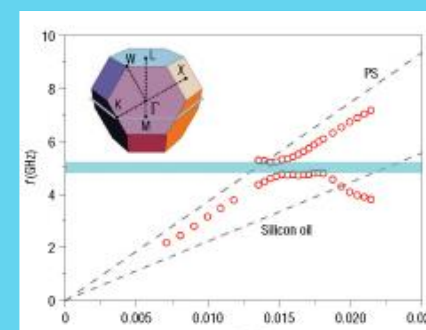
COLLOIDAL CRYSTALS



An ordered array of colloid particles (PS, 100-1000 nm) fabricated by self-assembly in a fcc structure. It presents phononic band gap, making it valuable for devices exploiting phonon control (acoustic isolator, heat management, acousto-optical



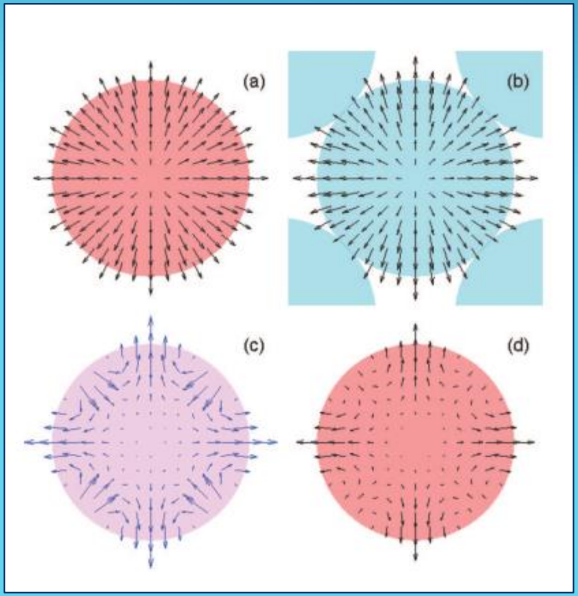




A matching index liquid infiltration is needed to overcome multiple scattering (and loss of q determination). But there is also an acoustic impedance matching.

Fytas et al, Nature Mat. 5, (2006) 830

CLUSTER AND CRYSTAL MODES



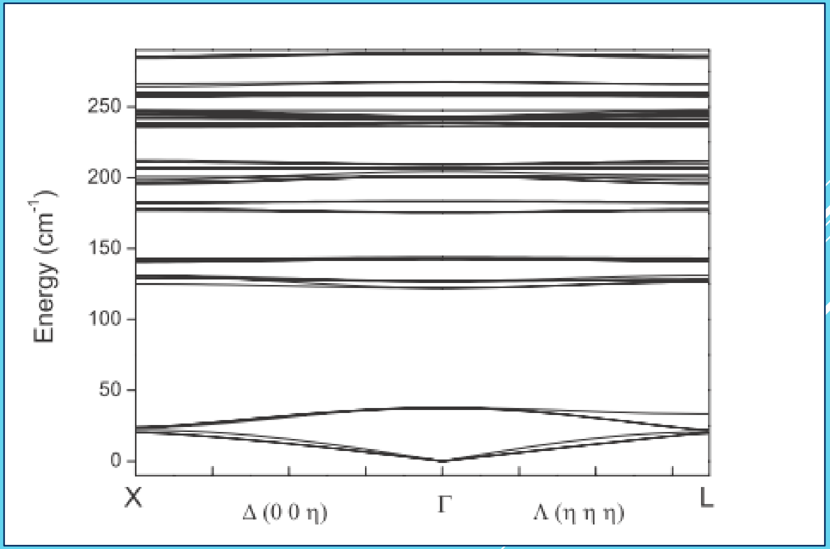
Band arise from the interaction between near particles

Coupling between different cluster modes, but limited lifting of the degeneracy.

Band Gaps in Phononic Crystals:

1) A mesoscopic periodicity breaks continuous acoustic bands

2) A tight binding approach: the weak interaction among the particles will couple the vibrations with the result that the discrete vibrational spectrum ω_α (α = (pnlm)) will be transformed into vibrational bands.




THE JOURNAL OF CHEMICAL PHYSICS 139, 174710 (2013)

Phononic crystals of spherical particles: A tight binding approach

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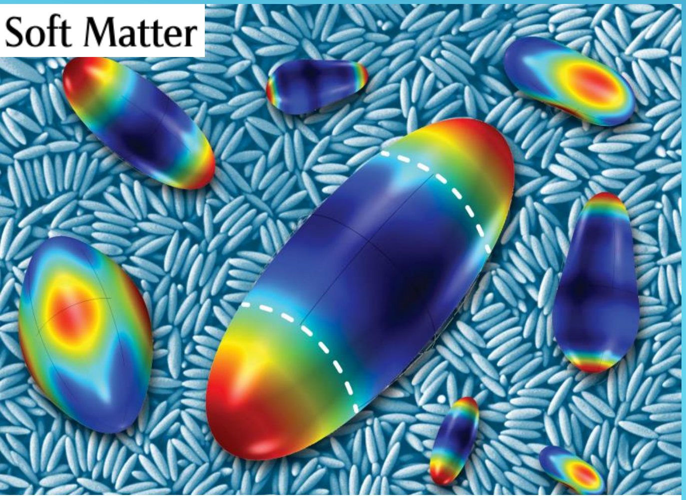
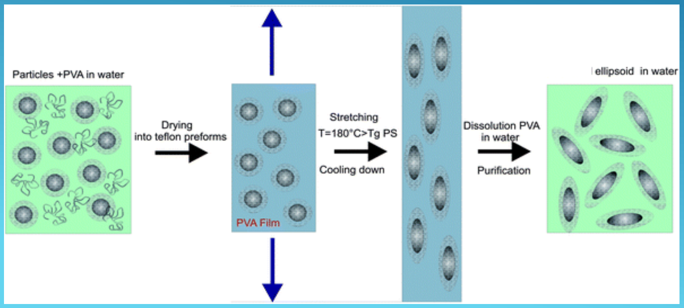


Elongated polystyrene spheres as resonant building blocks in anisotropic colloidal crystals†

Dirk Schneider,[a] Peter J. Beltramo,[b] Maurizio Mattarelli,[c] Patrick Pfleiderer,[d] Jan Vermant,[d] Daniel Crespy,[a] Maurizio Montagna,[c] Eric M. Furst[b] and George Fytas*[ae]

- Polystyrene particles were stretched by a matrix assisted elongation process



- **Elastic Properties**
- **Normal modes**

SPHEROIDAL PARTICLES

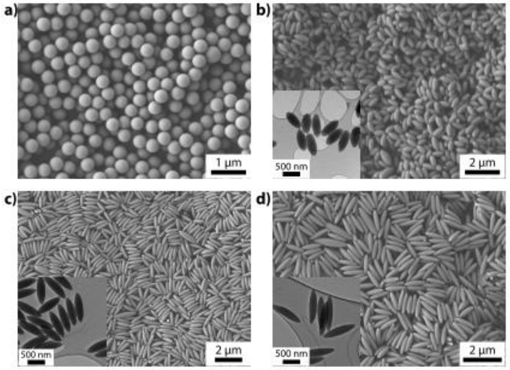


Fig. 1 SEM micrographs of seed spheres S0 (a) and spheroids S2–S4 (b–d) of various aspect ratio. Insets denote TEM images of the respective particles.

Table 1 Size characterization of particles studied and material parameters used in calculations. a and b being the long and short axes of the spheroids, respectively. ρ is the mass density and n_{ref} the refractive index at 532 nm

ID	a/b	a/nm	b/nm	ρ/kg m^{-3}	n_{ref} [b]
S0	1	400 ± 14	_	1050	1.599
S1 (ref. 30)	1.28 ± 0.07	459 ± 15	358 ± 16	965.1[a]	1.540
S2	2.12 ± 0.16	690 ± 42	325 ± 15	921.9[a]	1.511
S3	3.52 ± 0.20	986 ± 15	280 ± 15	869.4[a]	1.477
S4	3.99 ± 0.22	1078 ± 93	270 ± 23	854.7[a]	1.468

[a] Calculated based on stretched particle volume. [b] Calculated from density *via* the Clausius–Mossotti relation.

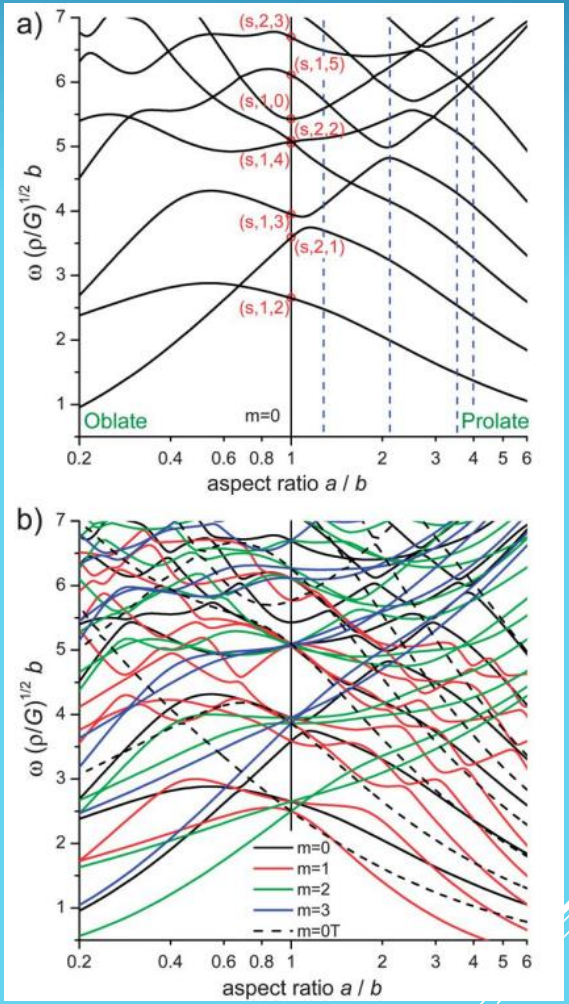
AXIS RATIO DISPERSION

- Rayleigh- Ritz method
  axis ratio and sound velocities as free parameters

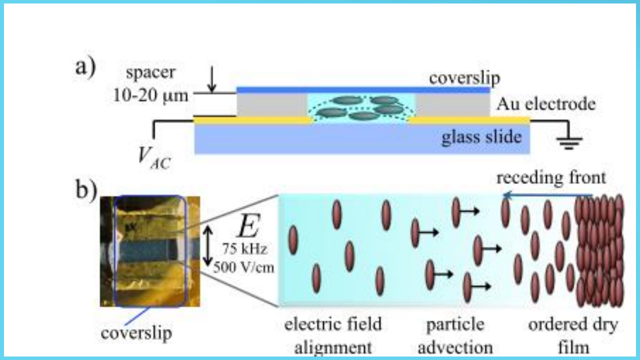
s12,0 s13,0 s10,0

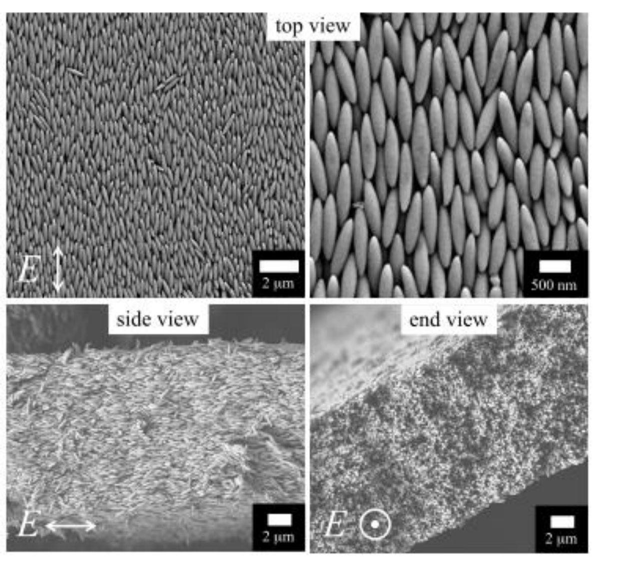
- Lifting of spherical degeneracy (toward disk or beam modes)

- There is important mixing between the various modes of the sphere, but m and parity remain good quantum numbers.



