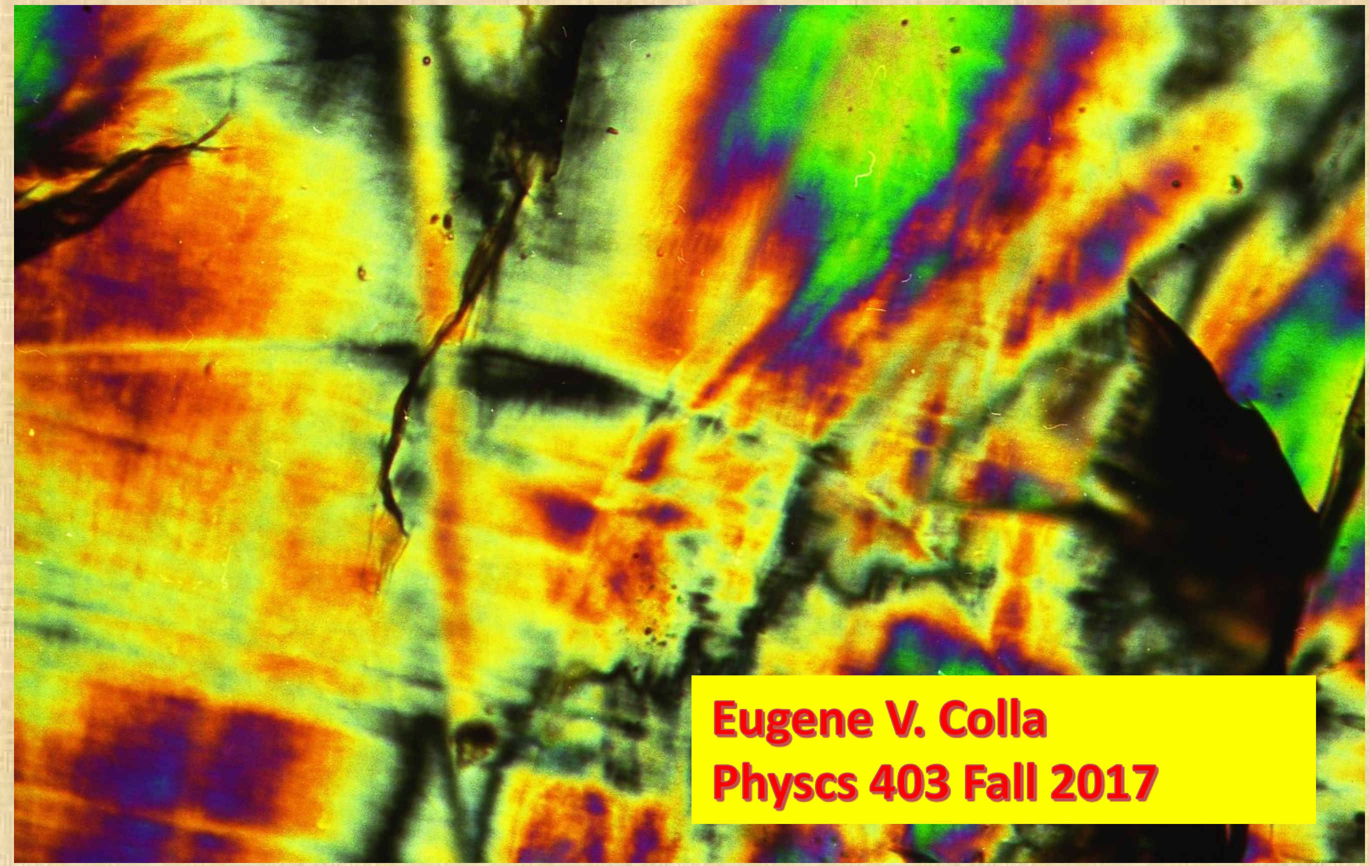
Ferroelectrics. Disordered Ferroelectrics – Relaxors.



Outline

- Ferroelctricity
  - Main properties
    - History. Discovery. Materials
      - Relaxors
        - Applications

Ferroelectricity. Definition.

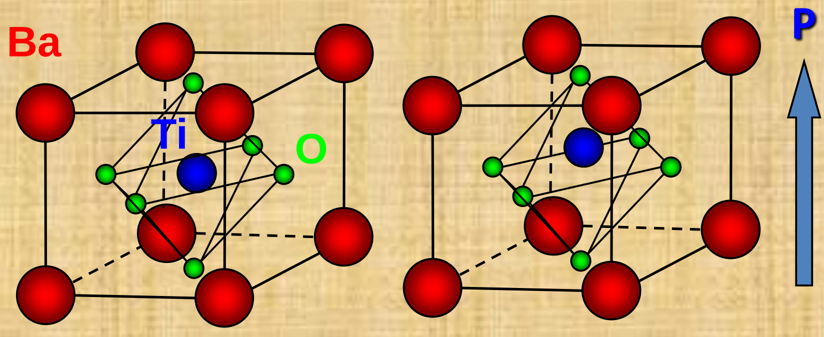
- **Ferroelectric Materials. A ferroelectric material is a material that exhibits, over some range of temperature, a spontaneous electric polarization that can be reversed or reoriented by application of an electric field.**

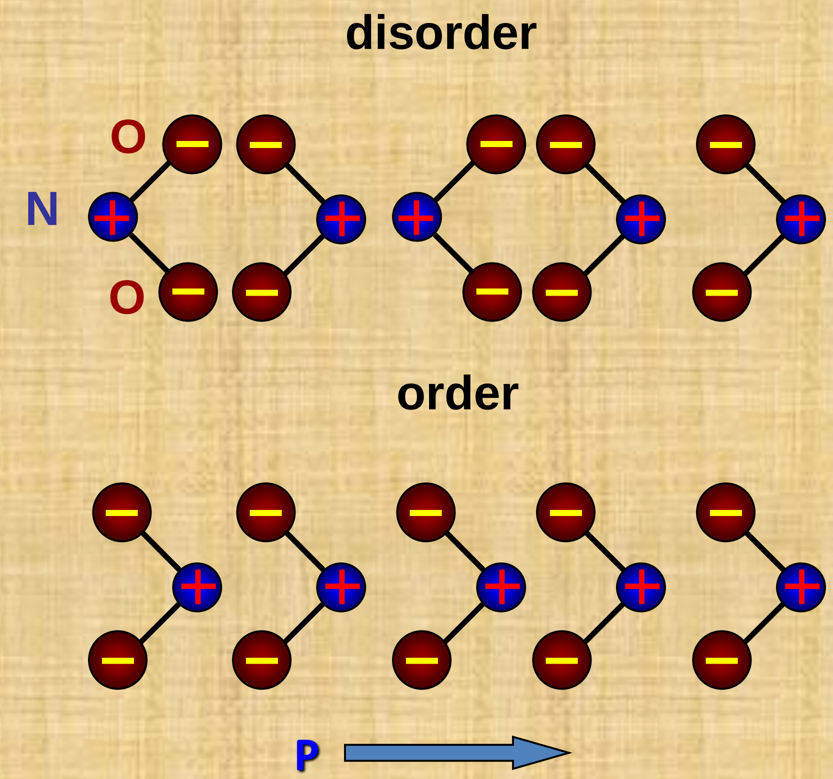
An American National Standard
IEEE Standard Definitions of
Primary Ferroelectric Terms

Ferroelectricity: Two classes of ferroelectrics

Order-Disorder

Displacement type

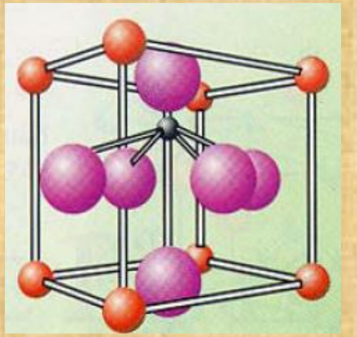


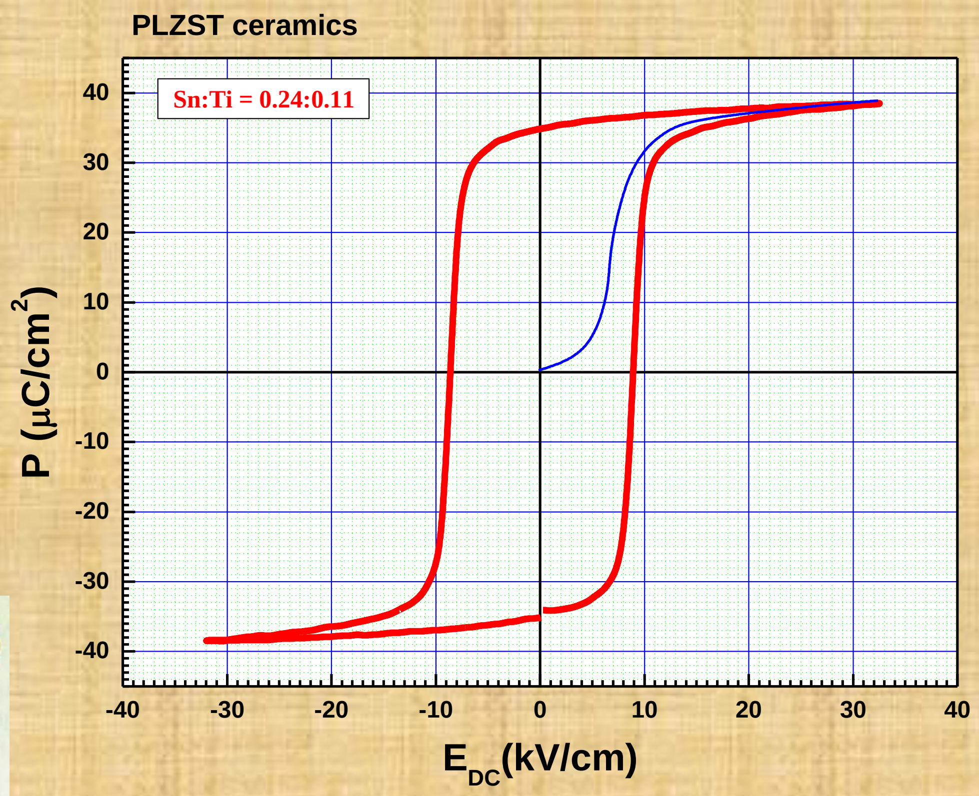


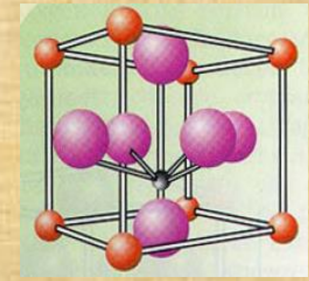
$BaTiO_3$

$NaNO_2$

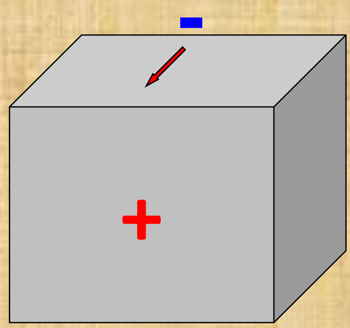
Ferroelectricity: Polarization reversible. (P-E hysteresis)



