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Innovative polymer-based composite systems
for high-efficient energy scavenging and storage

Training Material on Piezoelectric Materials

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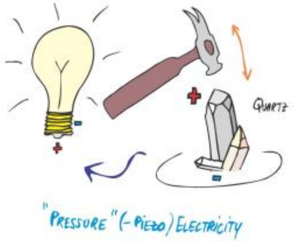
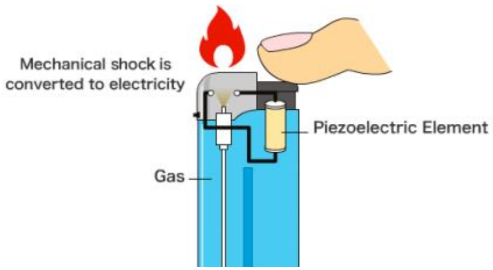
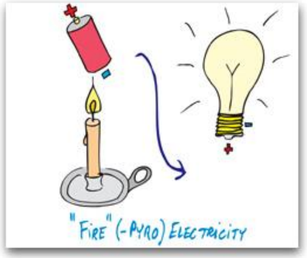
Electro active materials

- Piezo-electric polymer
  - Converts mechanical energy received into electrical energy:

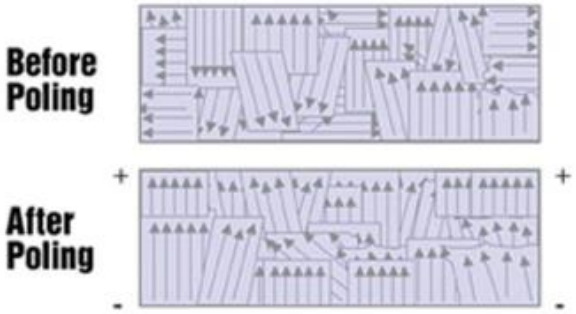




- Pyro-electric polymer
  - Converts heat into electrical energy:



- Ferro-electric polymer
  - Keeps oriented its polar crystals



- Ferrorelaxor polymer
  - Has a high dielectric constant above 20 and high strain with low applied voltage

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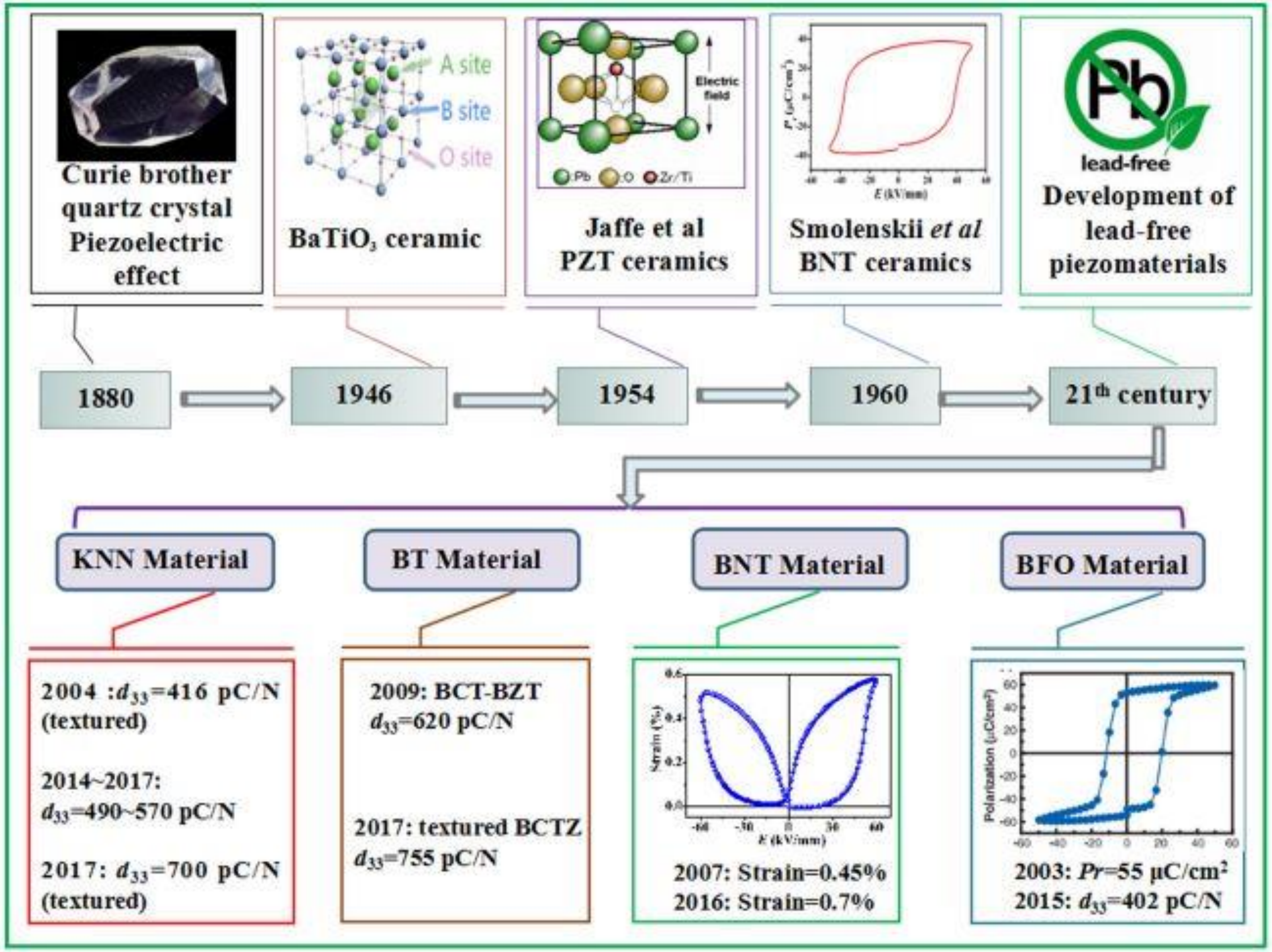
Evolution of lead-free piezoelectric materials