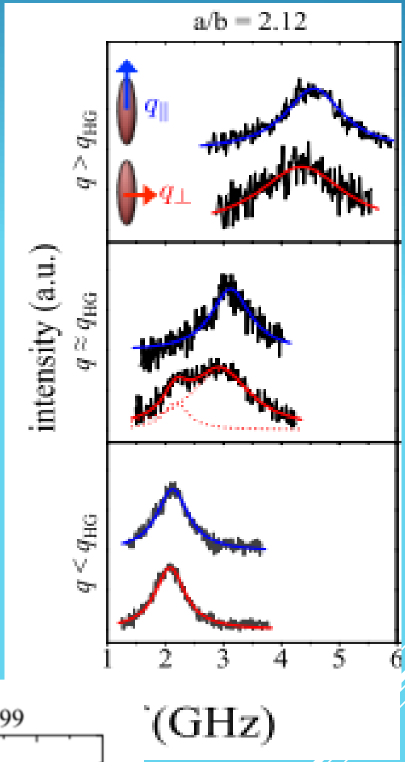
ORIENTED ELONGATED PARTICLES

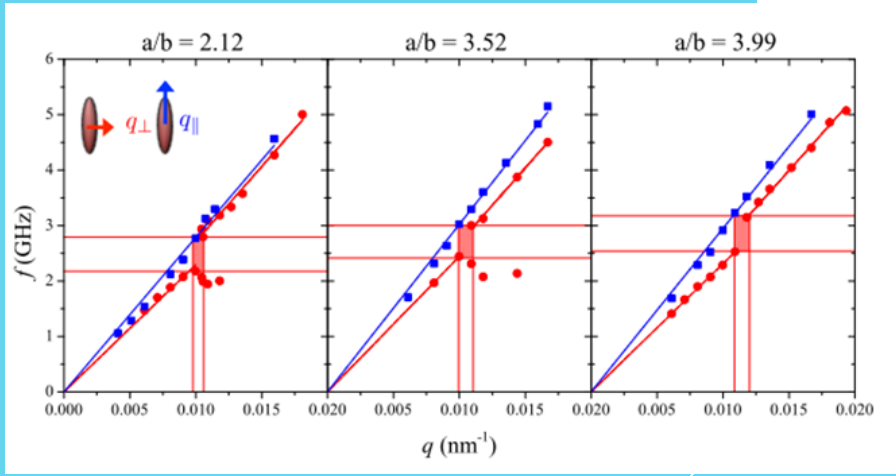




- The interaction of the acoustic phonon with other "optical" phonons <u>depends on their symmetry</u>

- Different gaps can occur for different propagation directions





TRANSDUCTION MECHANISMS AND MATERIALS

Mechanical action

Strain (cantilever, etc)

Motion («free» inertial mass,)

Strain conversion

- Piezoelectrics
- Electroactive polymers
- Magnetostrictive mat.
- Magnetoelectrics

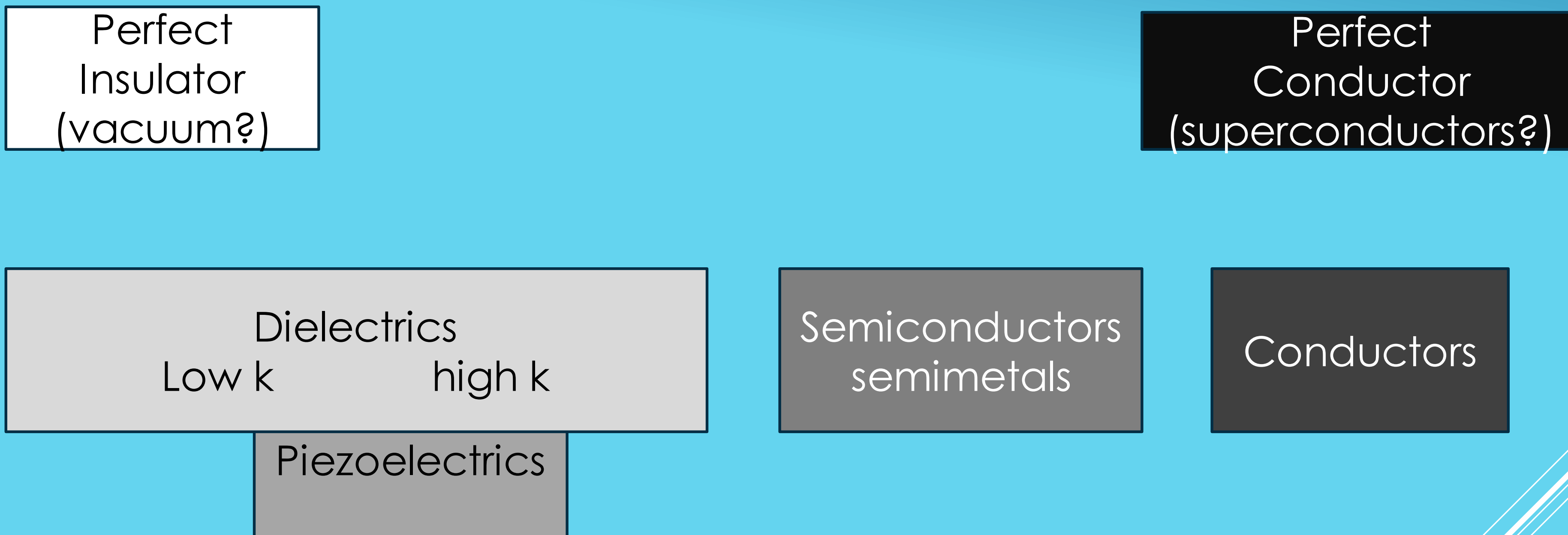
Electrostatic

- Electrets

Electromagnetic Induction

- Magnets

ELECTRIC BEHAVIOR OF MATERIALS



Depending on the external conditions (electric field intensity or frequency, temperature, shape, strain) the behaviour of real materials can move between these extrema

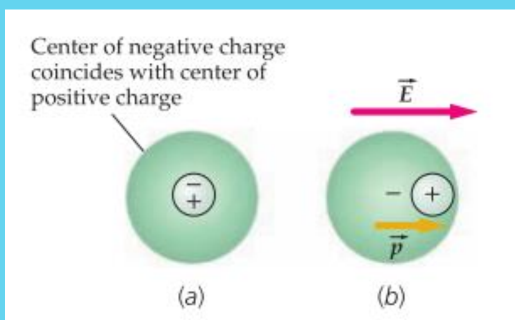
ELECTRIC POLARIZATION

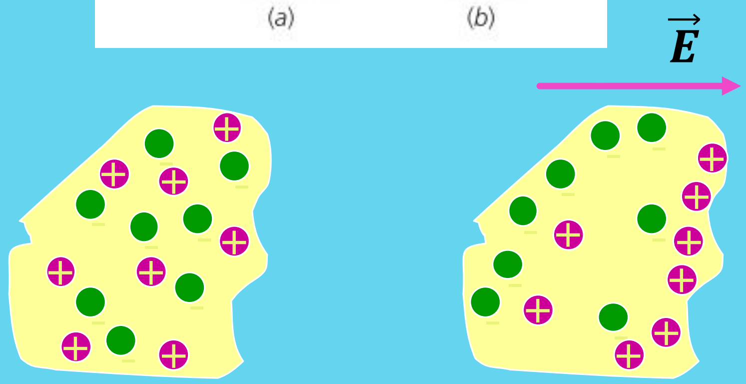
$$\boldsymbol{P} = \frac{\varepsilon - 1}{4\pi}\boldsymbol{E}$$

In an external electric field, materials acquire an induced dipole moment or POLARIZATION

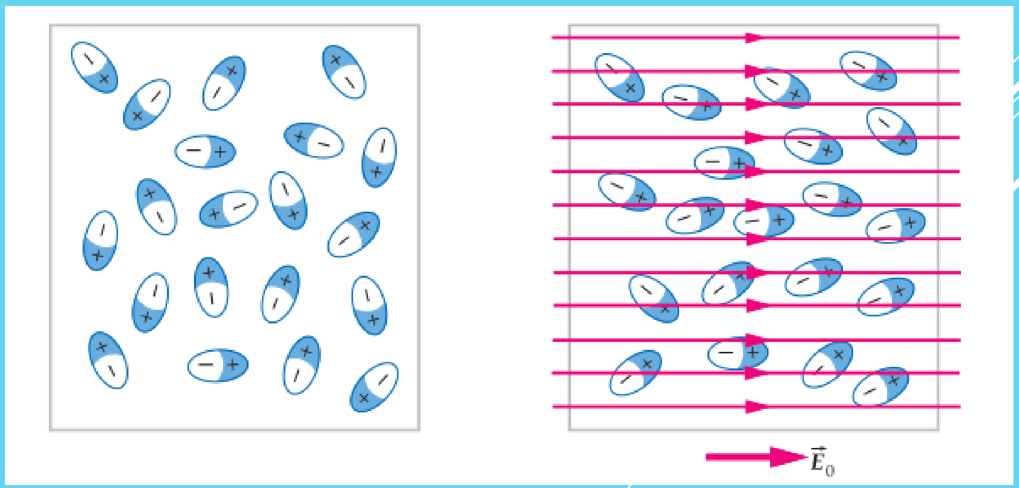
It can have different origins

Deformation
(of electron density or ions)

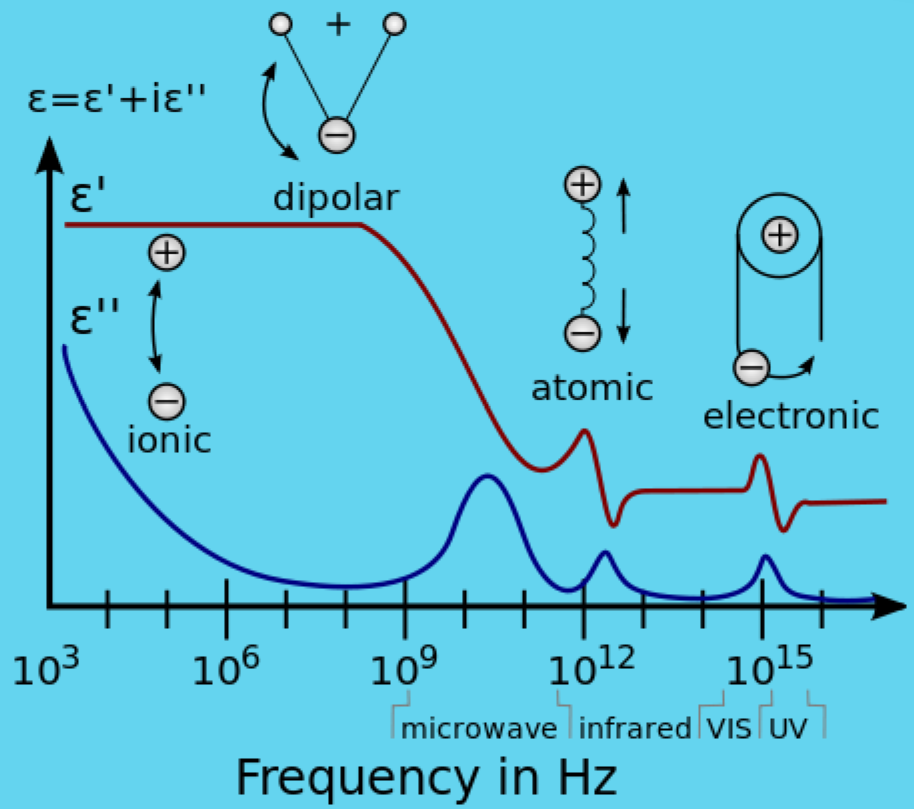




Orientation (of pre-existing dipoles)



FREQUENCY DEPENDENCE



- The response of the electroactive materials is strongly frequency dependent.
- They work best at resonance when the trasferred power is maximum.
- They still react at lower frequency, while at higher frequency they cannot rearrange following the external field

MATERIALS IN MAGNETIC OR ELECTRIC FIELDS

Diamagnetic

Its atoms have no permanent magnetic moment. The induced moment opposes the external field.

Paraelectric

The induced dipole in dieletrics is always aligned with the external field

Paramagnetic

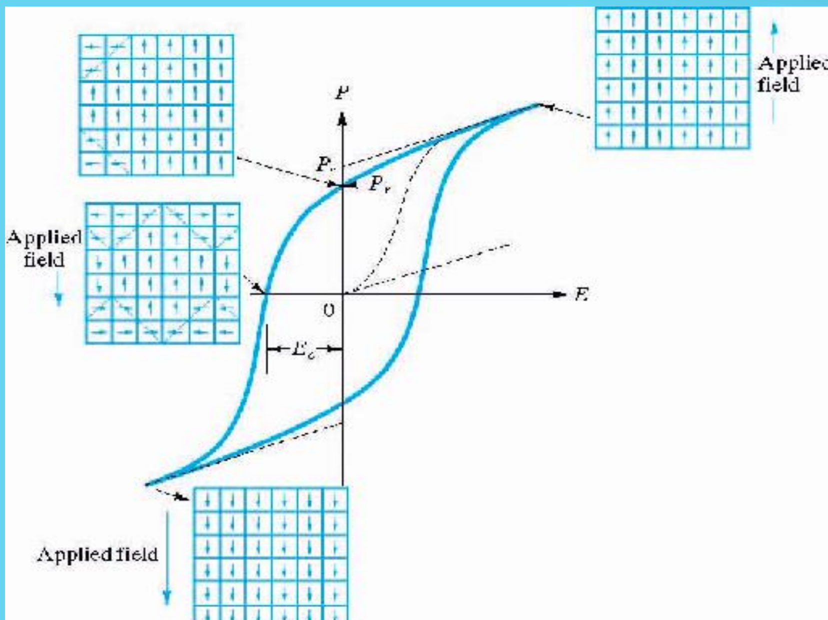
Its atoms have permanent magnetic moment, which aligns with the external field

Ferromagnetic

Its atoms have permanent magnetic moment and strong exchange energy connects them into domains

Ferroelectric

HYSTERESIS



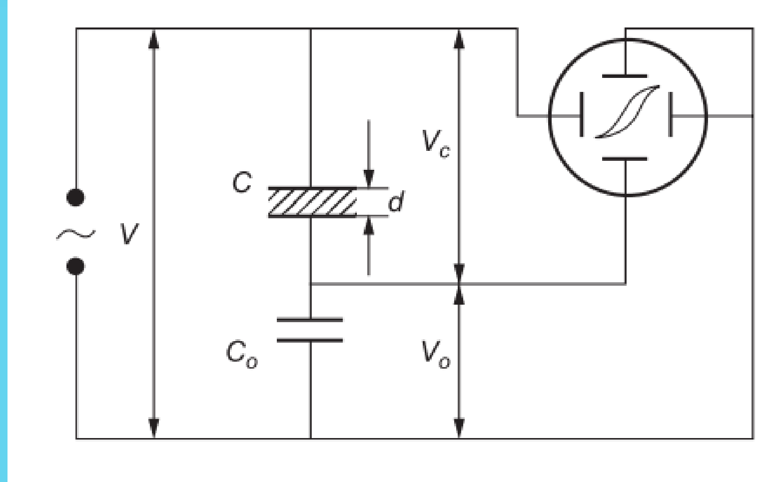


Figure 4-3 The Sawyer–Tower method for the measurement of the polarization-electric field (P–F) characteristics.