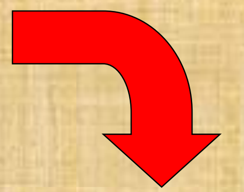




Ferroelectricity: Domains

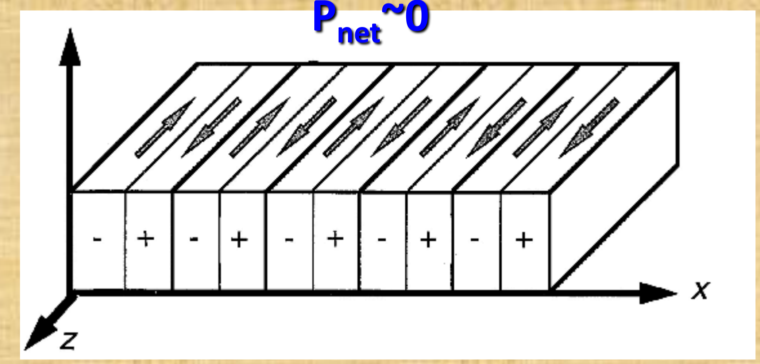


Single domain state



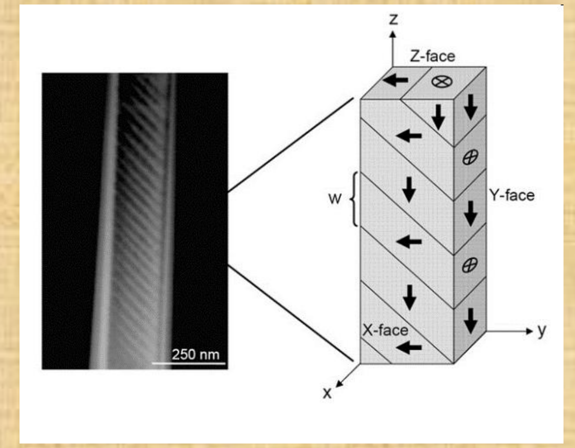
Multi domain state

P_{net}~0



180º domain pattern

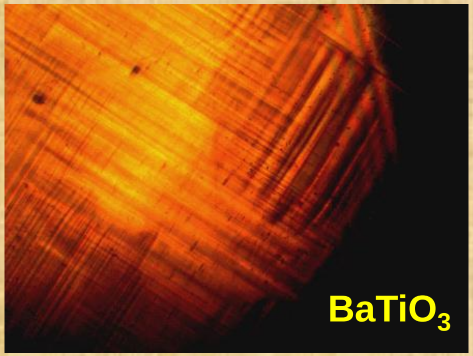
Y Lu et al. Science 1997;276:2004-2006



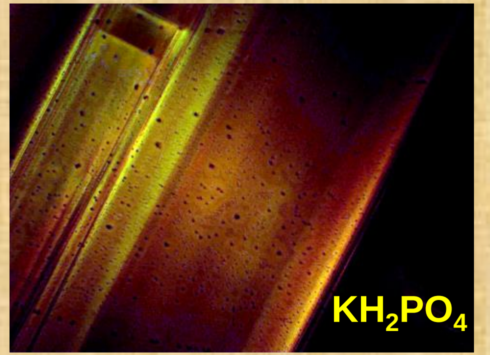
90º domains

Courtesy of Igor Lukyanchuk
http://www.lukyanc.net/stories/nano-worldofdomains

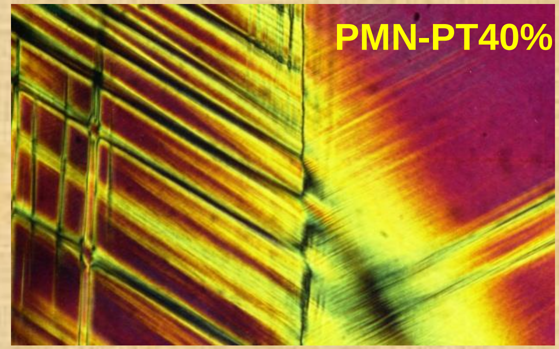
Ferroelectricity: Domains



Courtesy of Benjamin Vega-Westhoff and Scott Scharfenberg, P403, Fall2009

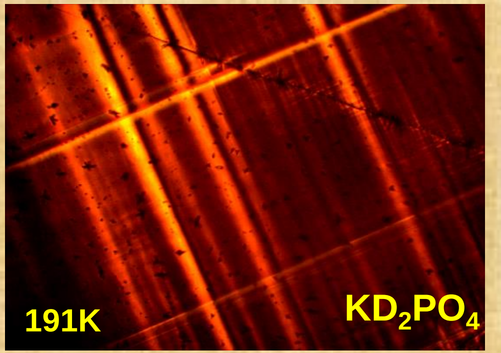


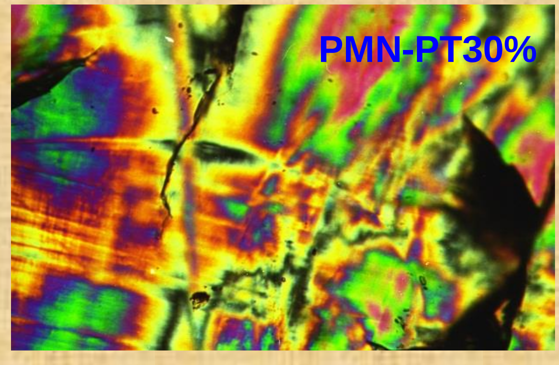
Courtesy of Allison Pohl, P403, Fall2009



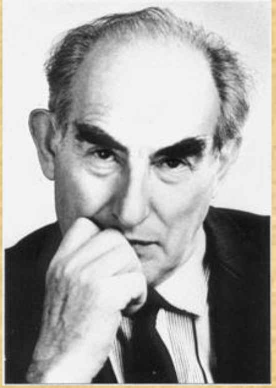
Crystal from Forschungsinstitut für mineralische und metallische

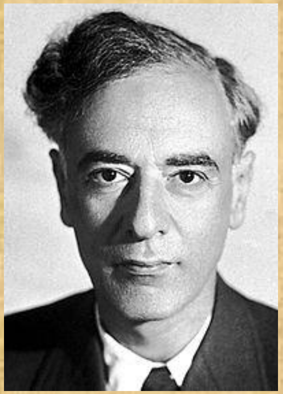
Werkstoffe -Edelsteine/Edelmetalle





Ferroelectricity: Landau-Ginzburg phenomenological theory


Vitaly Ginzburg
1916-2009


Lev Landau
1908-1968

Free energy; Order parameter (polarization); Electric field

$$F_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \ldots - EP$$

the equilibrium solution $$\frac{\partial F}{\partial P} = 0$$

Ignoring higher terms we can get the linear solution:

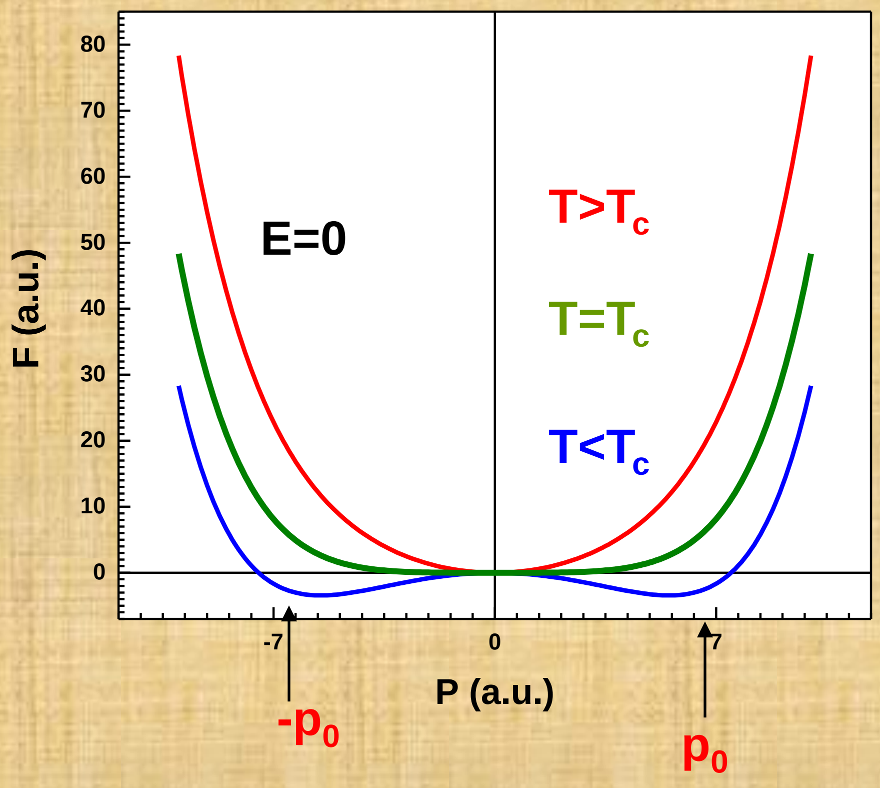
$$\frac{\partial F}{\partial P} = aP - E = 0 \qquad \chi = \frac{\partial P}{\partial E} = \frac{1}{a}$$