Zheng, T., Wu, J., Xiao, D., & Zhu, J. (2018). Recent development in lead-free perovskite piezoelectric bulk materials. *Progress in materials science*, *98*, 552-624.

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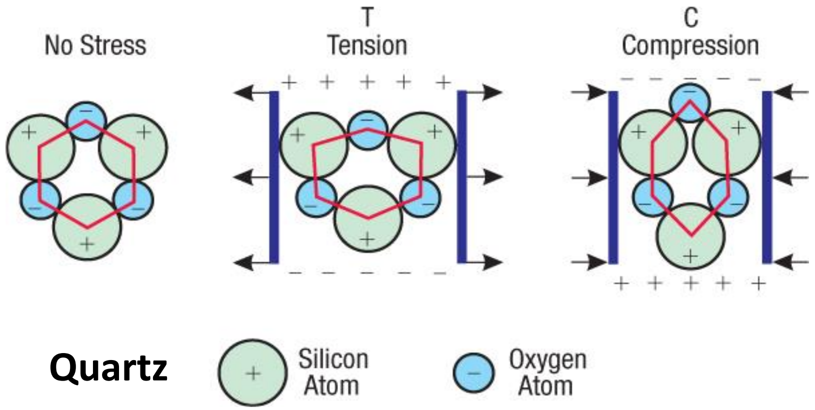
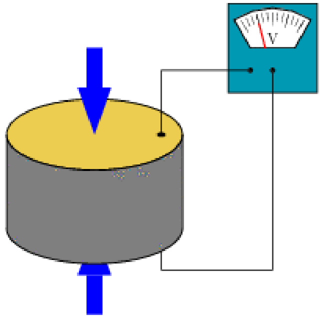
Piezoelectric materials

Piezoelectric effect





Mechanical Energy → *Electrical Energy*

$$D = dT + \varepsilon E$$

D: Dielectric displacement
d: piezoelectric coefficient
T: mechanical stress
ε: dielectric constant tensor under constant stress
E: electric field

Curie Jaques, Curie Pierre, Development, via compression, of electric polarization in hemihedral crystals with inclined faces]. *Bulletin de la Société Minérologique de France*. 3 (**1880**) 4 : 90–93.

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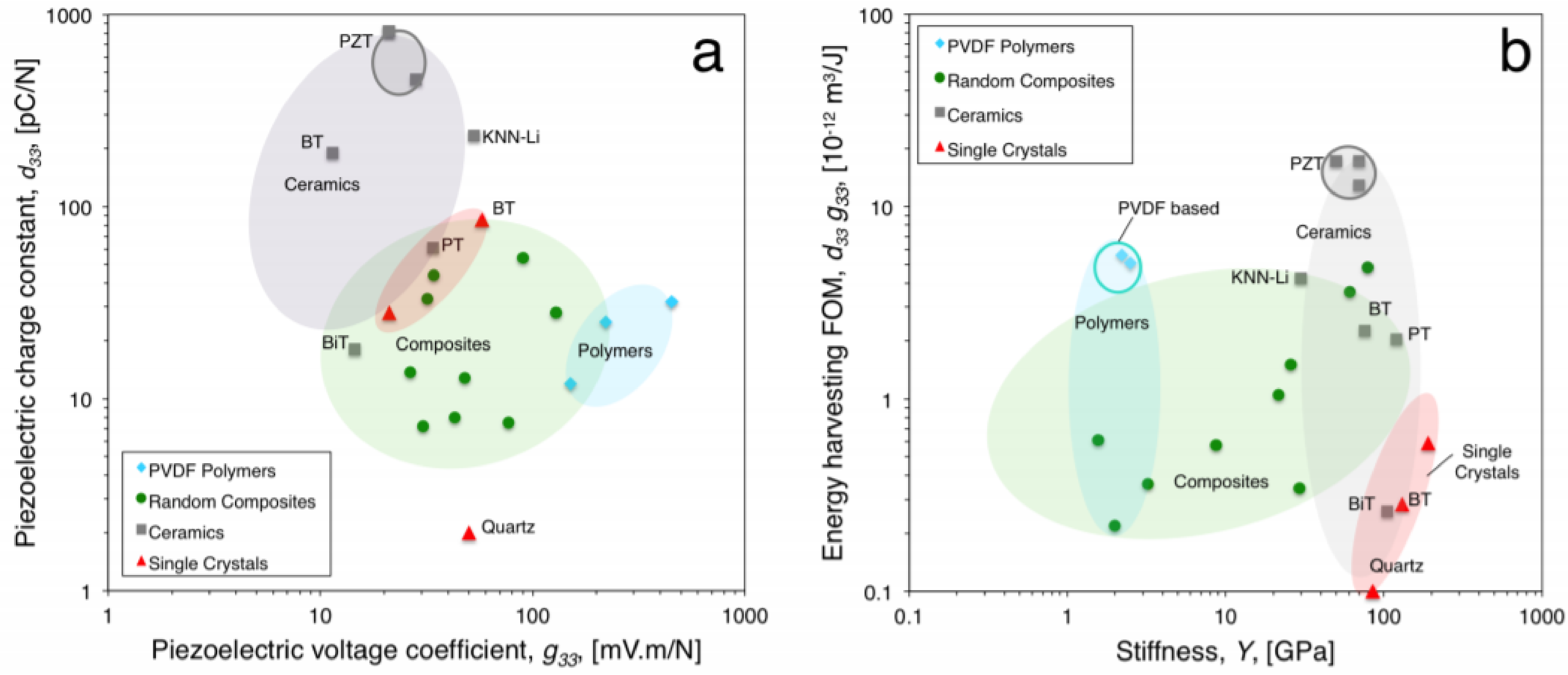
Piezoelectric behavior: ceramics, polymers, composites