In Ferroelectrics (Ferromagnetics) materials, the thermal agitation cannot overcome the alignement of the domains. A coercive field is needed to reverse polarization (magnetization).

THE MICROSCOPIC ORIGIN

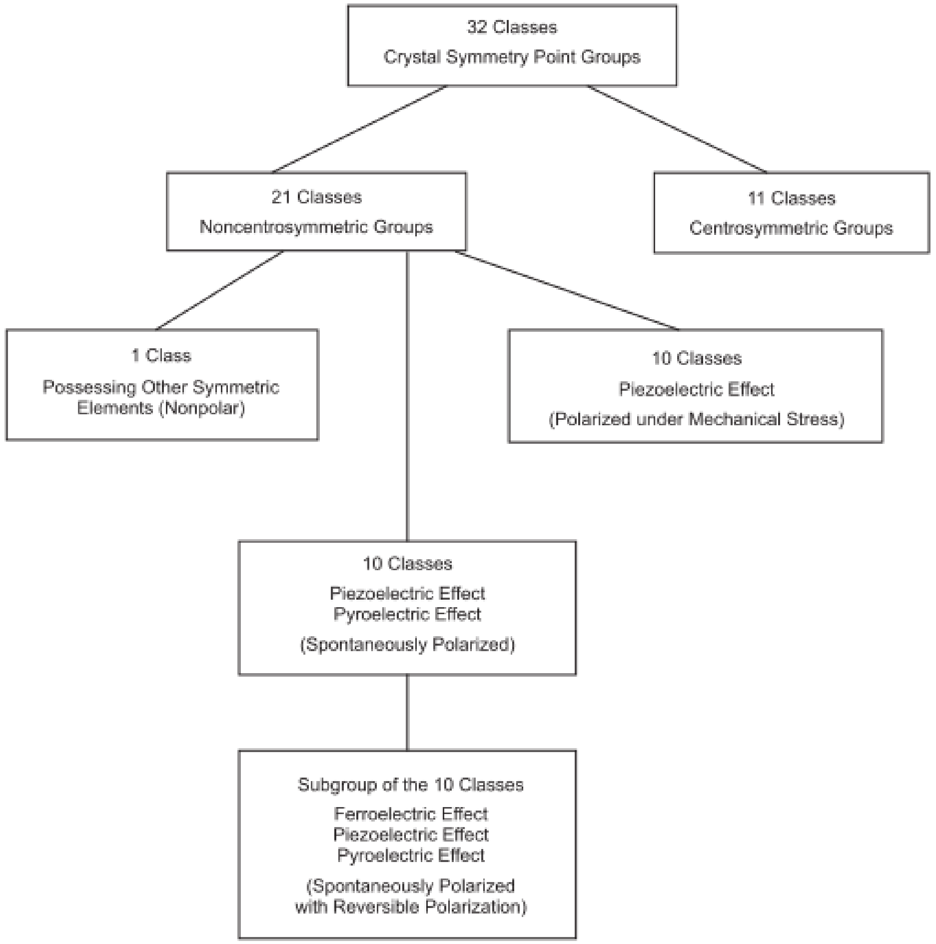
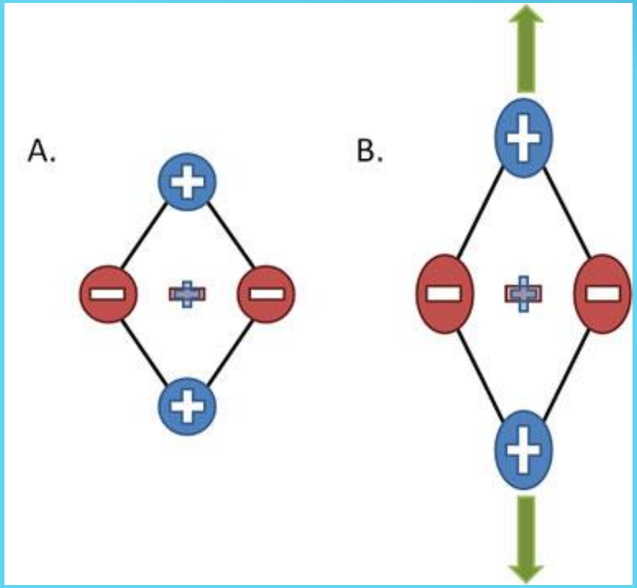


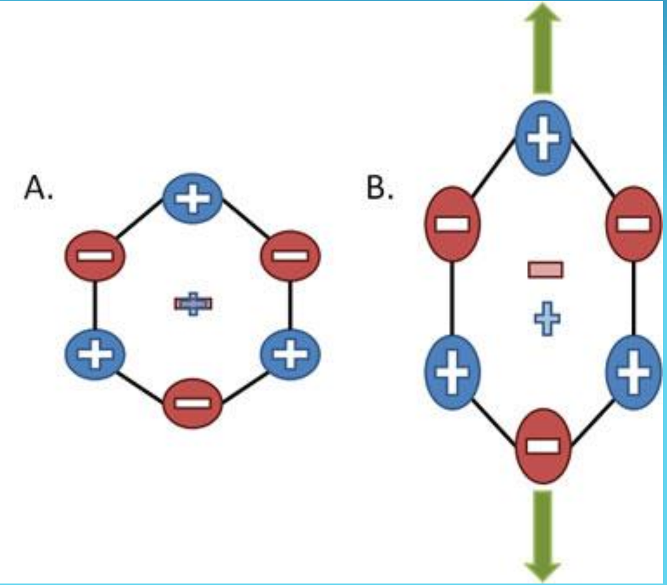
Figure 4-1 Classification of crystals showing the classes with piezoelectric, pyroelectric, and ferroelectric effects.

Simmetry of the unit cell is a necessary, but not sufficient condition.

Different charge distributions can cancel or strongly decrease the piezoelectric effect

PIEZOELECTRICITY





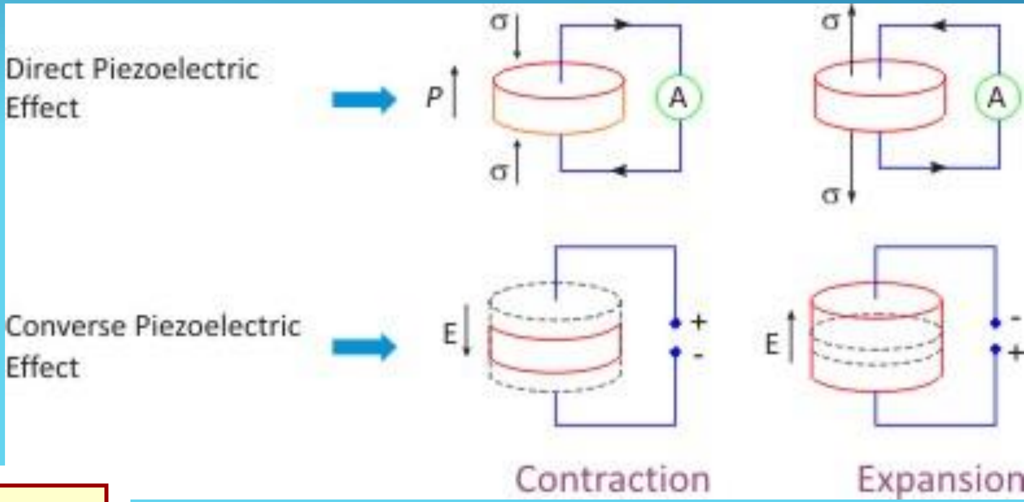
Centro-symmetric

Non Centro-symmetric

In centrosymmetric crystals the strain does not move the center of charge of the positive or negative charges. On the other hand, in in non centro-symmetric crystals, if the atoms have different charges because of the strain provokes the formation of an electric dipole.

PIEZOELECTRIC COEFFICIENTS

- $P = d\,\sigma$
- $\varepsilon = d^t\,E$



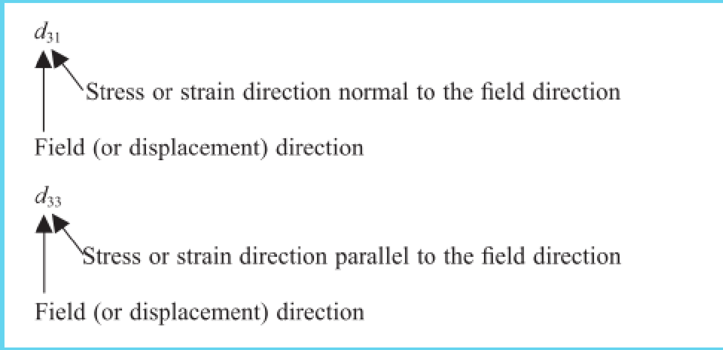
Material	Piezoelectric Constant, d (pm/V)
Quartz	2.3
Barium Titanate	100-149
Lead Niobate	80-85
Lead zirconate titanate	250-365

The direct piezoelectric effect is used as the basis for ENERGY HARVESTING (and force, pressure, vibration and acceleration sensors) while converse effect is used as a basis for actuator and displacement devices.

PIEZOELECTRIC COEFFICIENTS

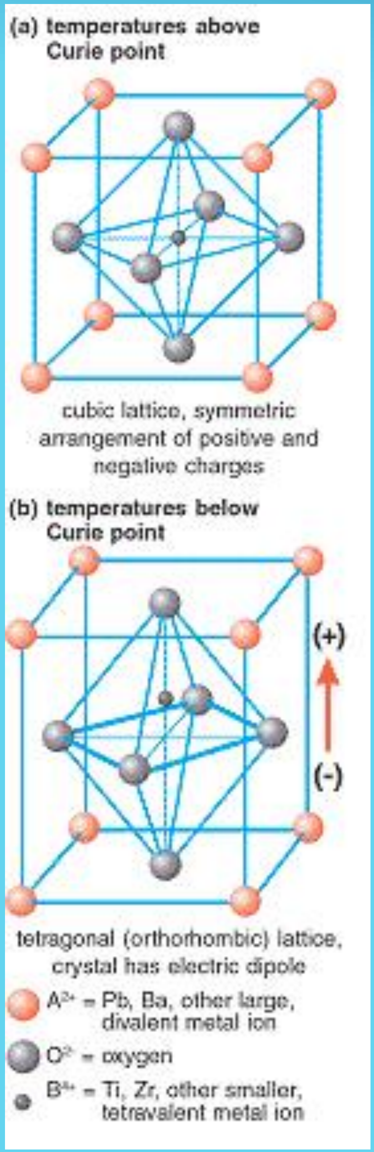
d is third-rank tensor (d_{ijk} 3x3x3) , as it links the effect of strain/stress (second order tensor) to the induced Polarization/Electric field (vector).

However, it is often written in a contract matrix form (3x6), where 4,5,6 index are used to express shear stress/strain



Axis «3» is usually the anomalous axis of uniaxial piezoelectric crystals and the one where the effect is stronger

FERROELECTRICITY

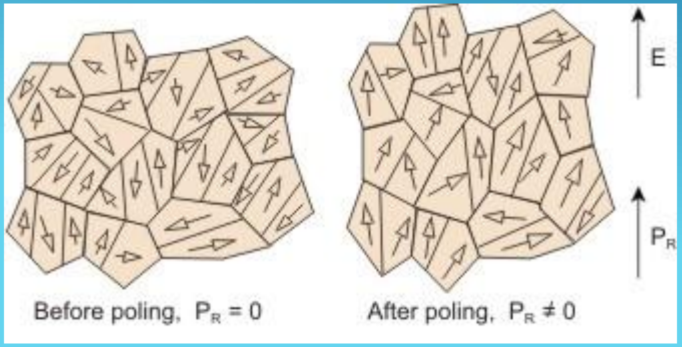


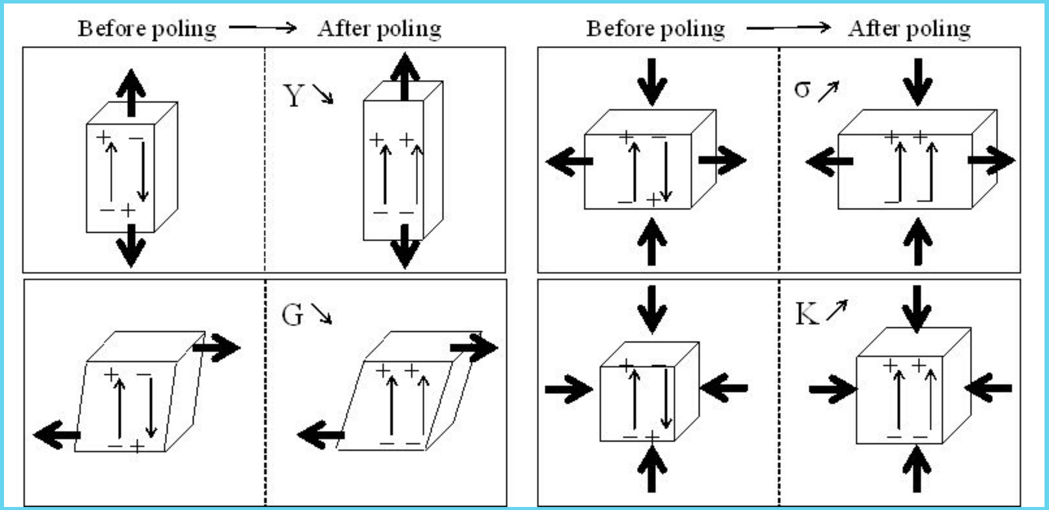
In BaTiO3 at room temperature the stable phase has the Ti4+ ion displaced form the center of the cell. It has two stable positions: above and below the 4 central oxygens.
Depending on its position, the dipole will be reversed.