Assuming linear dependence of a on temperature we will have:

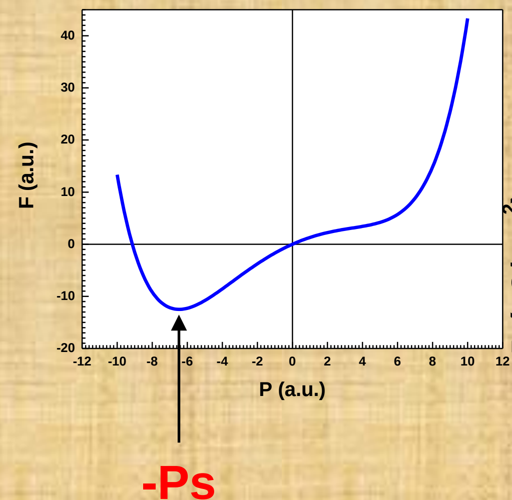
$$\alpha = \frac{1}{C}(T - T_c)$$ and finally we will have Curie-Weiss law $$\chi = \frac{C}{(T - T_c)}$$

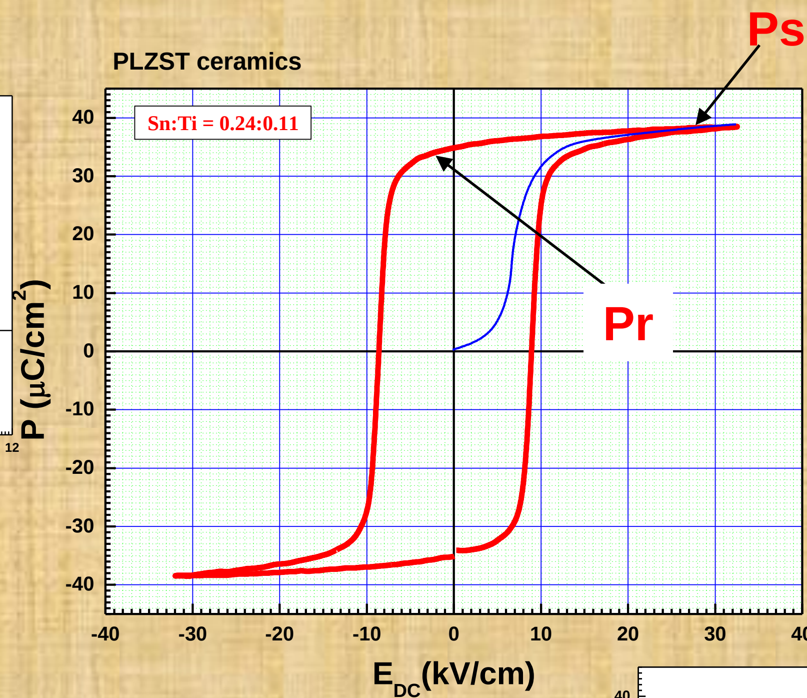
Ferroelectricity: Landau-Ginzburg phenomenological theory

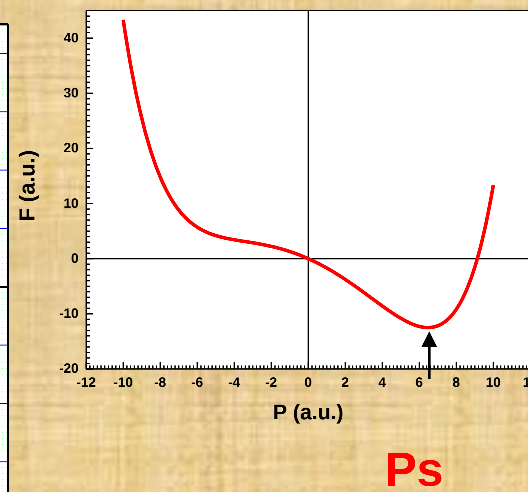
In case of b>) (C>0 also) We will have the solution for second order phase transition with two equilibrium points $-p_0$ and p_0. Both these states are equivalent



Ferroelectricity: Landau-Ginzburg phenomenological theory

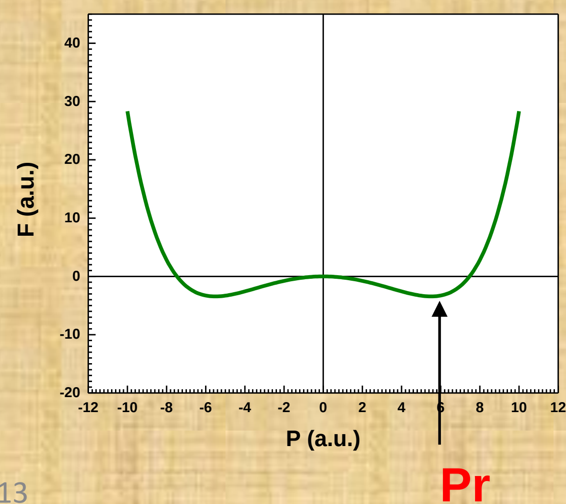






Including EP term can illustrate the P-E hysteretic behavior

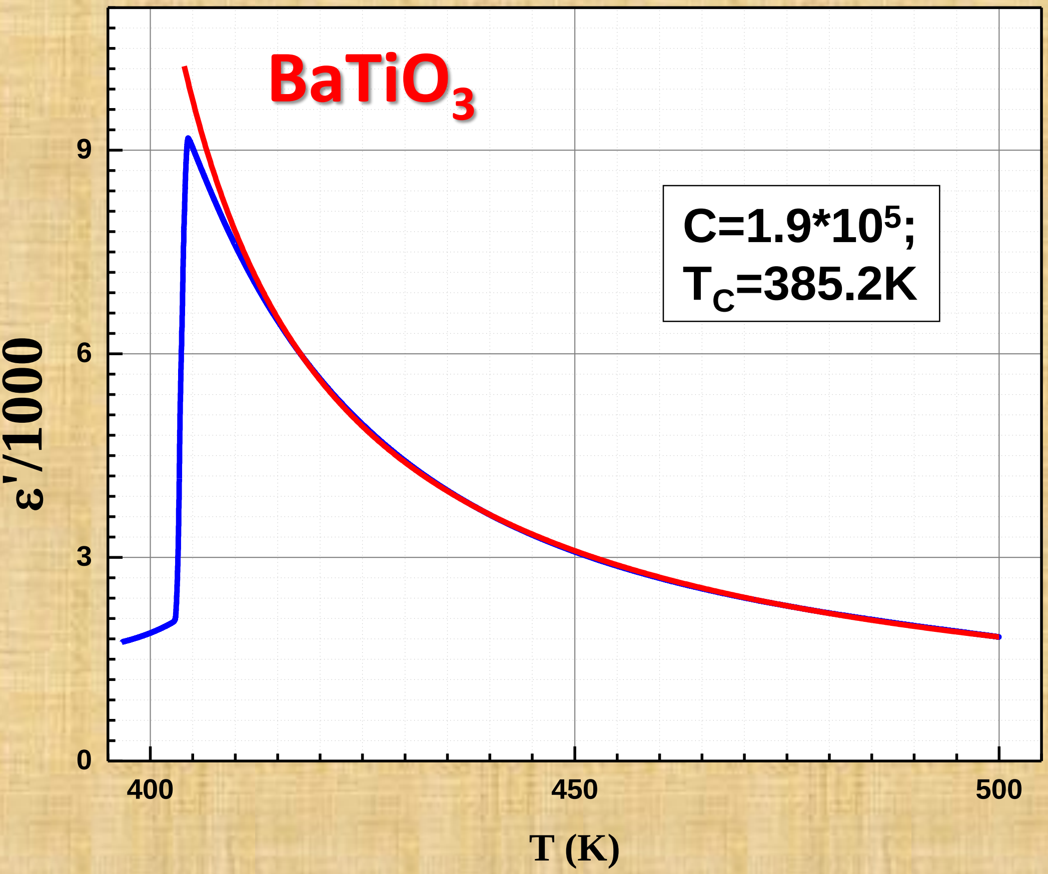
$$F_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots - EP$$



Ferroelectricity: Susceptibility

$$\vec{P} = \varepsilon_0 \chi \vec{E} \qquad \vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E} + \varepsilon_0 \chi \vec{E} = \varepsilon_0 (1 + \chi) \vec{E} = \varepsilon_0 \varepsilon \vec{E}$$

For ferroelectrics ε>>1 and $\varepsilon \approx \chi$



Curie-Weiss law:

$$\varepsilon = \frac{C}{(T - T_{CW})} + \varepsilon_{00}$$

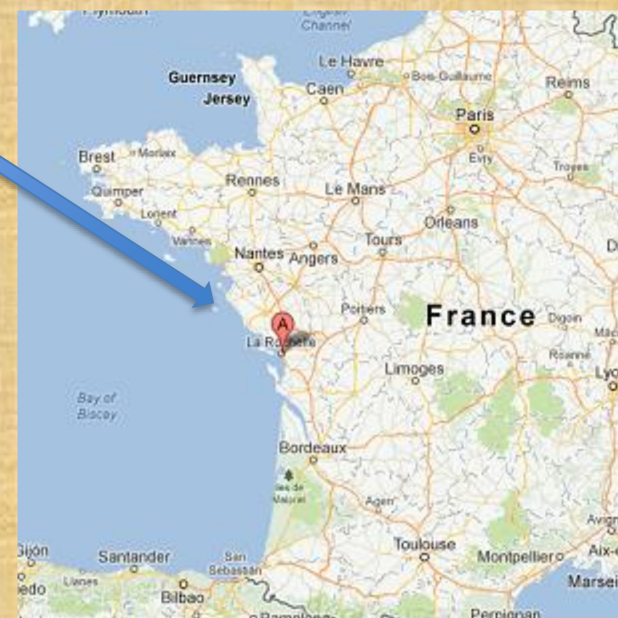
Ferroelectricity: Discovery

Rochelle Salt $KNaC_4H_4O_6*4H_2O$

Elie Seignette

Potassium sodium tartrate discovered (in about 1675) by an apothecary, *Pierre Seignette*