➢ Good compromise between piezoelectric coeficients (d_{33}, g_{33}) and mechanical properties

Deutz, D.. Flexible piezoelectric composites: Bridging the gap between materials and applications. 2017.

Piezoelectric materials

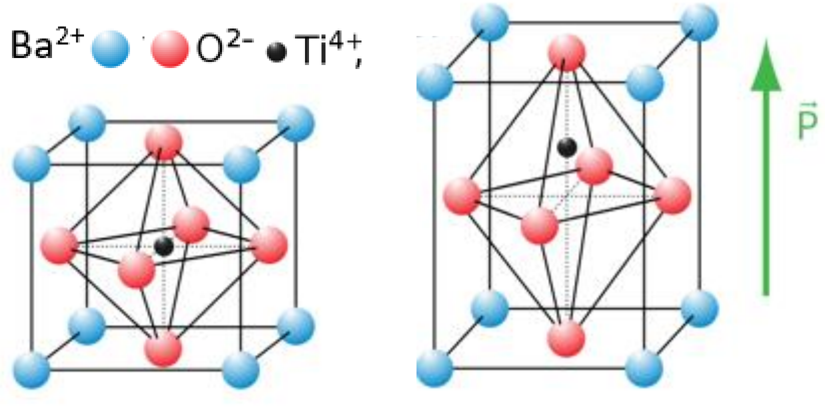
Piezoelectric effect is exhibited by most of the materials that possess a **non-centrosymmetric crystal structure**

Ceramics
($BaTiO_3$, PZT, KNN)

Composites
Polymers + ceramic fillers
(films, fibres)

Polymers
(PVDF, PVDF-TrFE)

$BaTiO_3$: Perovskite structure



Cubic structure
(no net polarization)

Tetragonal structure
(net polarization)

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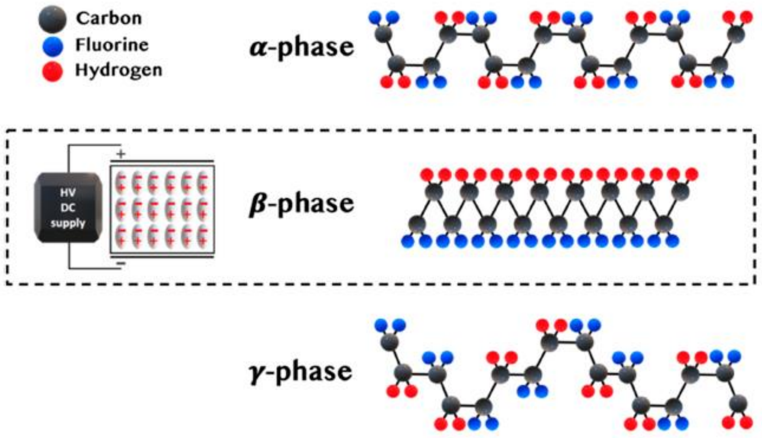
PVDF