Name (Abbreviation)	*Chemical Formula*	*Curie Temperature, T_c (°C)*	*Spontaneous Polarization P_s($\mu C m^{-2}$) at [T (°C)]*	*Crystal Structure* Above T_c	*Crystal Structure* Below T_c
Barium Titanate	$BaTiO_3$	120	26.0 [23]	Cubic	Tetragonal
Lead Titanate	$PbTiO_3$	490	50.0 [23]	Cubic	Tetragonal
Potassium Niobate	$KNbO_3$	435	30.0 [250]	Cubic	Tetragonal
Potassium Dihydrogen Phosphate (KDP)	KH_2PO_4	−150	4.8 [−177]	Tetragonal	Orthohombic
Triglycine Sulfate (TGS)	$(NH_2CH_2COOH)_3 \cdot H_2SO_4$	49	2.8 [20]	Monoclinic (Centrosymm.)	Monoclinic (Noncentrosymm.)
Potassium-Sodium Tartrate-Tetrahydrate (Rochelle salt)	$KNaC_4H_4O_6 \cdot 4H_2O$	24	0.25 [5]	Orthorhombic (Centrosymm.)	Monoclinic (Noncentrosymm.)
Antimony Sulfo-iodide	SbSI	22	25.0 [0]	Orthorhombic (Centrosymm.)	Orthorhombic (Noncentrosymm.)
Guanidinium Aluminium Sulfate Hexahydrate (GASH)	$C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$	None	0.35 [23]	Trogonal	—

POLING

- Under a strong external field it is possible to induce the poling of the ferroelectric material (i.e. to polarize it)



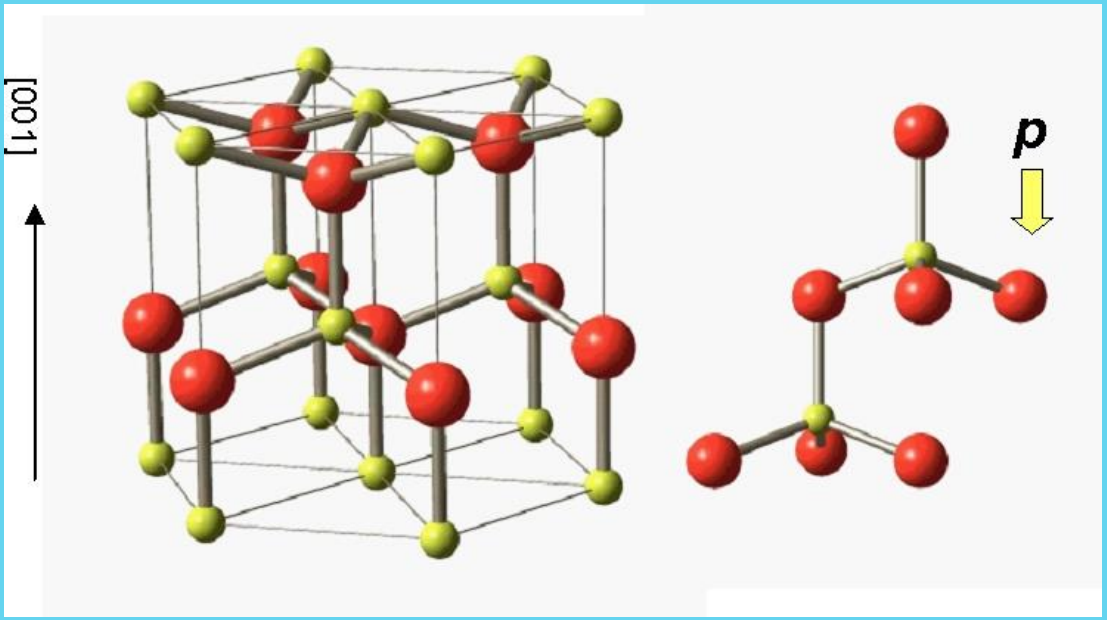


If the material is poled, the stress acting on it can generate an intense change of the electric dipole (usually stronger than in common piezolectric materials)

PYROELECTRICS

Crystal with a permanent dipole, not reversible.

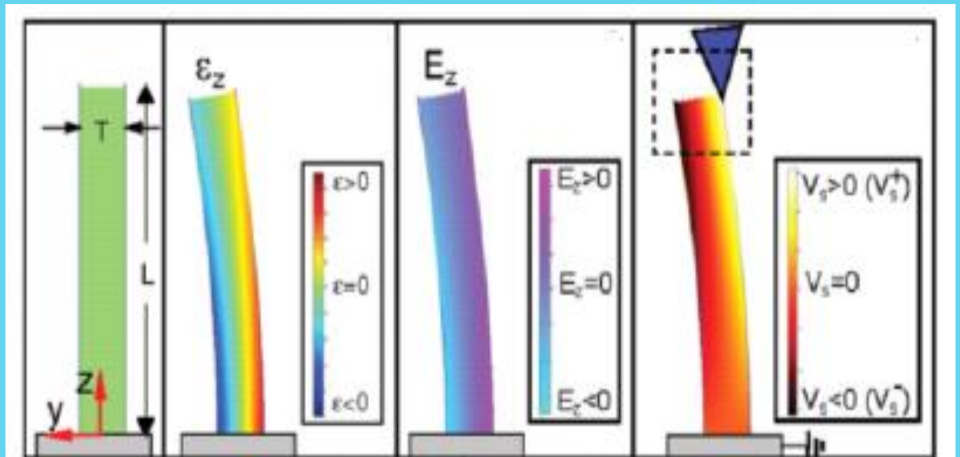
They have to be grown as single crystals.



Wurtzite structure crystals, such as ZnO, are asymmetric along the [001] axis, ([001] is different from [00-1])

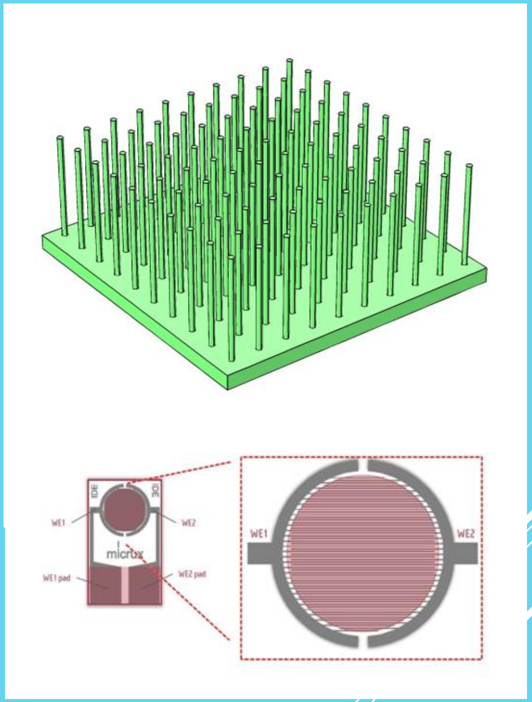
Because of thermal dilatation, the electric dipole increases

ZINC-OXIDE MICRORODS



Wang 2008

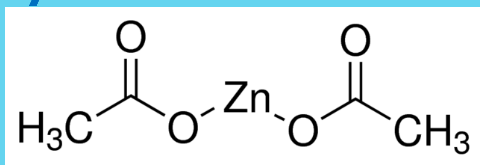
Growth of ZnO pillars on IDE



Objective: exploiting the difference of potential at the base of the pillar induced by the bending

FABRICATION

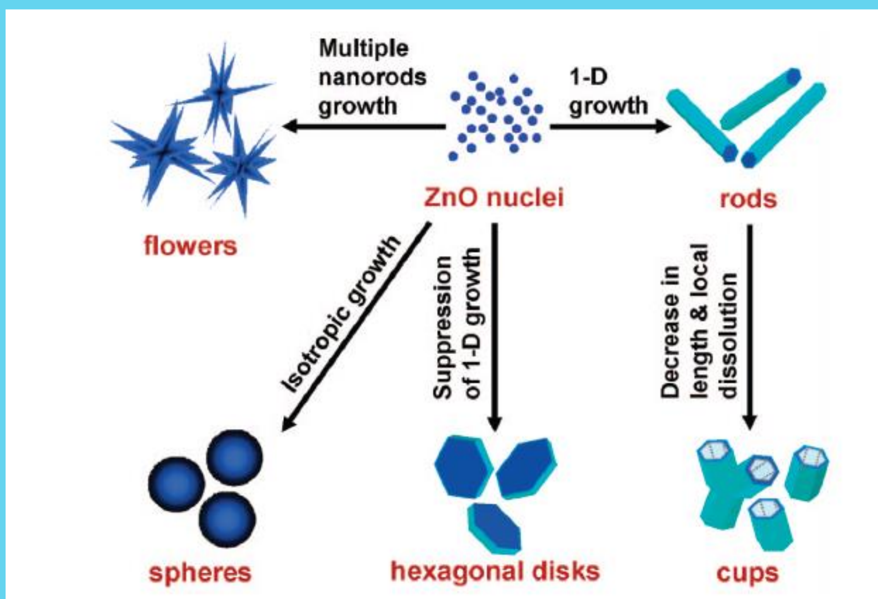
Hydrothermal Synthesis

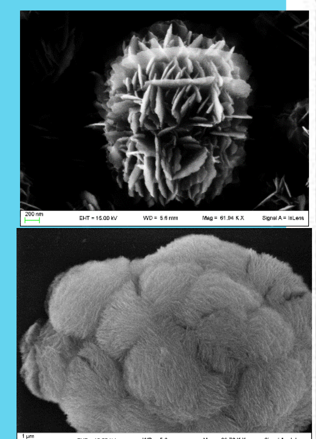


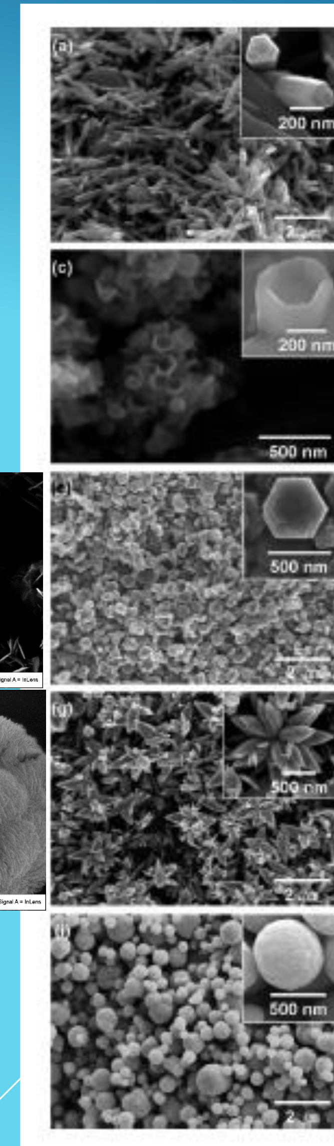
Acetato di zinco

basic environment

ZnO

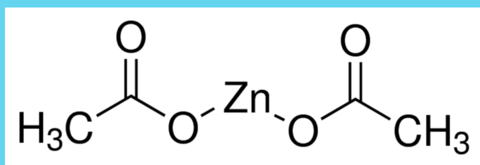






HYDROTHERMAL SYNTHESIS

ZnO nano and microrods

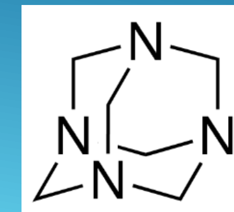


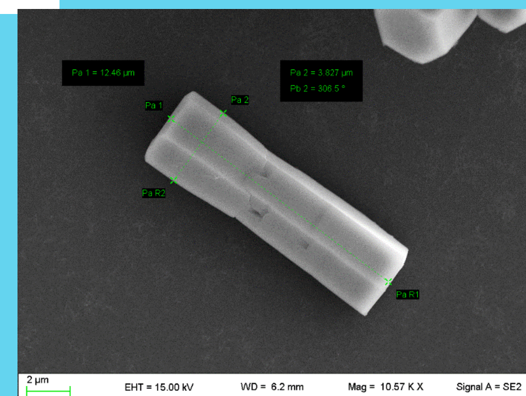
Acetato di zinco

HMTA

Hexamethylenetetramine

ZnO

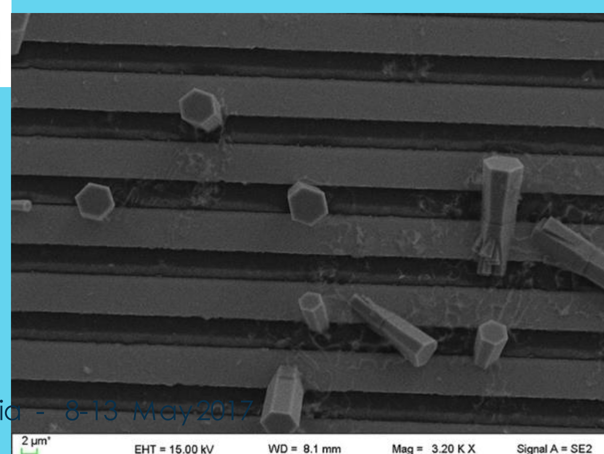


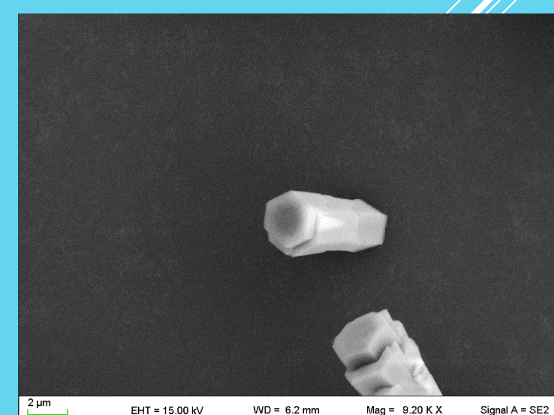


$$C_6H_{12}N_4 + 6H_2O \rightarrow 6CH_2O + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