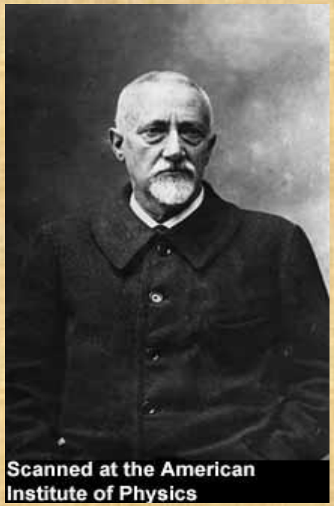
Rochelle Salt originates from French city of La Rochelle where it was produced by *Pierre Seignette* another name of this material is Seignette salt



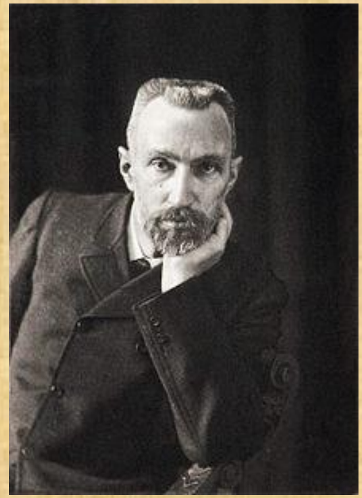
Rochelle Salt was used in medicine and food industry

Ferroelectricity: Discovery

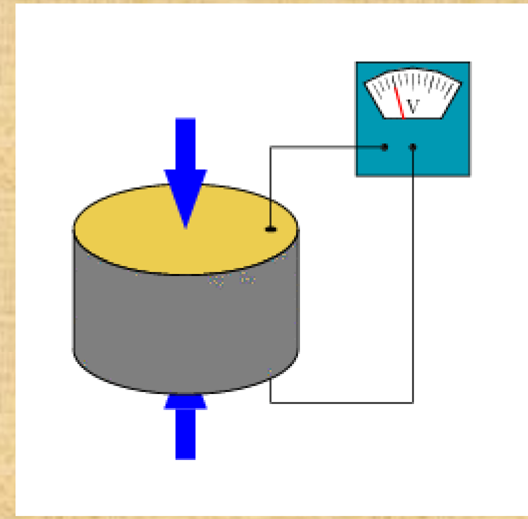
Rochelle Salt $KNaC_4H_4O_6*4H_2O$



Paul-Jacques Curie
1856 – 1941

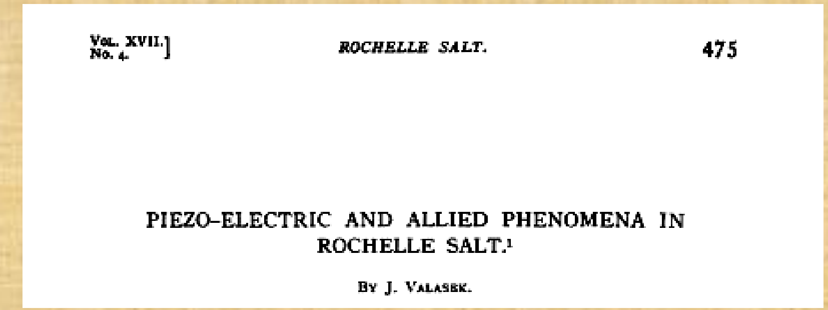


Pierre Curie
1859-1906



Brothers Curie discovered and investigated the piezoelectric effect I several materials including Rochelle salt

Ferroelectricity: Discovery



Vol. XVII.] No. 4. ROCHELLE SALT. 475

PIEZO-ELECTRIC AND ALLIED PHENOMENA IN ROCHELLE SALT.[1]

By J. Valasek.

Joseph Valasek (1897-1993)
University of Minnesota

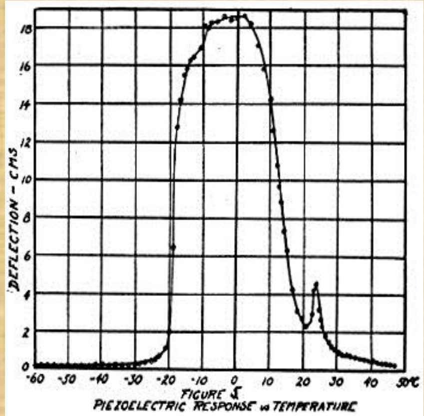


Fig3. Piezoelectric response as a function of temperature [2]

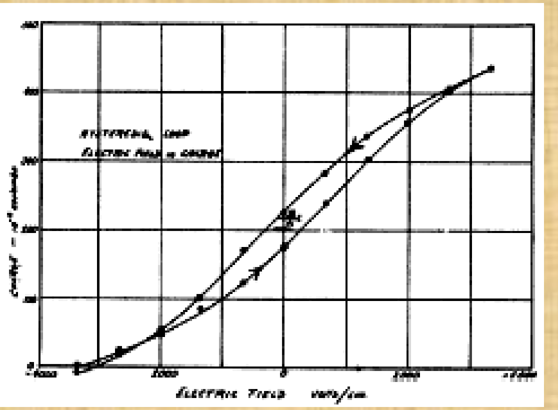
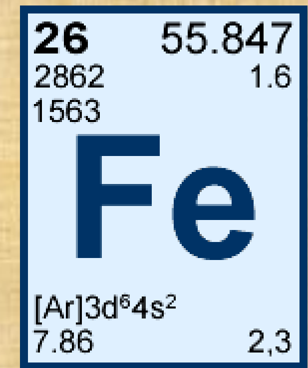


Fig.1. The first published hysteresis loop [1]

1. J. Valasek, Phys. Rev. 17, 475 (1921)
2. J. Valasek, Phys. Rev. 19, 478 (1922)

Rochelle Salt $KNaC_4H_4O_6*4H_2O$

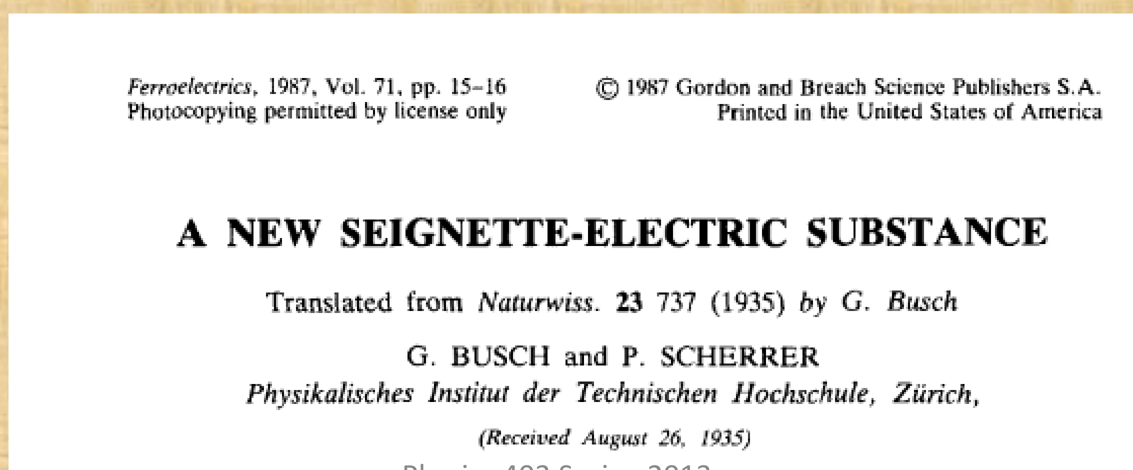
Ferroelectricity. Terminology.



ferrum (Lat) gave the name of the broad class of magnetic materials – *ferro*magnetics

Fe has no relation to the phenomenon of *ferro*elctricity but because of a lot of common features of *ferro*electric phase transition to *ferro*magnetic the "new" class of dielectrics was named as *ferro*electrics.

There is another name for this class of materials - Seignette-electrics named after the alternative name of the Rochelle salt



Ferroelectrics, 1987, Vol. 71, pp. 15–16
Photocopying permitted by license only

A NEW SEIGNETTE-ELECTRIC SUBSTANCE

Translated from *Naturwiss*. **23** 737 (1935) *by G. Busch*

G. BUSCH and P. SCHERRER
Physikalisches Institut der Technischen Hochschule, Zürich,

(Received August 26, 1935)

Materials. KDP

KDP (KH_2PO_4) - potassium dihidrophosphate

1935 G. Busch and P. Scherrer, Naturwiss. **23**, 737 (1935). Eine neue *Seignetteelektrische* Substanz.

Georg Busch
1908-2000

Paul Scherrer
1890-1969

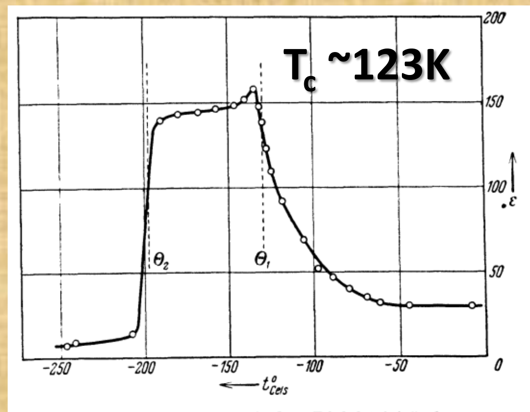


Fig. 1. Temperaturverlauf der Dielektrizitätskonstanten ε_{33} an KH_2PO_4.