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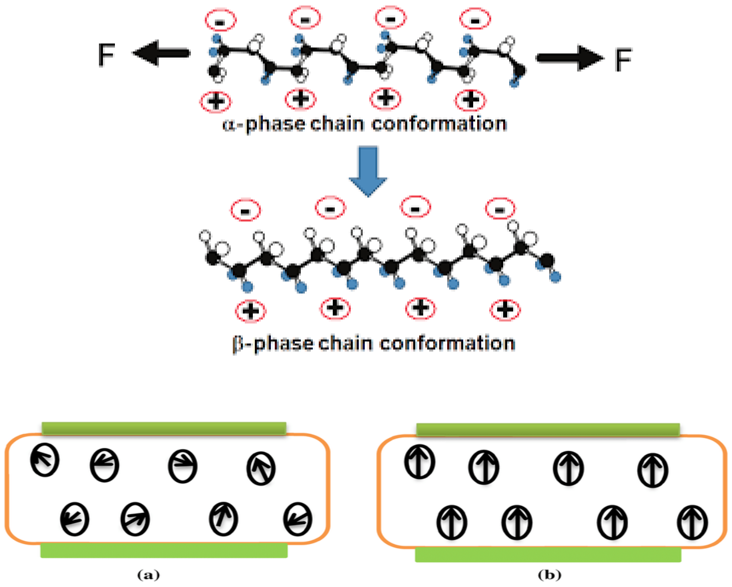
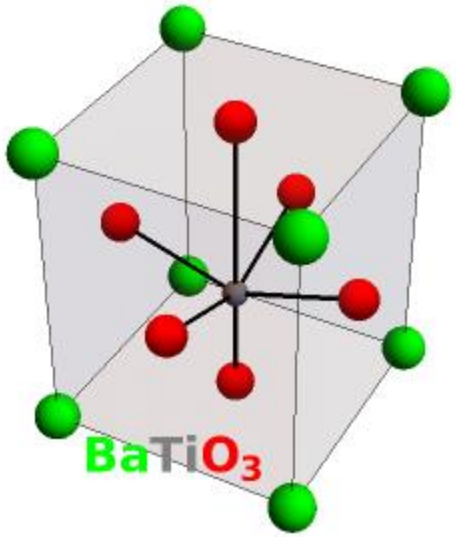
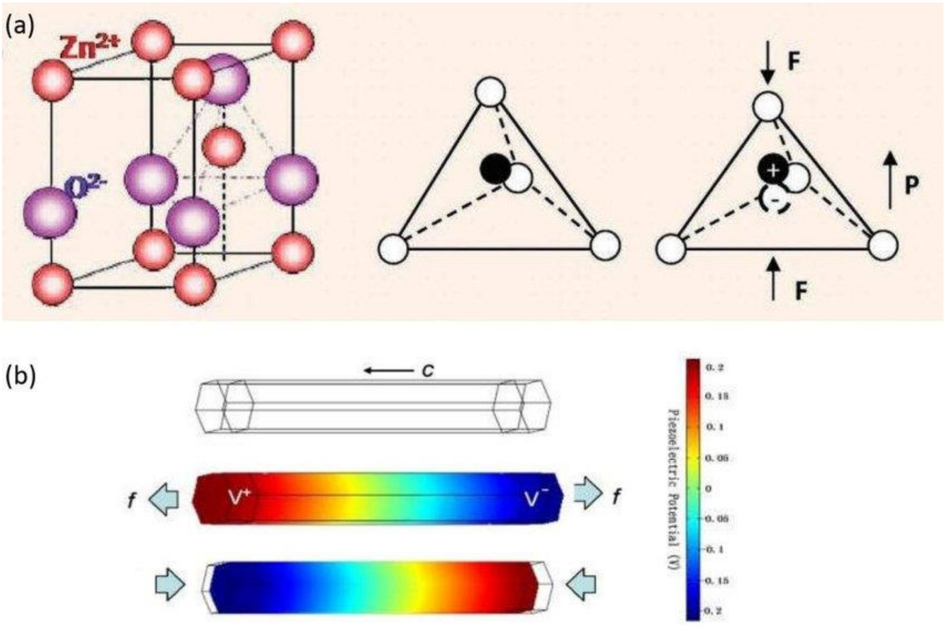
Lead free materials with piezoelectric properties

Orientation







PVDF structure

BTO structure

ZnO nanorods structure

Polarization process

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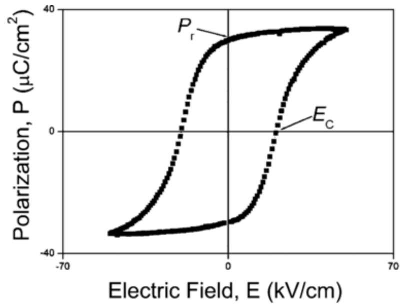
Ferroelectric & Piezoelectric Materials