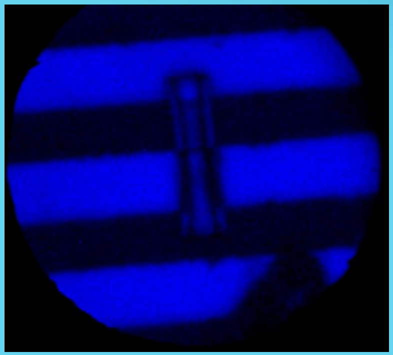
$$2OH^- + Zn^{2+} \leftrightarrow ZnO + H_2O \quad (3)$$

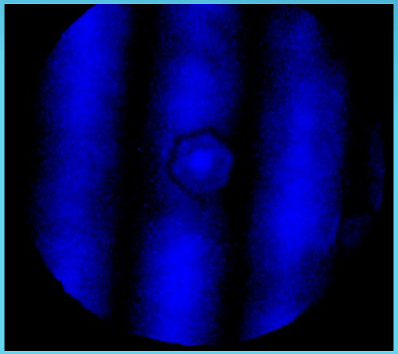




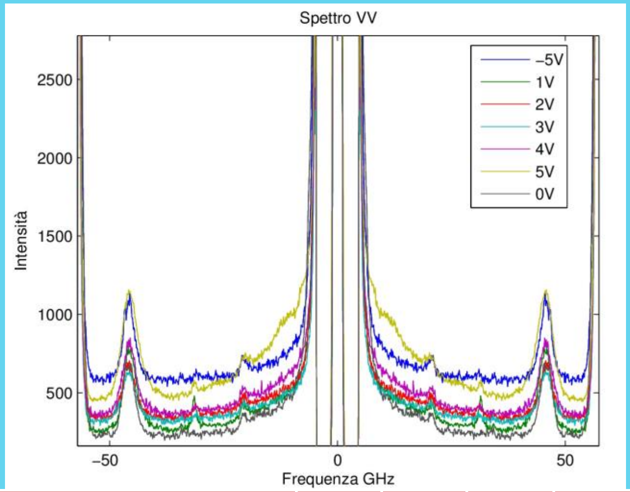
Size in the order of tens of micrometes

SPECTROSCOPIC CHARACTERIZATION

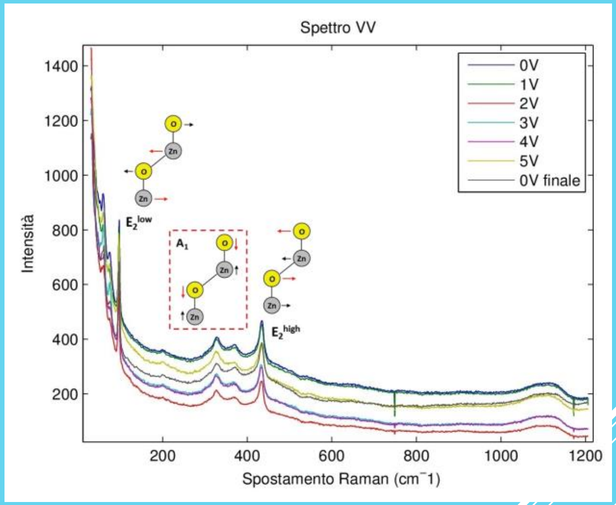




Raman and Brillouin spectroscopy on single crystals

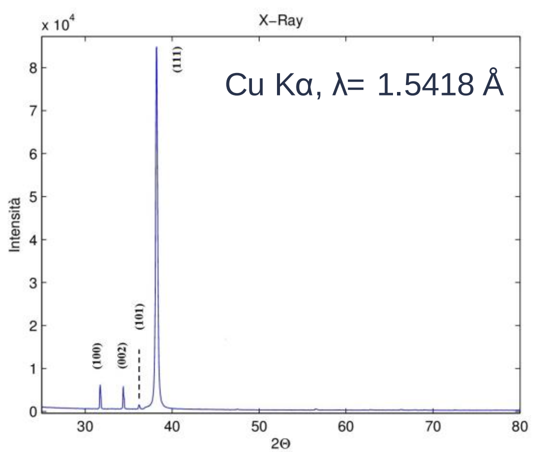


Elementi Matrice C (GPa)	C_{11}	C_{33}	C_{44}	C_{66}
Ref. Bhat et al.	209	210	42	44
Risultati	209	198	42	43

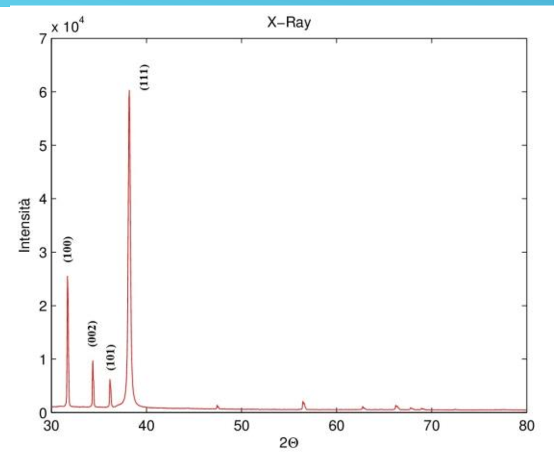


Raman Shift (cm^{-1})	E_2^{low}	$A_1(E_2)$	$A_1(E_1,E_2)$	A_1	E_2^{high}
Ref. Damen et al.	101	208	332	380	437
Risultati	101	205	332	379	438

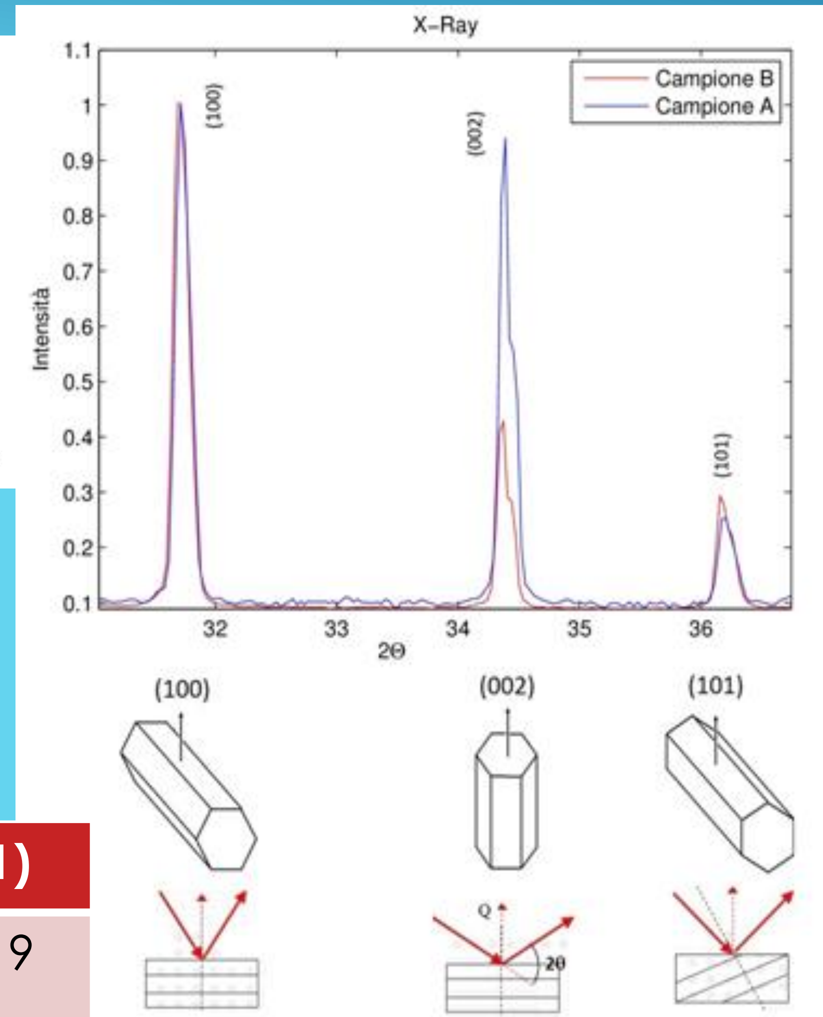
XRD CHARACTERIZATION



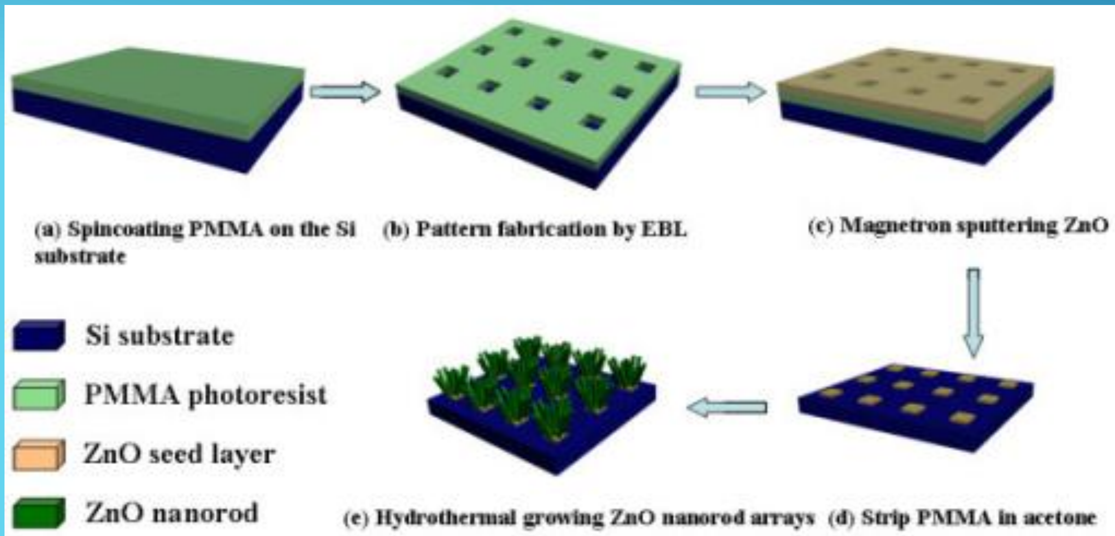
A (HMTA:ZnAc, 2:1)

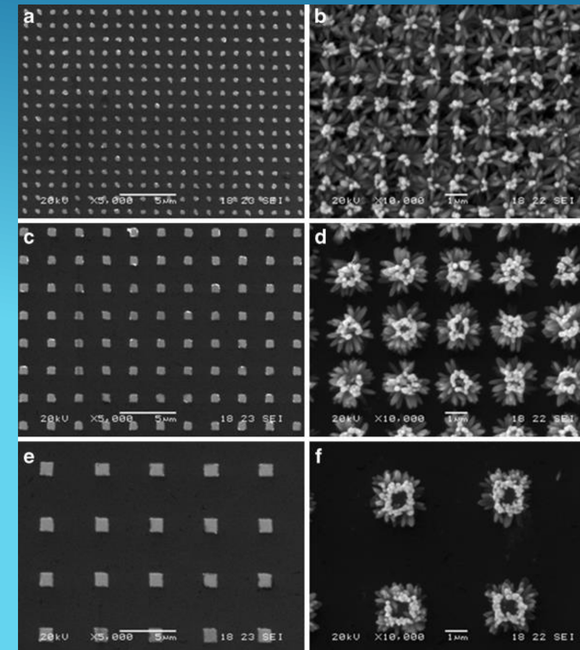


B (HMTA:ZnAc, 3:1)



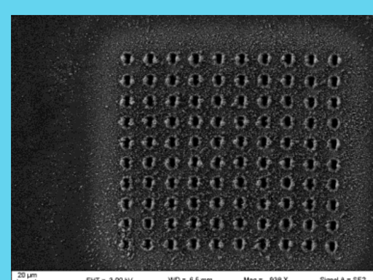
2Θ (Deg)	(100)	(002)	(101)	(111)
Ref. Martinez et al.	31.73	34.40	36.21	38.19
Results	31.73	34.40	36.21	38.21

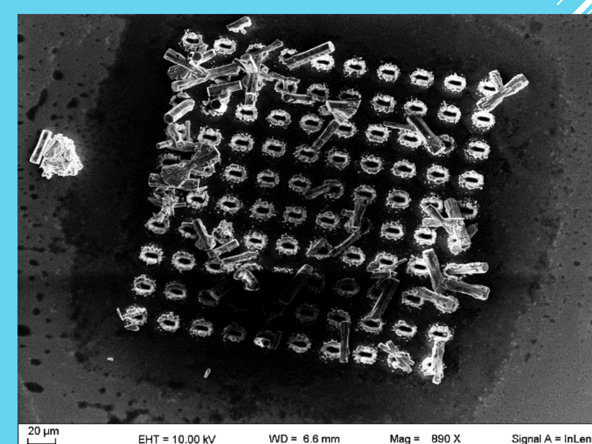




Wang et al. Nanoscale Research Letters 2012, 7:246

Template made by laser ablation on PMMA





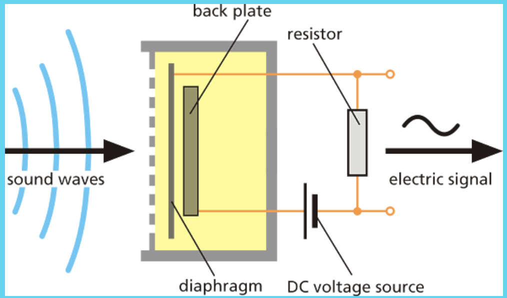
ELECTRETS

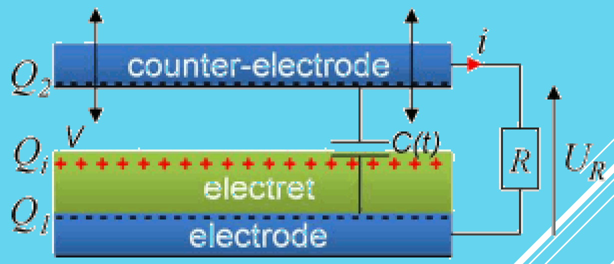
Dielectrics with unbalanced charge (permanent oriented electric dipoles or a net charge.)