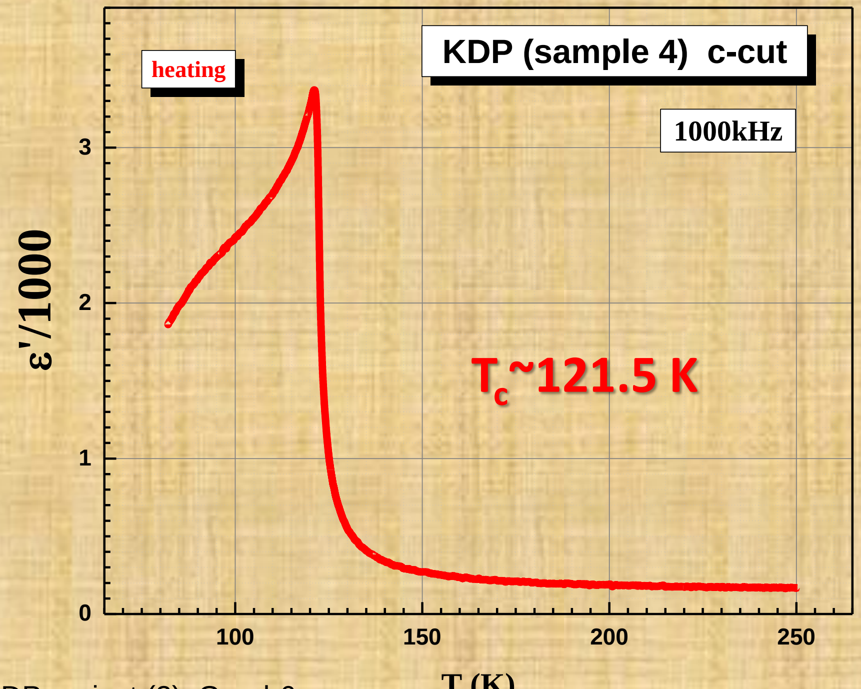
DIE NATURWISSENSCHAFTEN

23. Jahrgang 25. Oktober 1935 Heft 43

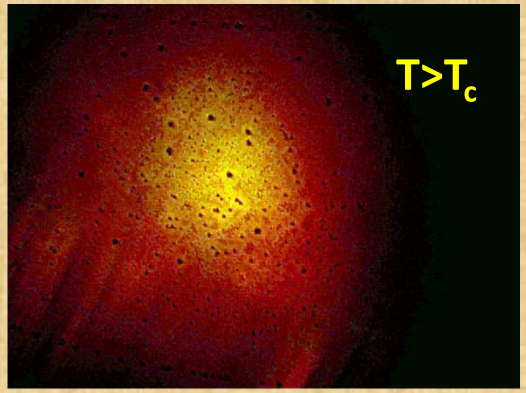
Eine neue seignette-elektrische Substanz.

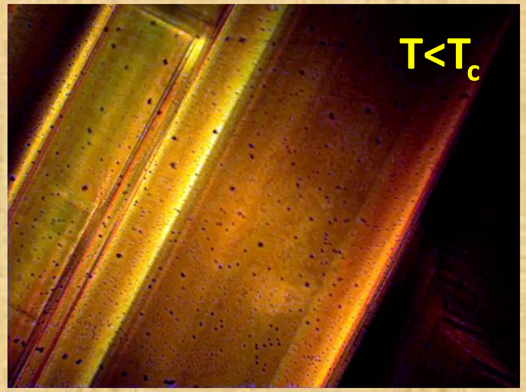
Materials. KDP

KDP (KH_2PO_4) - potassium dihidrophosphate T_c ~123K



KDP project (2): Graph6





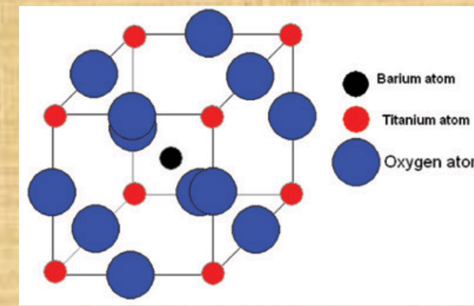
Courtesy of Tim S. Thorp, Zhangji Zhao, Physics 403, Spring 2013

Courtesy of Alison Pohl, Physics 403, Spring 2009

Materials. Barium Titanate.

1943 – material with high (>1200) value of the dielectric constant (Wainer, Solomon (USA); Wul, Goldman (USSR))

1945 – discovered the ferroelectric properties of $BaTiO_3$ A. von Hippel (USA); Wul, Goldman (USSR))



T_c ~400K

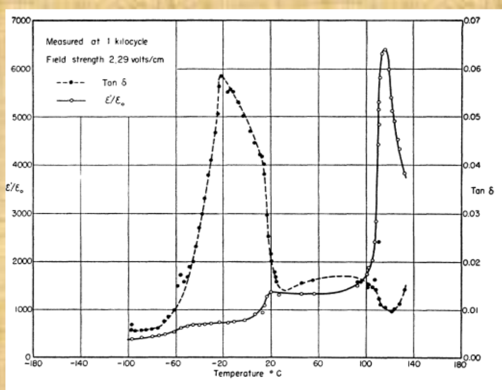


FIG. 6. Dielectric constant and loss of barium titanate ceramic.

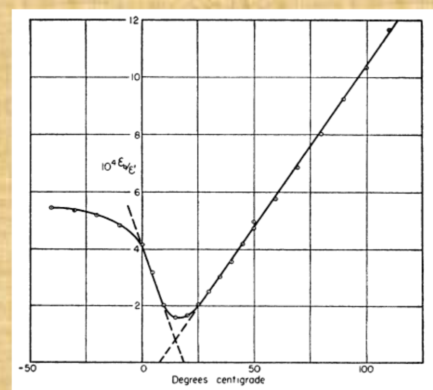
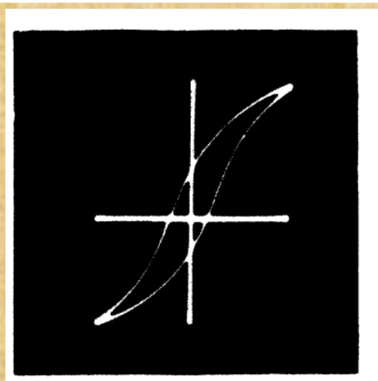
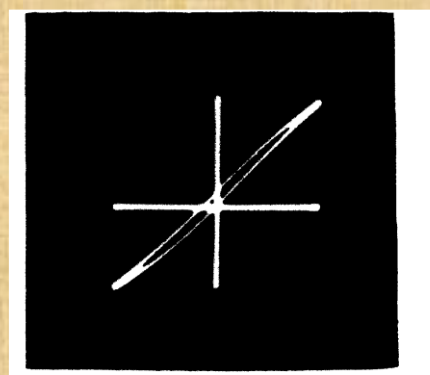


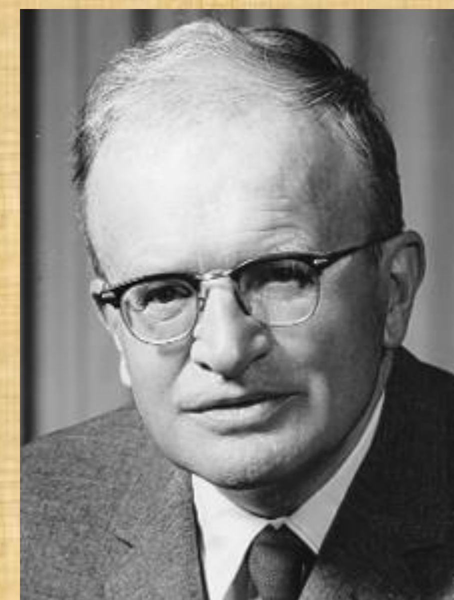
FIG. 15. Confirmation of Curie-Weiss laws in (Ba-Sr)TiO_3 (400 kc).



+75°



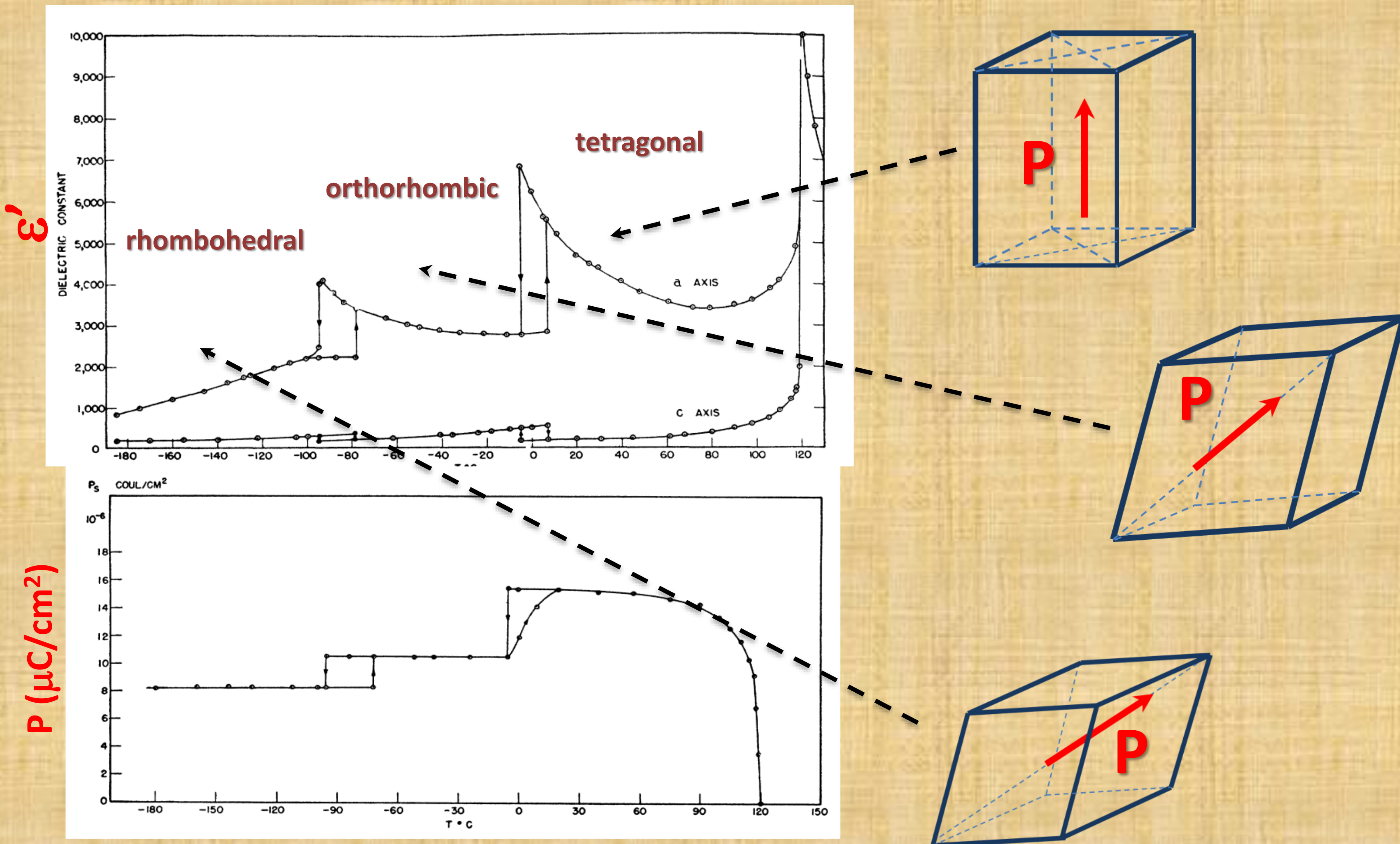
+125°



Arthur R. von Hippel
1898-2003

A. Von Hippel, Rev. Mod. Phys. 22,221, 1950

Materials. Barium Titanate.