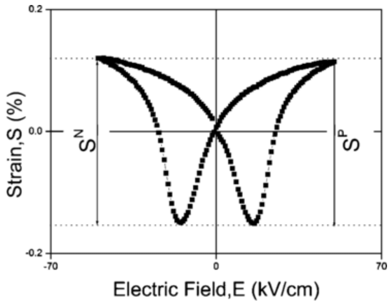
Ferroelectric

Exclusive features of ferroelectric (FE) materials

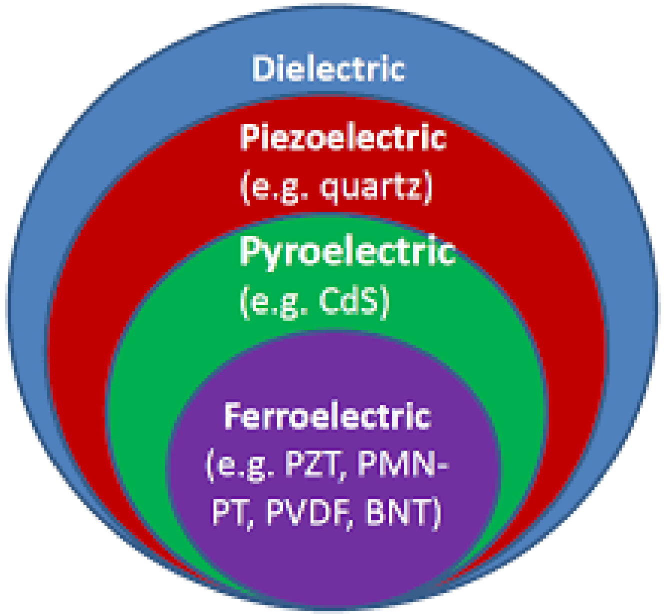
Permanent dipole moment



Spontaneous polarization

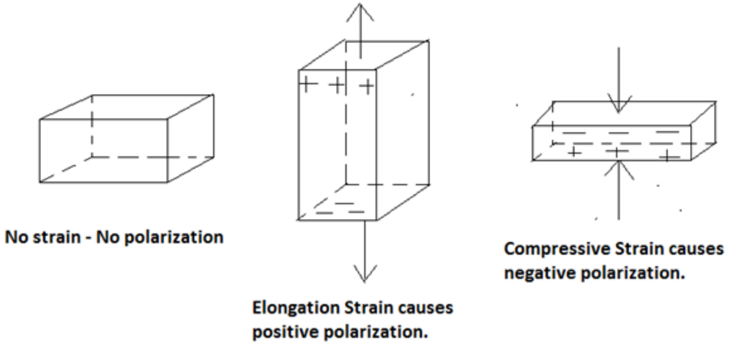


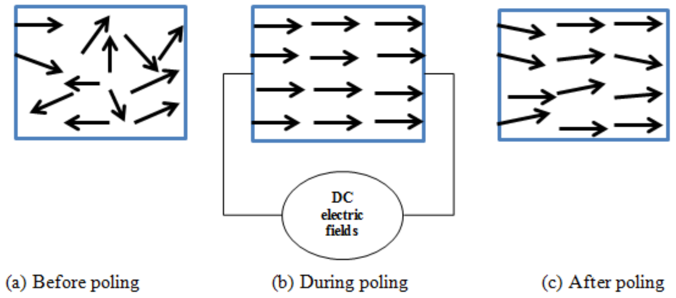
All ferroelectrics are also piezoelectric, with the additional property that their natural electrical polarization is reversible



Piezoelectric

Piezoelectric Materials: dielectric materials that can be polarized by means of an external electric field or by the application of a mechanical stress.





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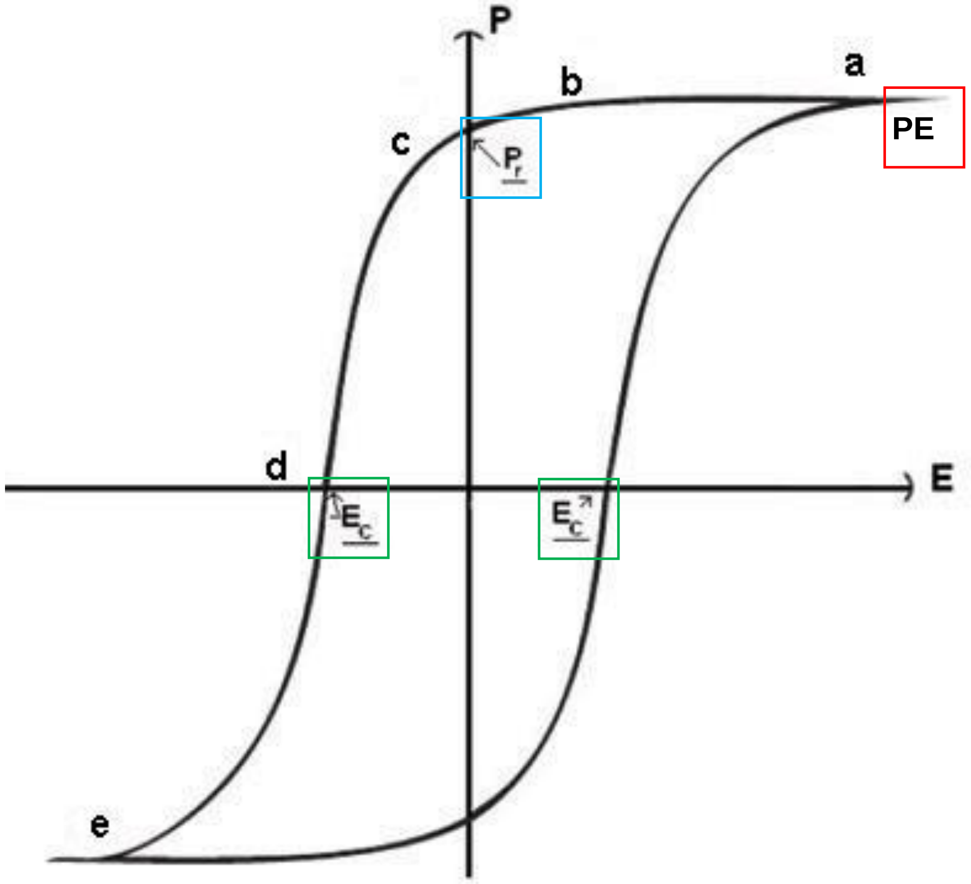
Polarization hysteresis: Ferroelectric Materials