Electrical analogue of a magnet: able to generate an electric field

MATERIALS: dielctrics (polymers, oxides) with high dielectric strength and low conducibility

Old applications: microphone





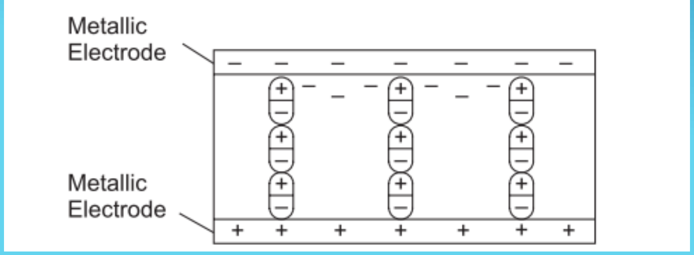
S Boisseau et al. Smart Materials and Structures 20, 105013, 2011

New ones : energy harvesting devices

FORMATION OF ELECTRETS

Two types of electrical charges in an electret :

- monocharges (also called real charges)
- dipolar charges (such as in ferroelectrets)

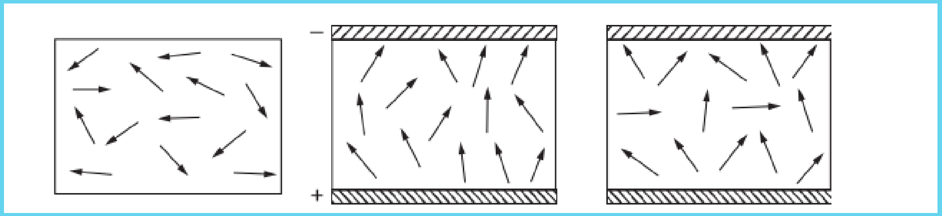


Several fabrication techniques:

- Thermo-Electrical Method (dipolar)
- Electromagnetic Radiation Method (dipolar)
- Liquid-Contact Method (real charges)
- Corona Discharge Method (real charges)
- Electron-Beam Method (real charges)

THERMO-ELECTRICAL METHOD

Dipolar molecules are randomly arranged but they will actively orient under an electric field at a temperature higher than the glass transition temperature, Tg



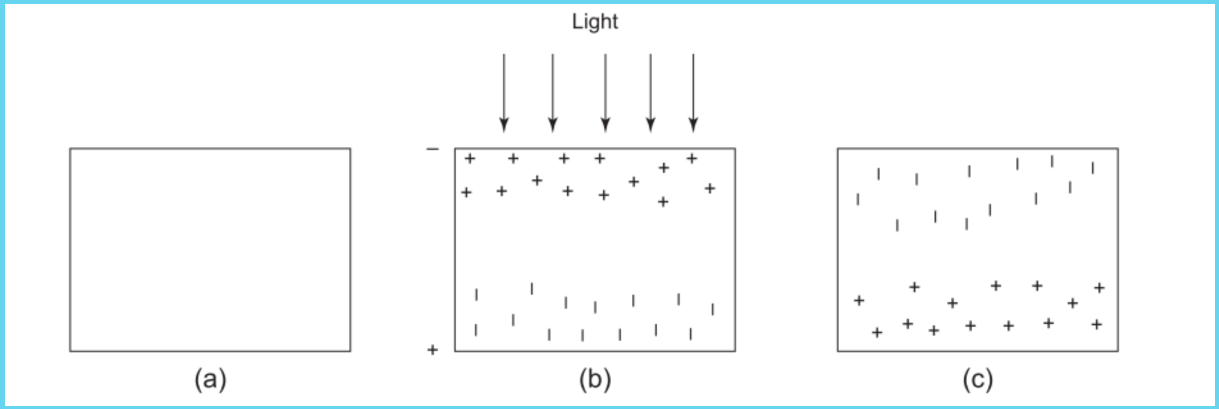
Typycal materials is the Carnauba wax–beeswax (first electret, made by Eguchi in 1919)

Drawback: stability

Ferroelectrets can be considered electrets obtained by thermoelectrical method (the poling) but with, possibly, much higher Tg

ELECTROMAGNETIC RADIATION METHOD

Displacement of the charge carriers generated by penetrating radiation (x-rays or ultraviolet light), under an externally applied electric field.

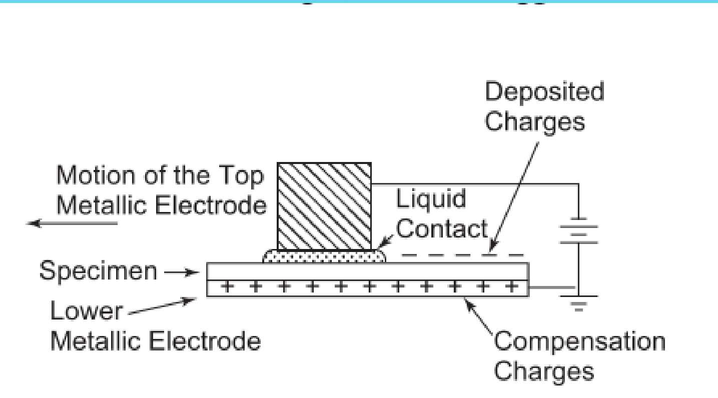


These carriers can be trapped near the electrodes to create a space charge polarization.

The polarization remains after the external field removal

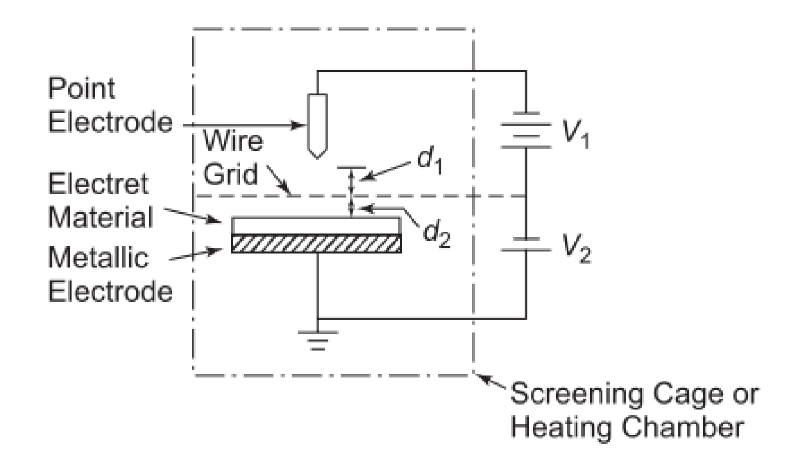
(LIQUID) CONTACT METHOD

Transfer of real charges into the material, by a conductive contact. This can be made at large scale down to the nanoscale (AFM)



The advantage of the conductive liquid is in the possibility to move the metallic contact all over a large surface

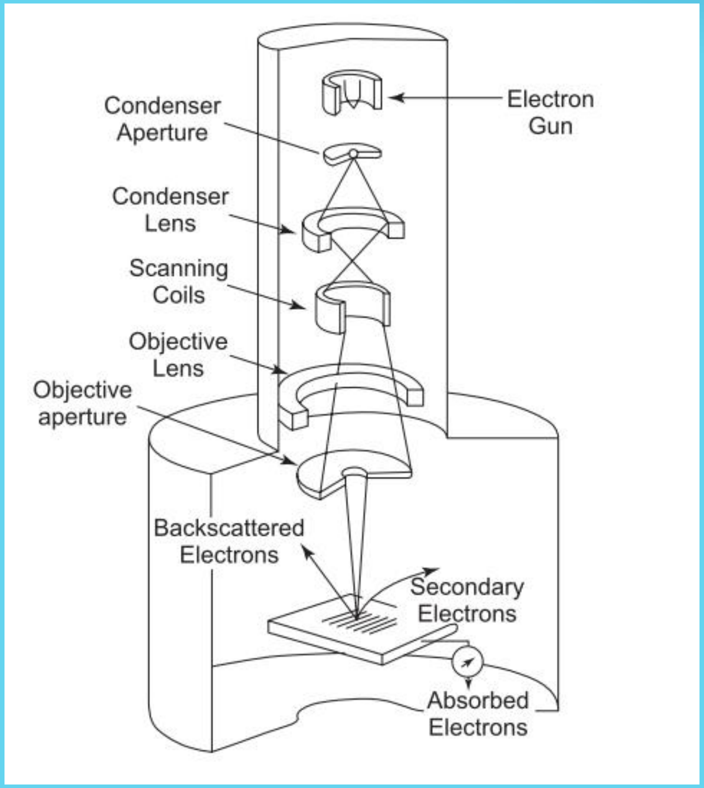
CORONA DISCHARGE



The bottom electrode is a vacuum-deposited metallic film on the material surface, and the top forming metallic electrode is usually made of a metallic wire

Around the point electrode it is possible to exceed
the breakdown strength of the air in a region of a few millimeters.
The so formed ions/free electrons can be accelerated toward the grid
and so be implanted in the target dielectric material

ELECTRON BEAM METHOD

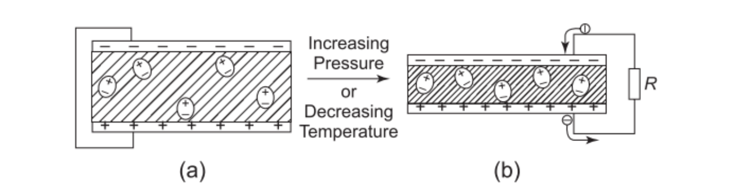


It is possible to inject/extract real charges (electrons) into the electret by SEM

The energy of the electron beam (<50 keV) should be controlled according to the structure and thickness of the material specimens to be used for forming electret

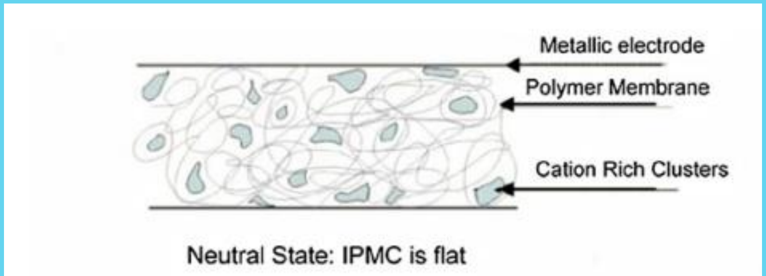
A similar mechanism can be used with ion implantation instrument

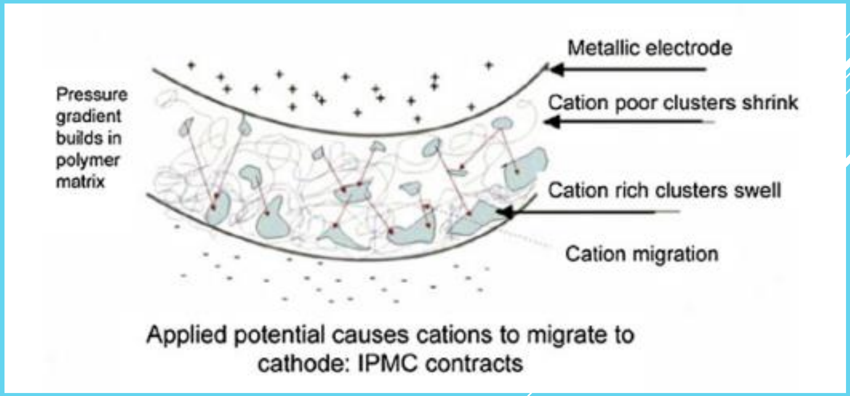
ELECTROACTIVE POLYMERS
(ARTIFICIAL MUSCLES)



Dipolar «soft» electrets have interesting properties similar to piezolectric materials . They can react to external field changing shape or , viceversa, change their own dipolar field because of a change in shape

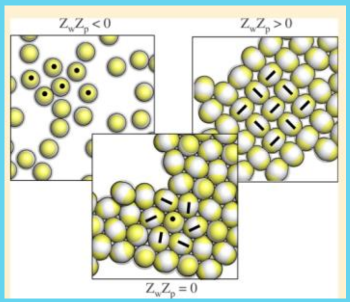
More complex structures can be engineered. Polymer are especially intersting.



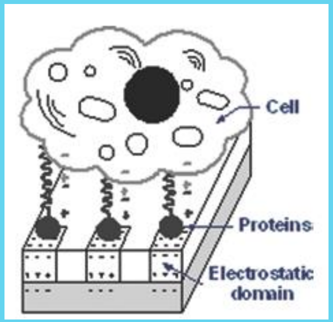


SIZE REDUCTION OF ELECTRETS

- **Miniaturization** of devices (EH, MP)
- The charge provides a further way to **functionalize** the nano/micro- material



Bianchi et al, Nano Lett. 2014, 14, 3412 − 3418



Tofail, Biological Interactions with Surface Charge in Biomaterials (RSC Publ.)