Walter J. Merz, Phys. Rev. 76, 1221, 1949

Materials. $BaTiO_3$. Domains.

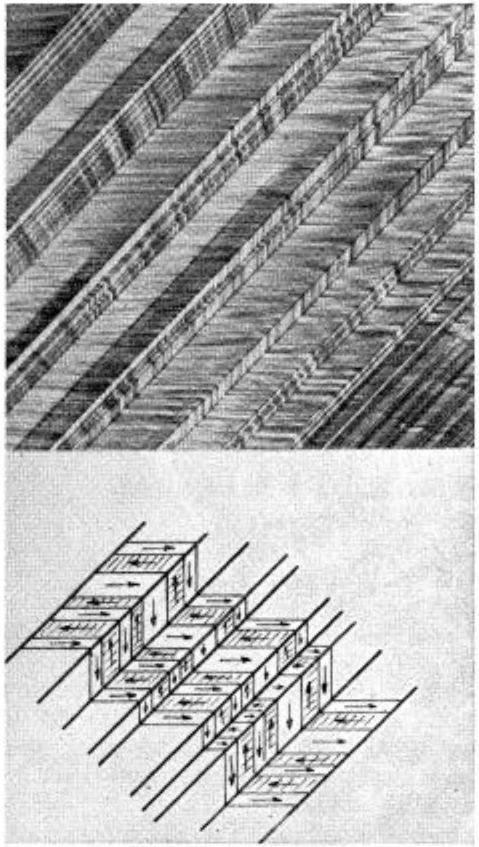
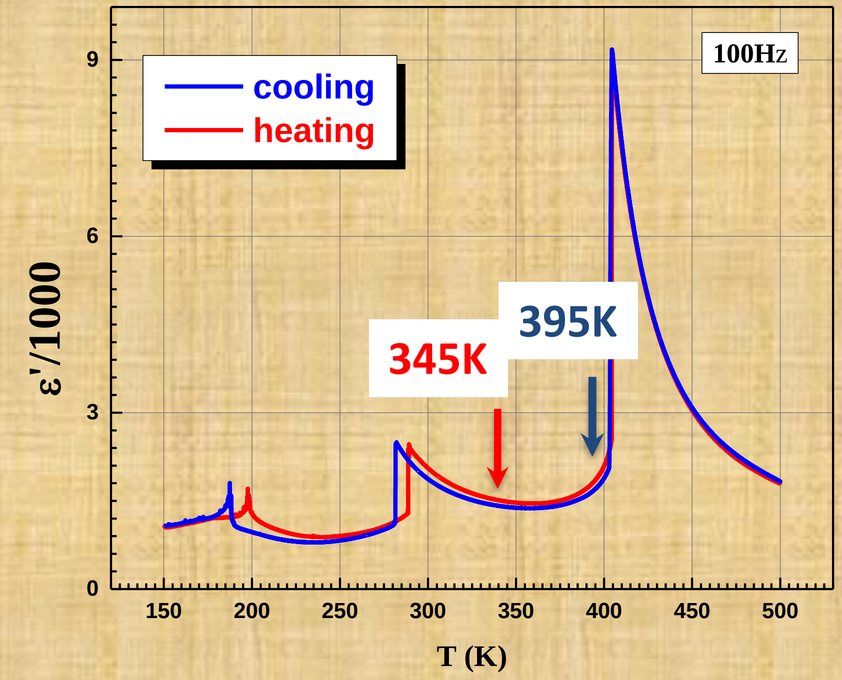


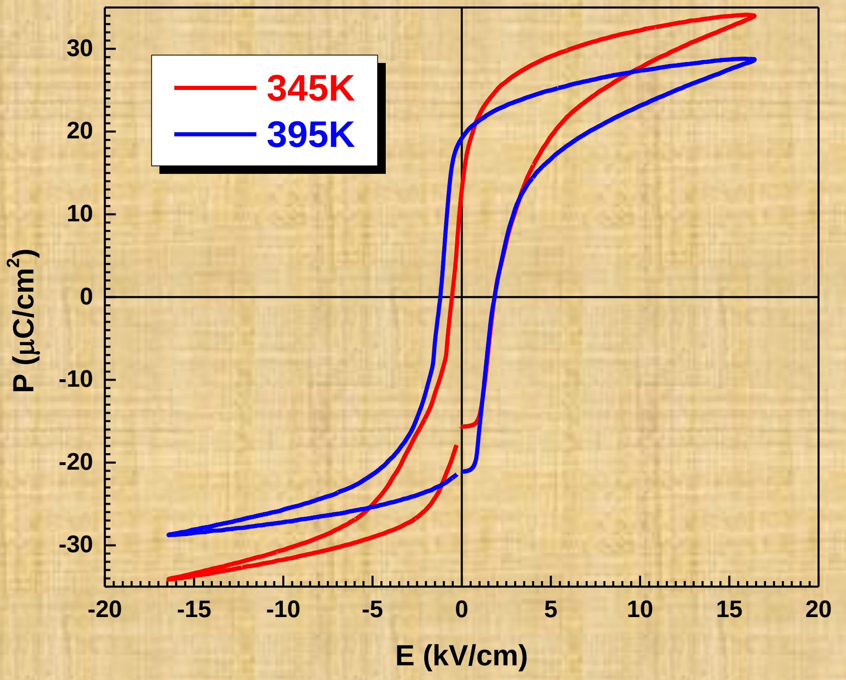
FIG. 4. Surface of an *a*-domain crystal showing 90° walls and antiparallel domains.

John A. Hooton, Walter J. Merz, Phys. Rev. 98, 409,1955

Physics 403 Lab, August 2011

Materials. $BaTiO_3$. P-E hysteresis.

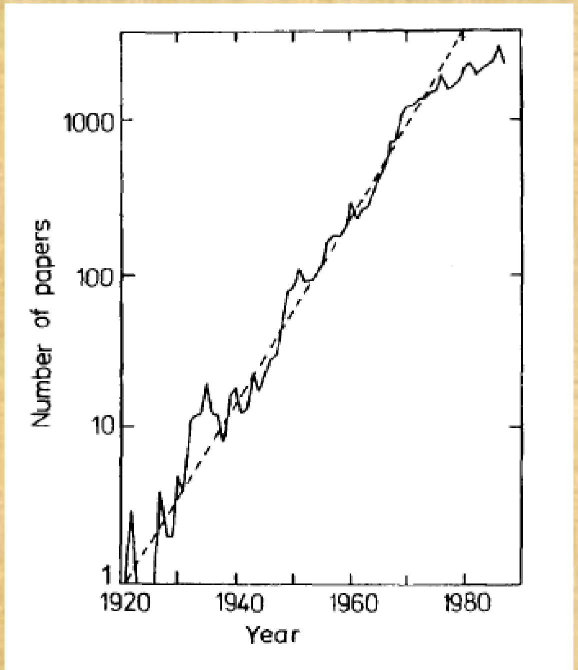




Courtesy of Liu M. & Lopez P,
Physics 403, Spring 2013

Ferroelectricity: Typical ferroelectric materials

		T_C(K)	Ps (μC/cm^2)
KDP type	KH_2PO_4	123	4.75
	KD_2PO_4	213	4.83
	RbH_2PO_4	147	5.6
Perovskites	$BaTiO_3$	408	26
	KNbO3	708	30
	$PbTiO_3$	765	>50
	$LiTiO_3$	938	50
	$LiNbO_3$	1480	71



Number of publications concerning ferroelectricity. From Jan Fousek "*Joseph Valasek and the Discovery of Ferroelectricity*"

ABO_3

Springer Handbook of Condensed Matter and Materials Data

New Perovskite Materials - Relaxors

B-site complex	Lead magnesium niobate (PMN)	$PbMg_{l/3}Nb_{2/3}0_3$
	Lead scandium tantalate (PST)	$PbSc_{1/2}Ta_{1/2}0_3$
	Lead zinc niobate (PZN)	$PbZn_{l/2}Nb_{1/2}0_3$
	Lead indium niobate (PIN)	$PbIn_{1/2}Nb_{1/2}0_3$
A-site complex	Lead lanthanum titanate (PLT)	$Pb_{1-x}La_xTiO_3$
Both sites complex	Lead lanthanum zirconate titanate (PLZT)	$Pb_{1-x}La_xZr_yTi_{1-y}O_3$
	Potassium lead zinc niobate	$K_{1/3}Pb_{2/3}Zn_{2/9}Nb_{7/9}0_3$