-E_c: Coercive field Voltage threshold to start crystals polarization

-P_r: Remnant polarization
Residual polarization after electrical field removed

-PE Maximum polarization achievable near to breakdown voltage

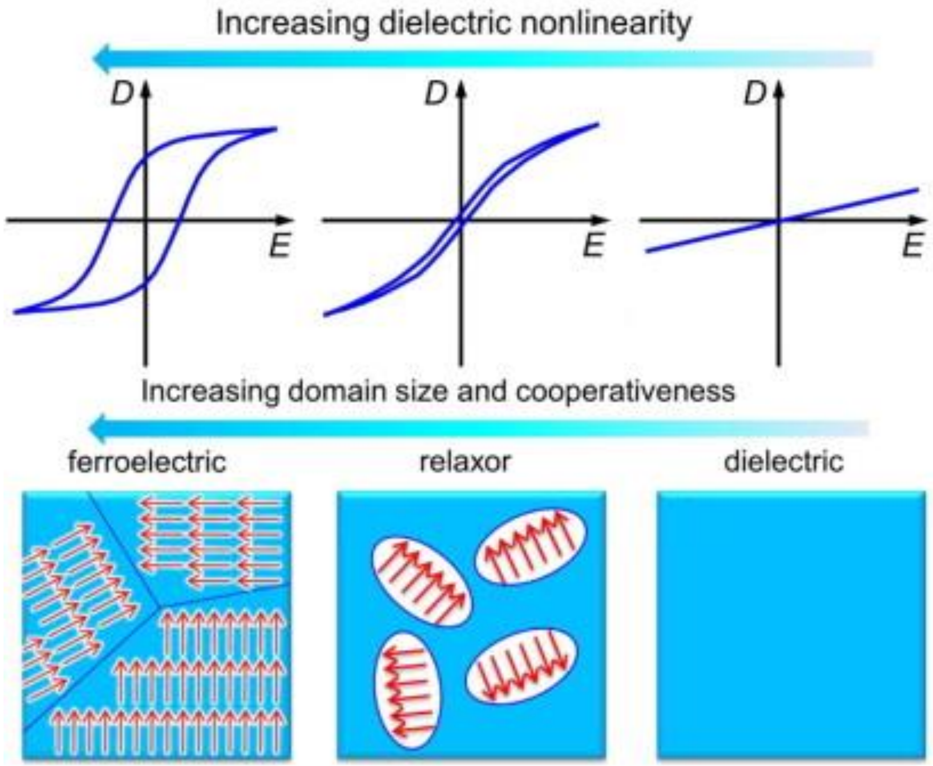
-d_{33}: Piezo coefficient
Capability of a material to generate an electrical signal under a mechanical stress



Typical Values

PVDF-TRFE copolymers

- Large crystalline domains
- **ε_r** : 11
- **P_r** : 8 µC/cm^2
- **E_c** : 55 V/µm
- **d_{33}** : - 27 pC/N



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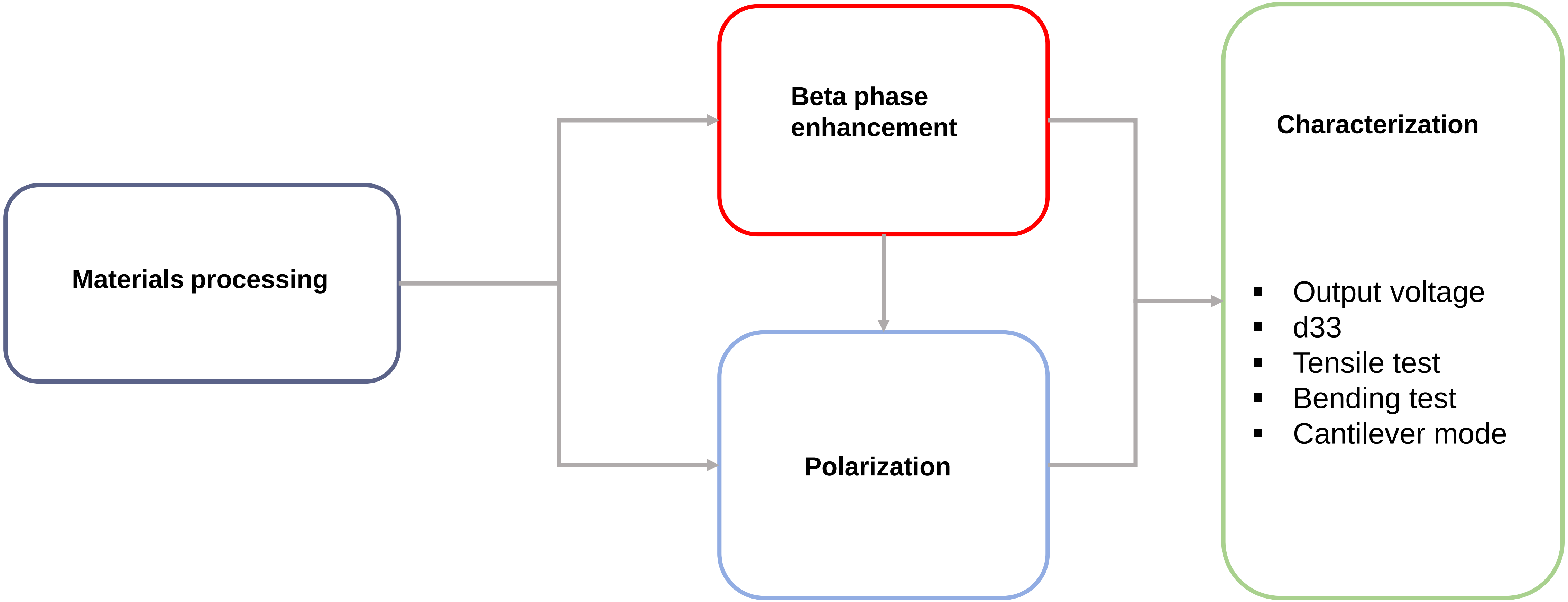
Fabrication and characterization process