Drawbacks

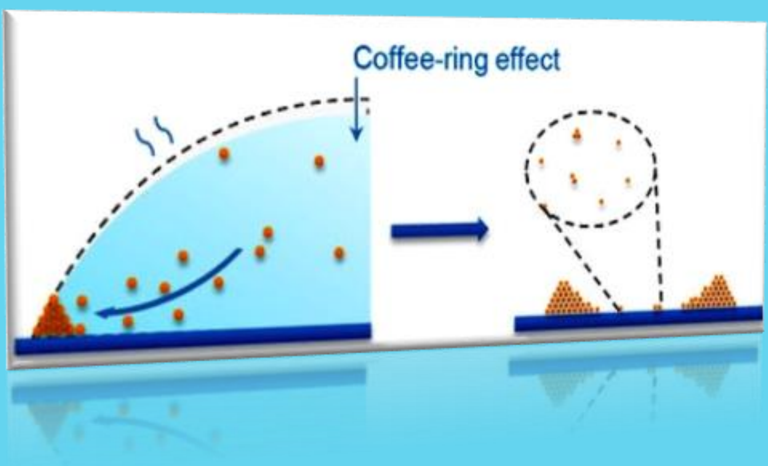
Stability of charging (surface vs space)
Control of charging

But also dynamic applications

Electro-Mechanical resonators

SAMPLES

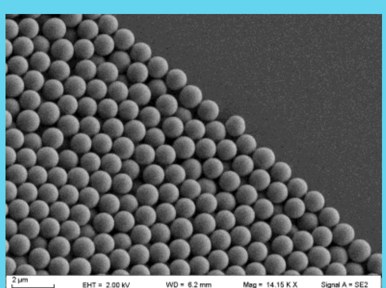
- SiO_2 particles (0.5 e 1 µm) deposited by drop casting on a polished copper substrate

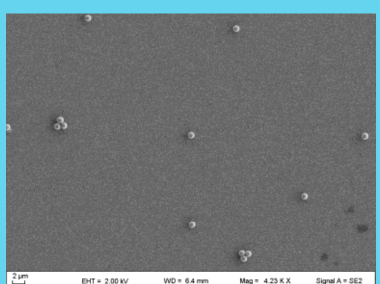


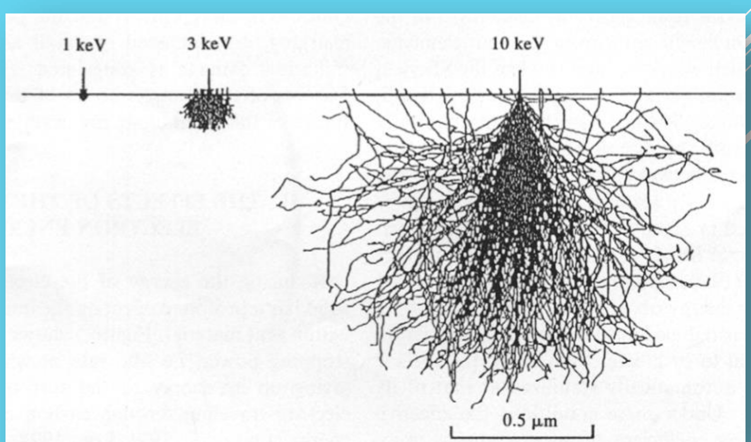
Fabrication by SEM

1) ***High lateral resolution (5 nm at 20 keV)***
2) ***Energy dependent penetration***

$$R = (76/\rho)E_0^{\,1.67}$$







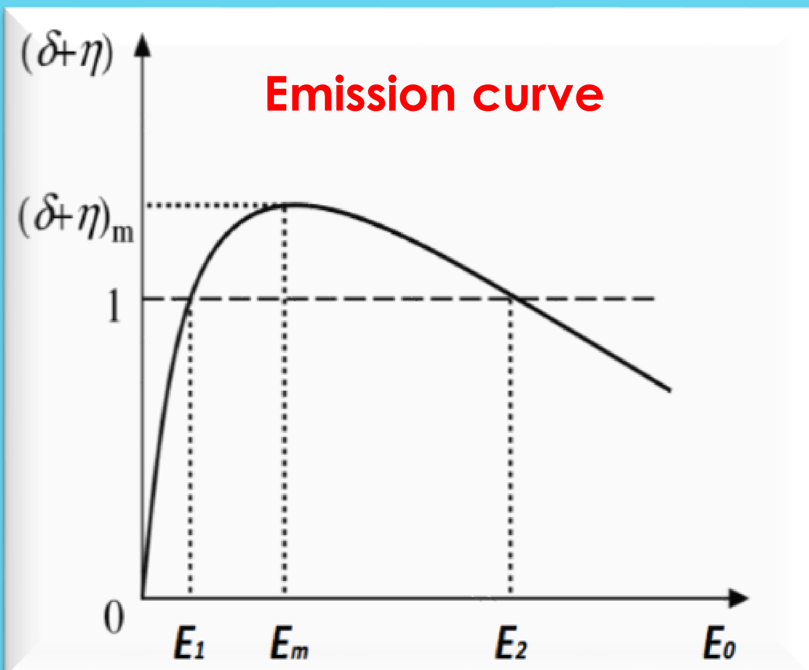
CHARGING MECHANISM

Total Yield Approach

$$\frac{\partial Q}{\partial t} = \left(1-\sigma(E_0)\right)\cdot I_B - I_L$$

1) ***Crossover energies*** **(E_1 e E_2)**

2) Three chraging region: ($\sigma>1$ e $\sigma<1$)



Charge effect:

$E_L = E_0 - eV_s$

Small size material:

1) Leakage current I_L can be significant

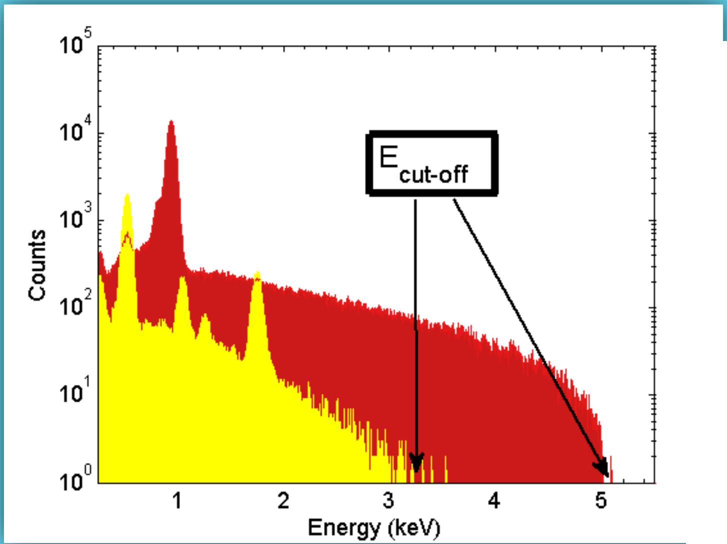
2) Surface potential V_S up to 200-300 V

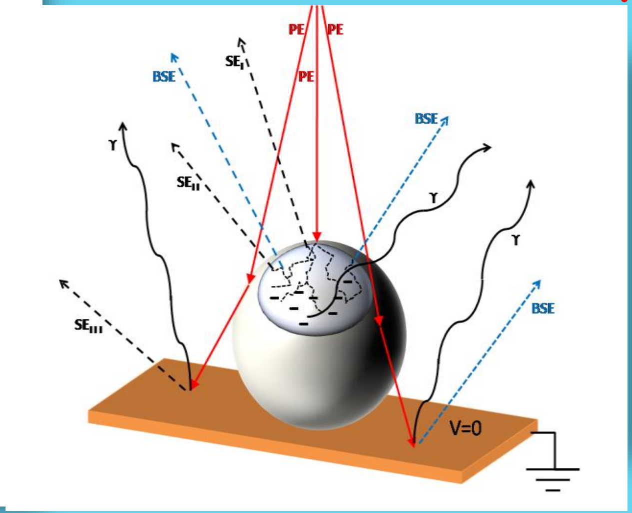
DUANE-HUNT LIMIT SHIFT

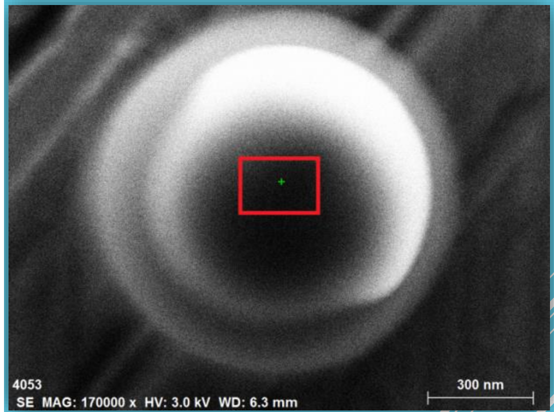
$E_L = E_0 - eV_s$

Bremsstrahlung x-ray spectrum

$$V_S = \frac{E_0 - E_{cut-off}}{e}$$





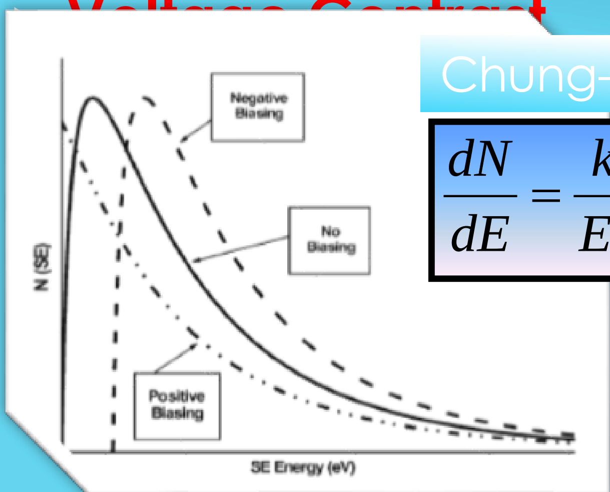


η(π/2)→1

$$V_S < 2R \cdot r.d. \approx 350V \Rightarrow Q \approx 10^5 e^-$$

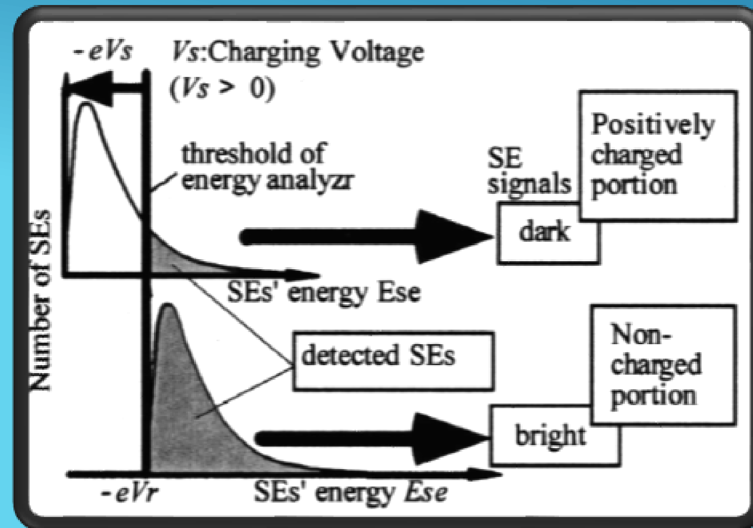
ELECTRONIC SPECTROSCOPY

Voltage Contrast



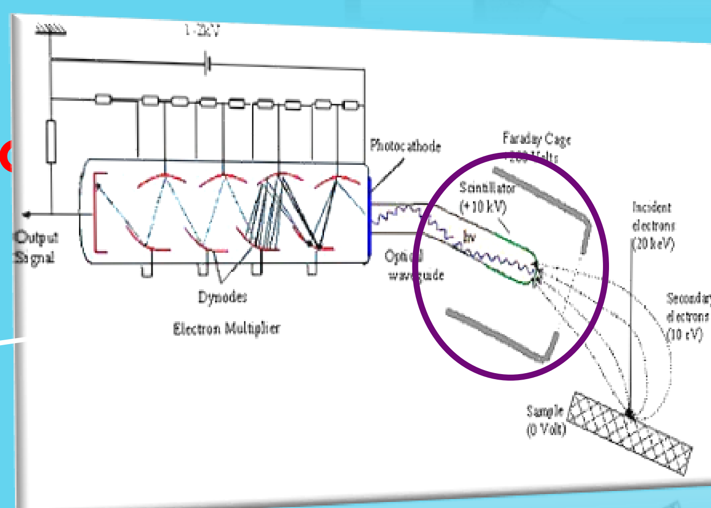
Chung-Everhart

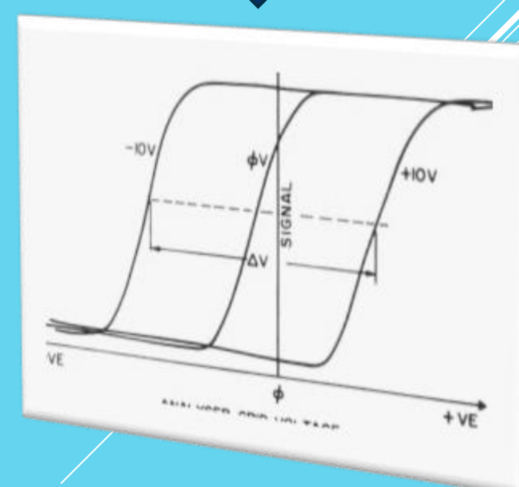
$$\frac{dN}{dE} = \frac{k}{E_0} \frac{E}{(E+\phi)^4}$$



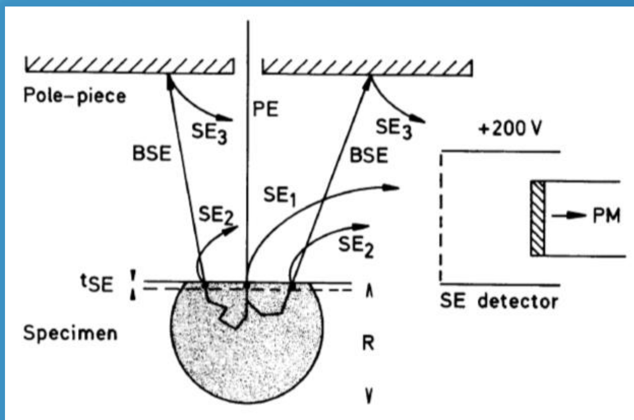
- **Output depends o[n] potential**

Everhart-Thornley detector (E-T)