L. Eric Cross[1] (1923-2016)

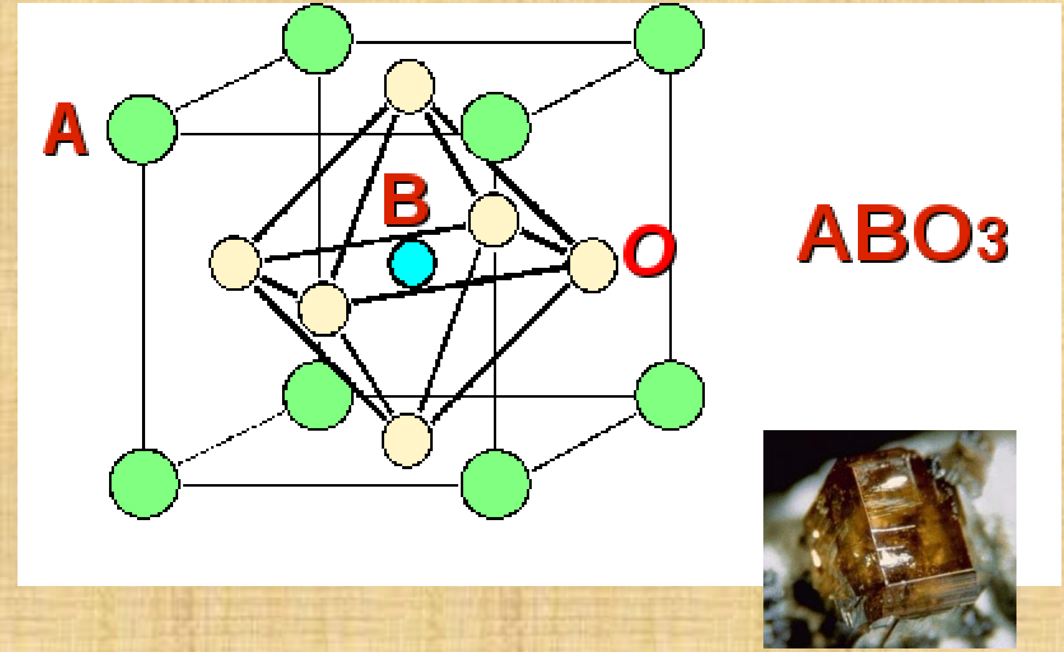
Smolenskii G.A.[2] (1910 – 1986)

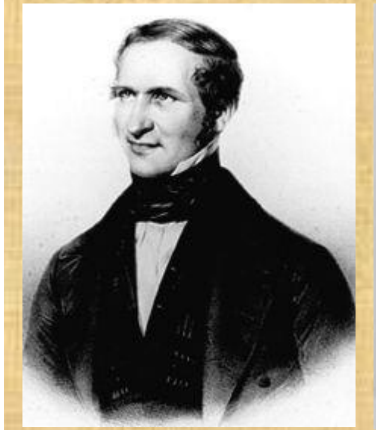
1. Pennsylvania State University, USA
2. A.F. Ioffe Institute, USSR

$AB1_{(1-x)}B2_xO_3$ $A1_{(1-x)}A2_xBO_3$ $A1_{(1-x)}A2_xB1_{(1-y)}B2_yO_3$ typical complex oxides with perovskite structure

Perovskite Structure

Perovskite is a mineral $CaTiO_3$. The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist Lev Perovski.





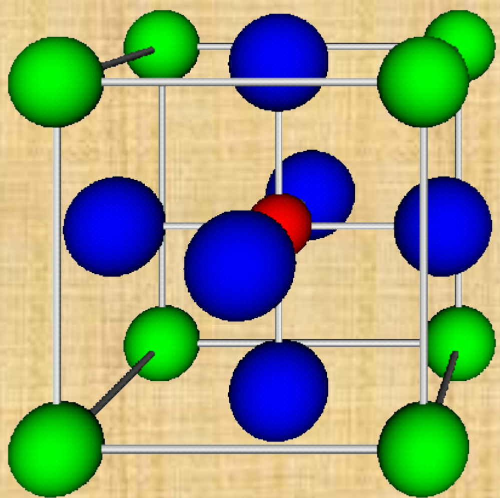
Gustav Rose
1798-1873

Lev Perovski
1792-1856

$AB1_{(1-x)}B2_xO_3$ $A1_{(1-x)}A2_xBO_3$ $A1_{(1-x)}A2_xB1_{(1-y)}B2_yO_3$ typical complex oxides with perovskite structure

Relaxors

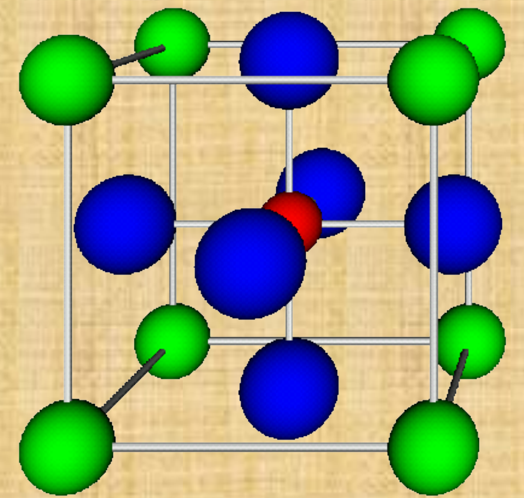
Regular ferroelectric $BaTiO_3$



$T > T_c$ (cubic)

Ba O Ti

Relaxor - PMN $Pb(Mg_{1/3} Nb_{2/3})O_3$

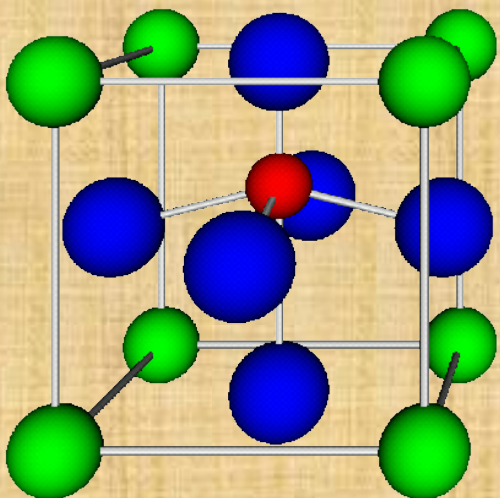


(cubic)

Pb O Mg^{+2} or Nb^{+5}

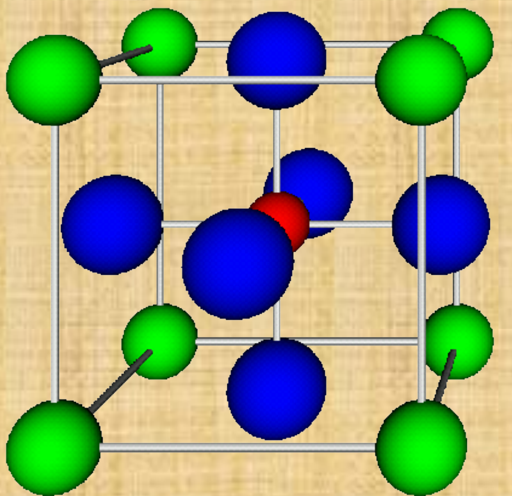
Relaxors

Regular ferroelectric $BaTiO_3$ | **Relaxor - PMN $Pb(Mg_{1/3}\,Nb_{2/3})O_3$**



$T < T_c$ (tetragonal)

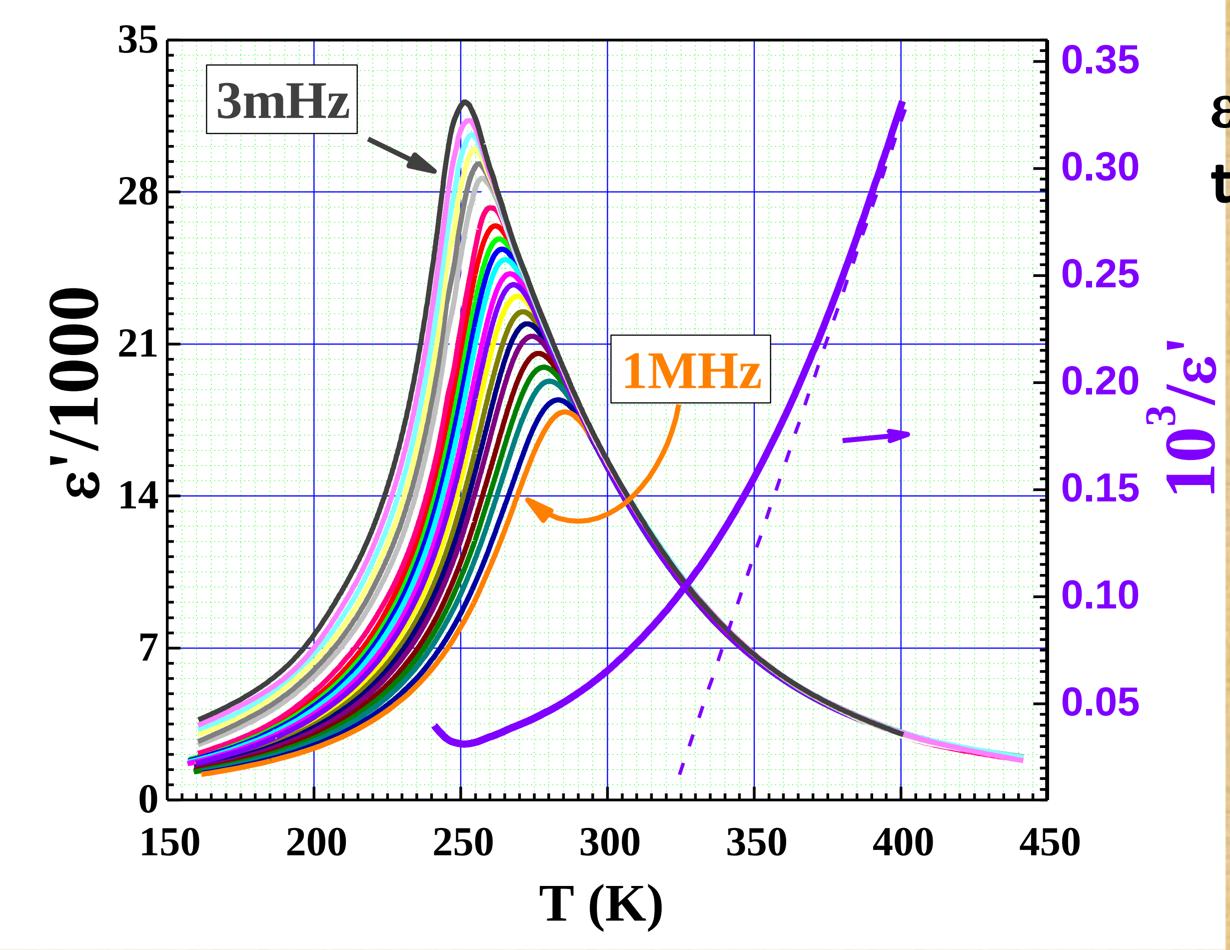
Ba O Ti



(cubic)