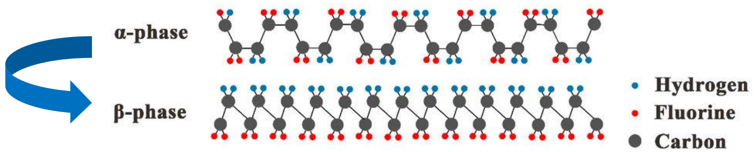
Development of lead-free piezoelectric composite films

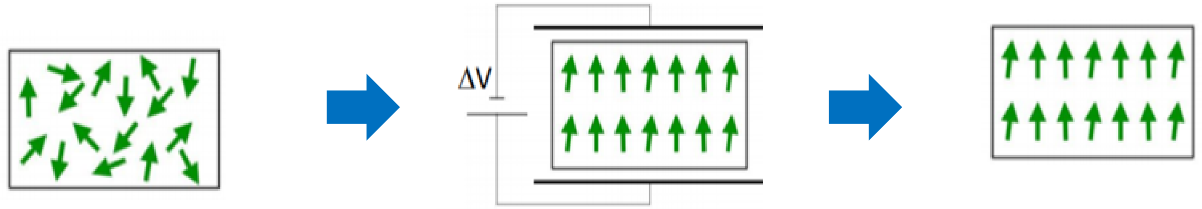
Development of PVDF, PVDF/$BaTiO_3$ films/strips

1) Filament extrusion/compounding;
2) Fabrication of the tapes
3) Drawing process (under strain & temperature) for enhanced **β-phase content of PVDF matrix**

& **subsequent polarization** (under electric field in oil bath)

4) Testing





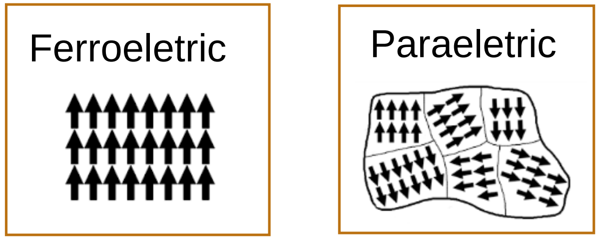
Non-poled
Dipoles randomly oriented

Poling process
(application of DC voltage)

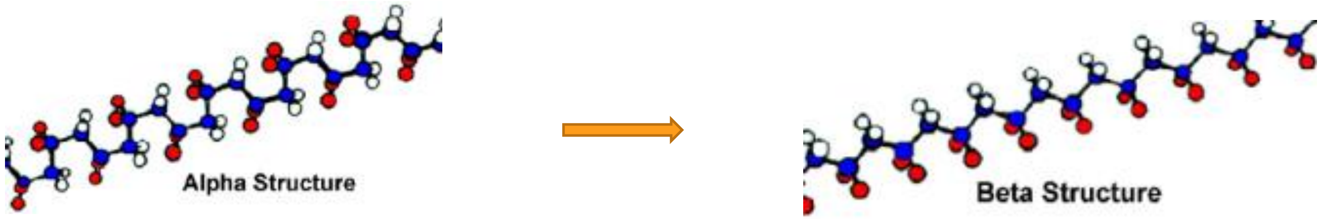
Poled material
Dipoles oriented

Electro active materials

- **β-phase PVDF** the most widely used polymer for Piezo application since 1969 showing a very high value of Curie Point.
- Curie transition point is the Thermal transition between the ferroeletric (ordered crystalline state) and paraelectric phase (disordered crystalline state)



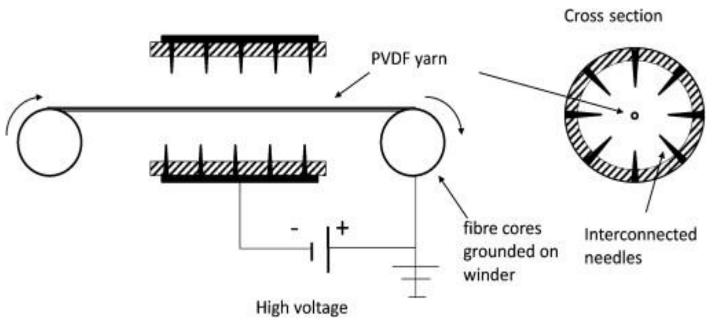
- To make PVDF piezo we need to **convert crystalline α-phase into β-phase** by:



  - Stretching it mechanically
  - Annealing under a very high Pressure
  - Poling by applying a very high electrical field