ELECTRONIC SPECTROSCOPY



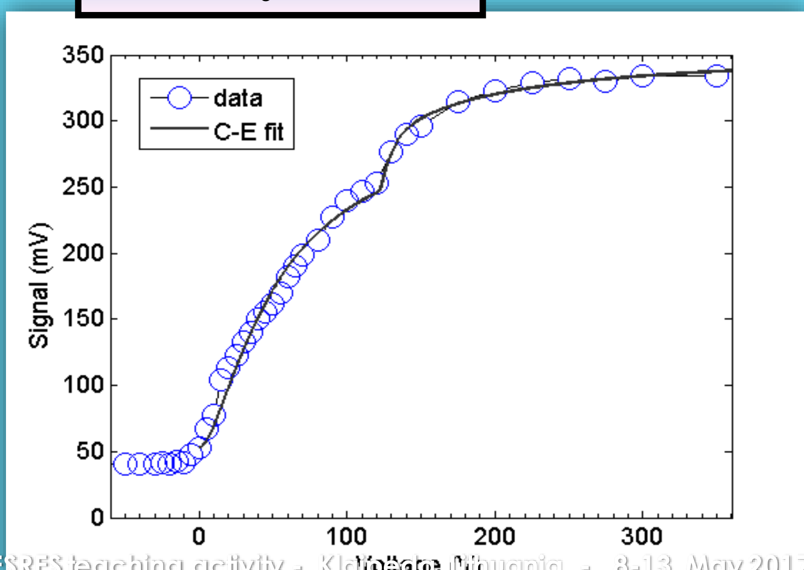
Strong background from the SEM chamber

Increasing Working Distance WD

Increasing Φ

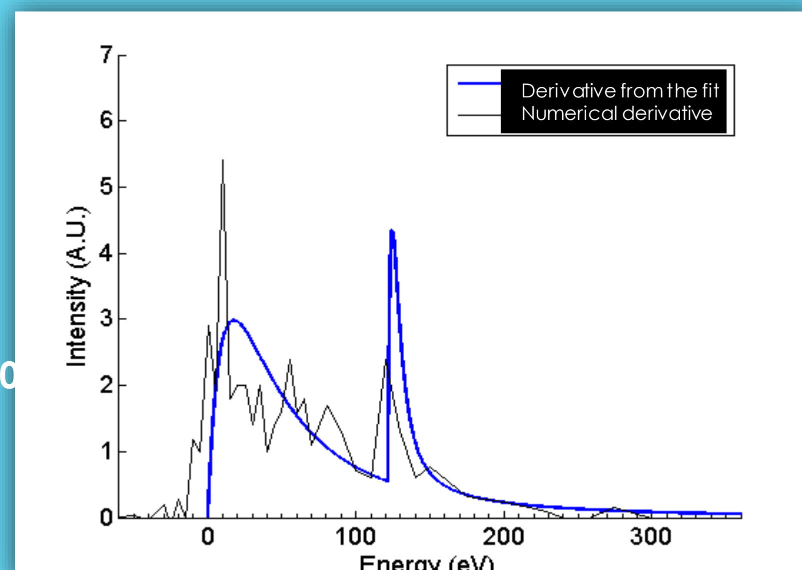
$$\frac{dN}{dE} = \frac{k}{E_0} \frac{E}{(E+\phi)^4}$$

$$S_{SE} = f_1(\delta \sec(\phi) + \delta\eta\beta) + f_2\delta_{ext} + f_3(d\eta / d\Omega)\Delta\Omega$$

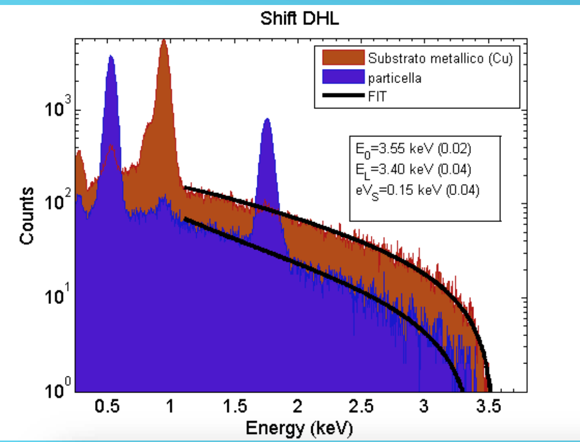


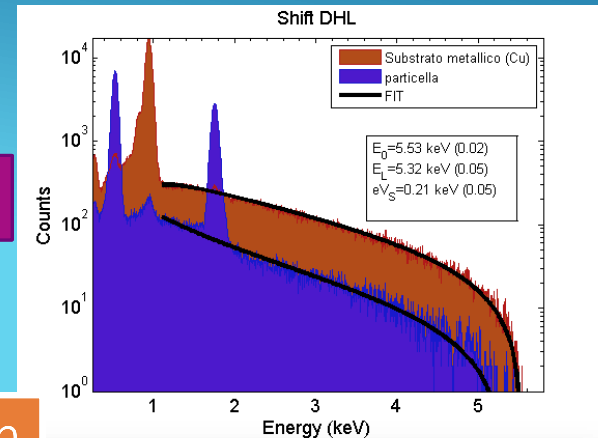
=1.8 keV
D=6.8mm
ag=150KX

=(121±19)V
prems=(130 ±50



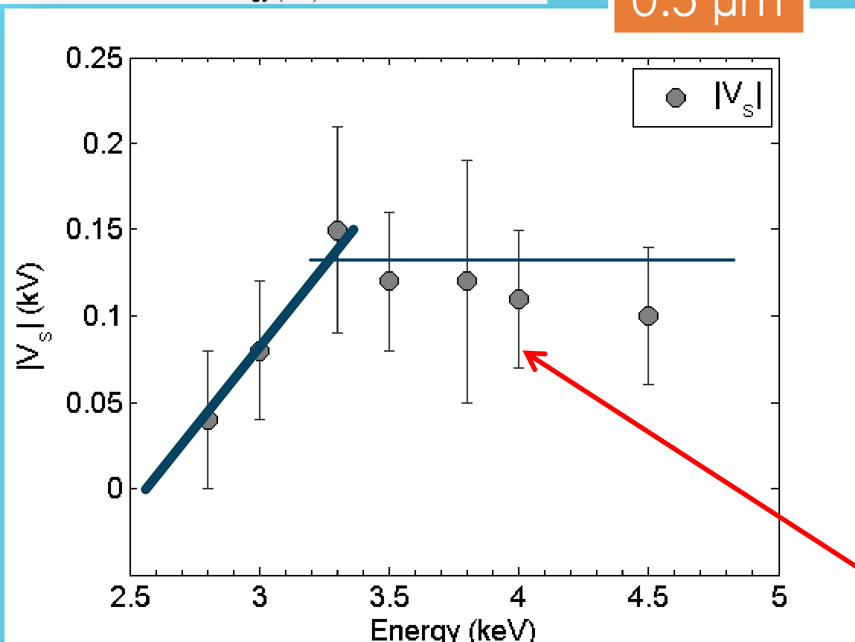
CHARGING VS ENERGY



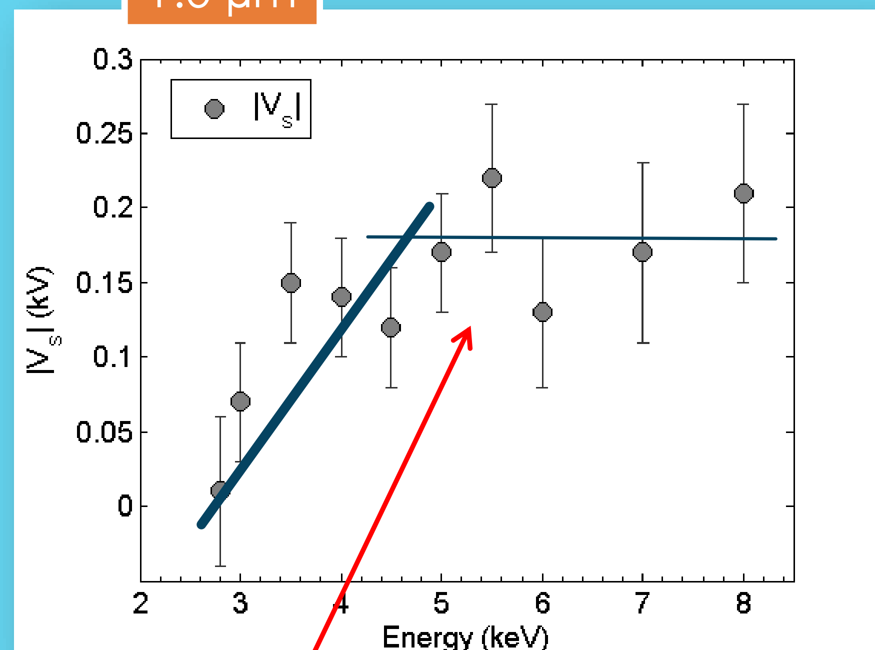


Initial linear increase

0.5 µm



1.0 µm



Potential saturation

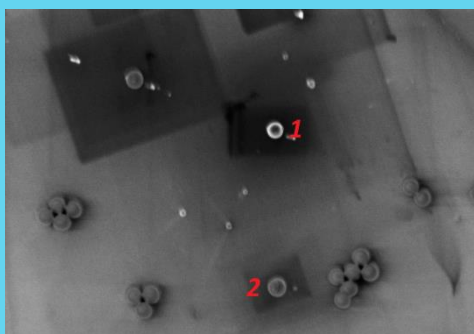
CHARGE TEMPORAL EVOLUTION

Samples in air

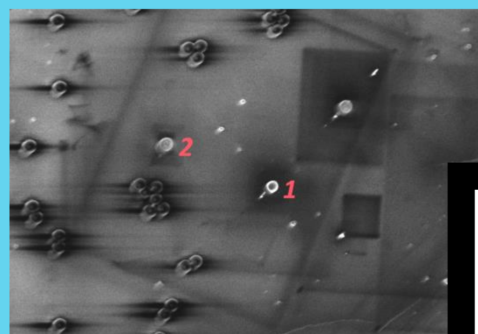
Monitoring charge by non penetrating electrons (0.5-1.5 keV)

Observations by In Lens detector

→ More electrons detected from charged particles

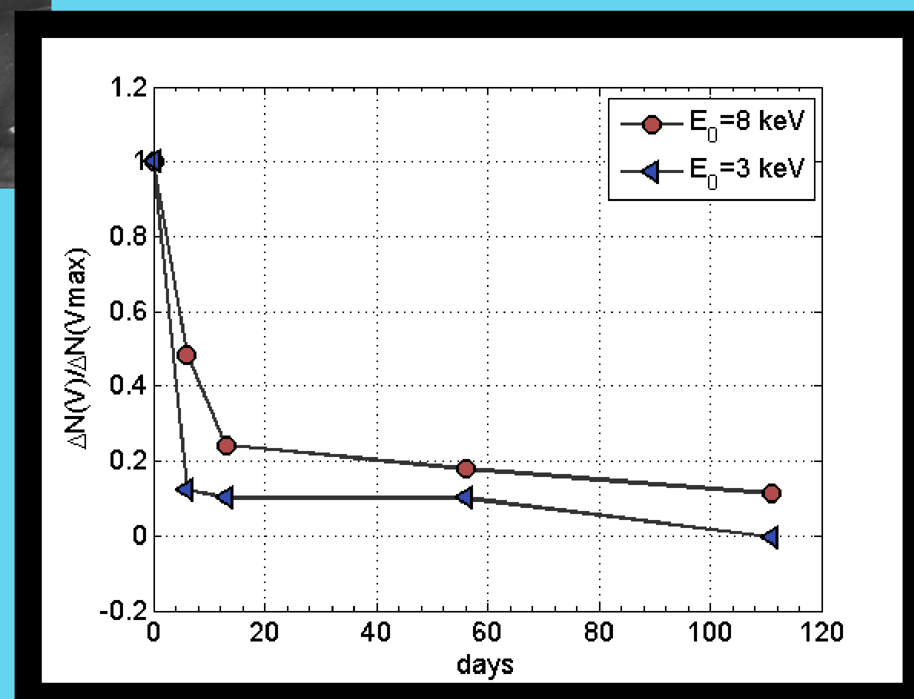


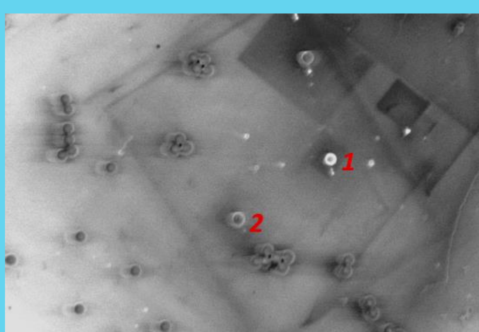
13 days



56 days

$$\Delta N(V_s) = N_{charged}(V_s) - N_{neutral}$$





111 days

Two characteristic lifetimes:

1) ***fast*** (***surface***)
2) ***Slow*** (***space***)

FINAL COMMENTS

- EH device and materials are strongly correlated
- Thermoelectric materials convert thermal gradient into electric energy. The optimization of thermoelectric generators depends on the separation of phononic and electronic properties.
- Electro active materials are effective ways to harvest mechanical energy (noise vibration and direct forces)
- Piezoelectrics materials change their polarization state after a shape change. Their properties depend on the asymmetric structure of the crystal cell.
- Electrets are artificial materials,where the natural charge distribution has been modified. They can provide significant permanent external electric fields.