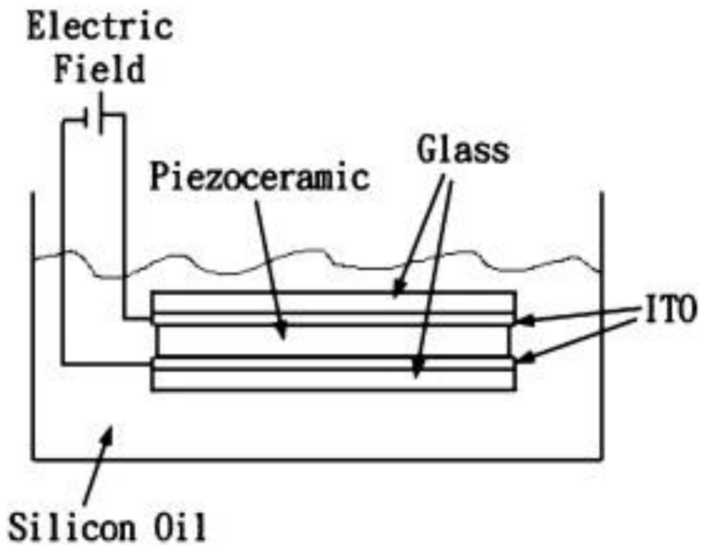
Piezoelectric polarization process methodologies

Inline-polarization



- One step process
- Can be combined with fibre fabrication processes

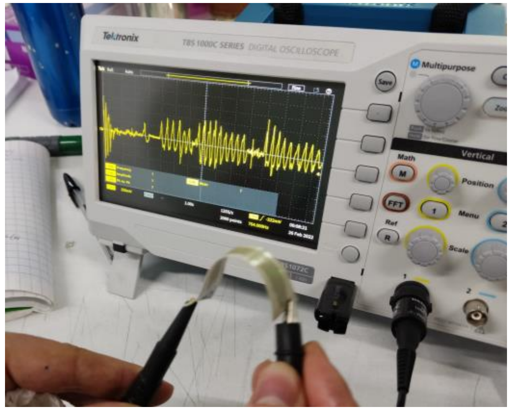
Offline-polarization



- It takes several minutes
- It is necessary to do the polarization after the material integration

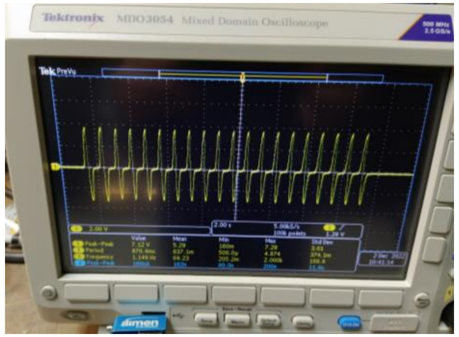
Characterization of lead-free piezoelectric composite films

- **Analysis of d_{33} piezoelectric coefficient & output voltage**



- d_{33} piezoelectric coefficient (pC/N) measured after polarization process
- Output voltage response measured with an oscilloscope (with a 10:1 10MΩ probe) upon bending cycles applied by hand

- **Output voltage – bending & tensile tests** (universal tensile machine)



- Peak-to-peak voltage response monitored with an oscilloscope (10MΩ internal resistance) when subjecting the piezoelectric films to tensile tests

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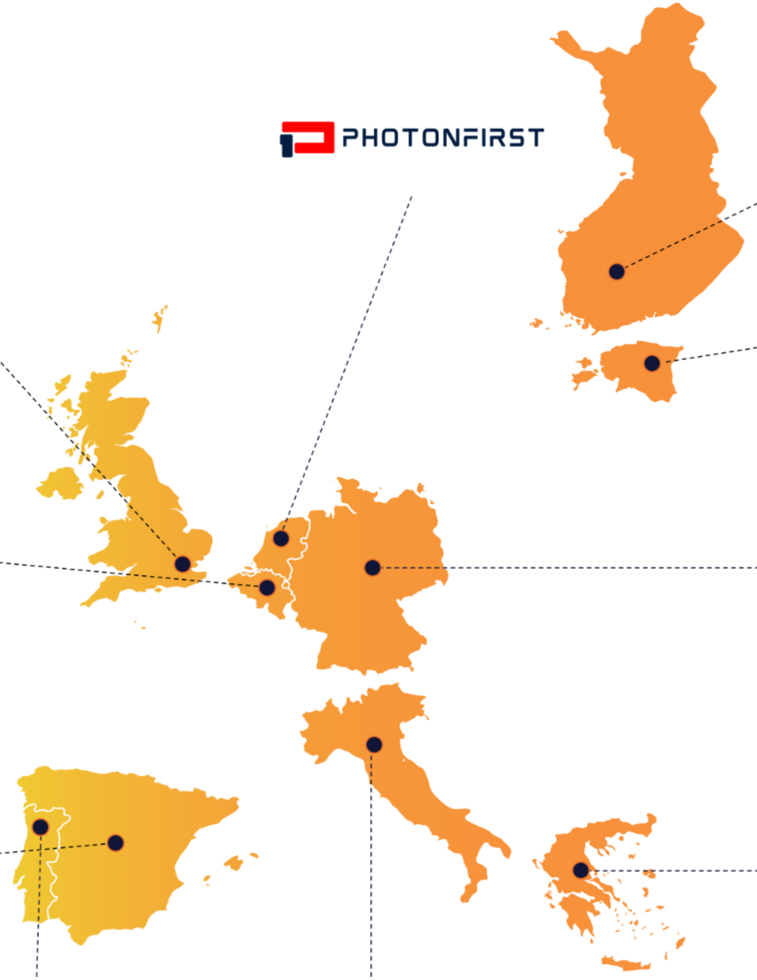

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Innovative polymer-based composite systems
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Thank you

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