Pb O Mg^{+2} or Nb^{+5}

Relaxor. PMN dielectric susceptibility

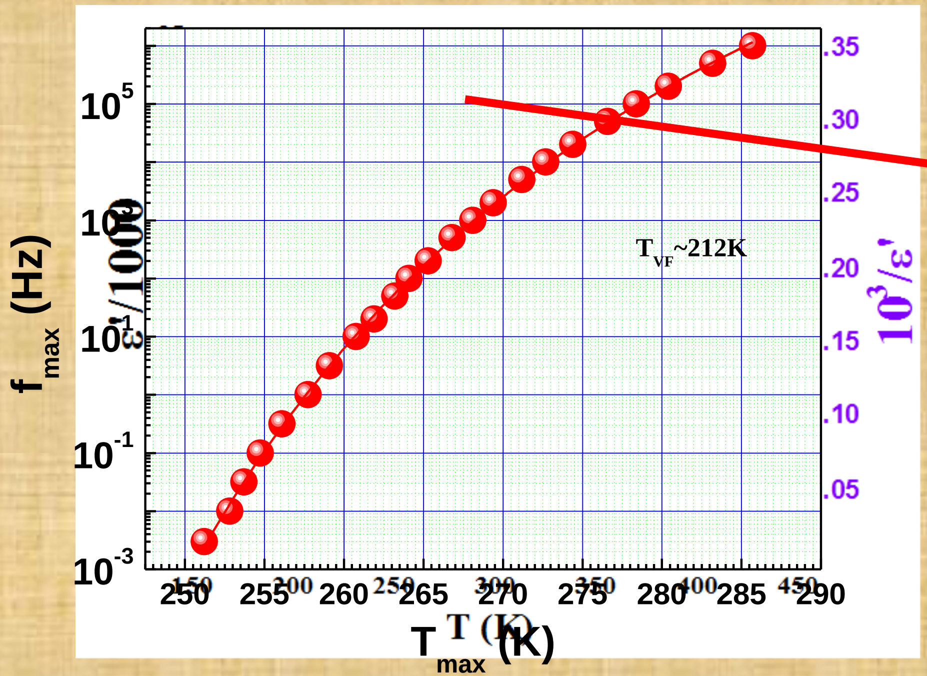


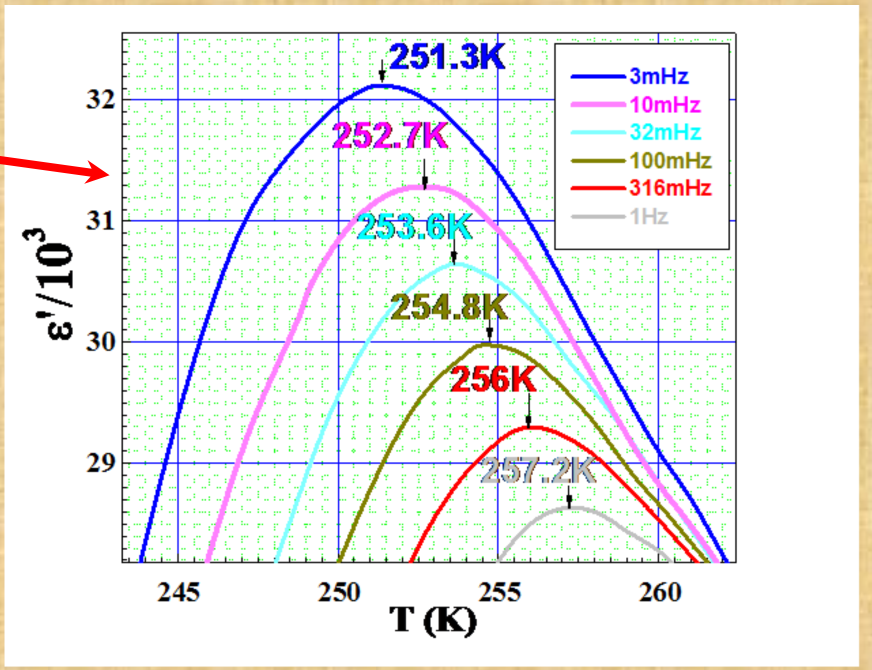
ε'_{max} and T_{max} depend on the measuring frequency

ε' does not follow Curie-Weiss law

Temperature dependencies of ε' measured in a broad frequency range: 3mHz -1MHz

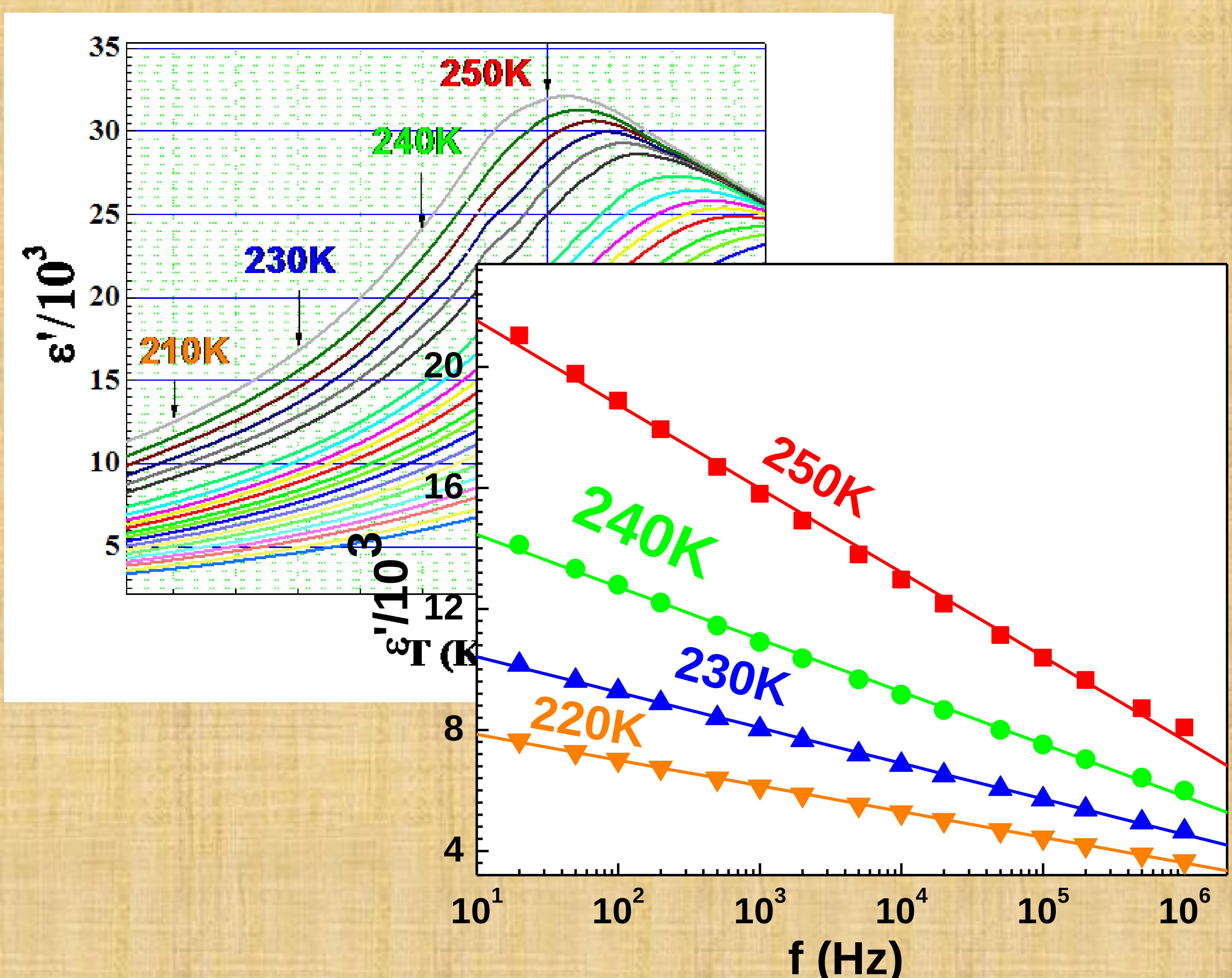
PMN. *Vogel – Fulcher* dependence



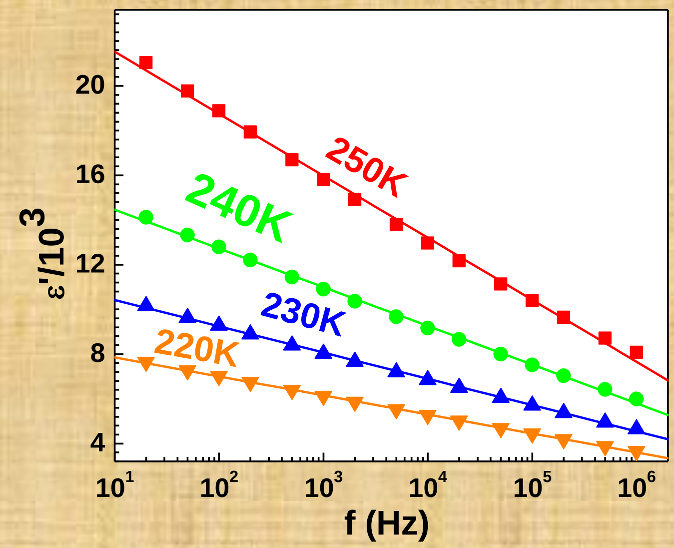


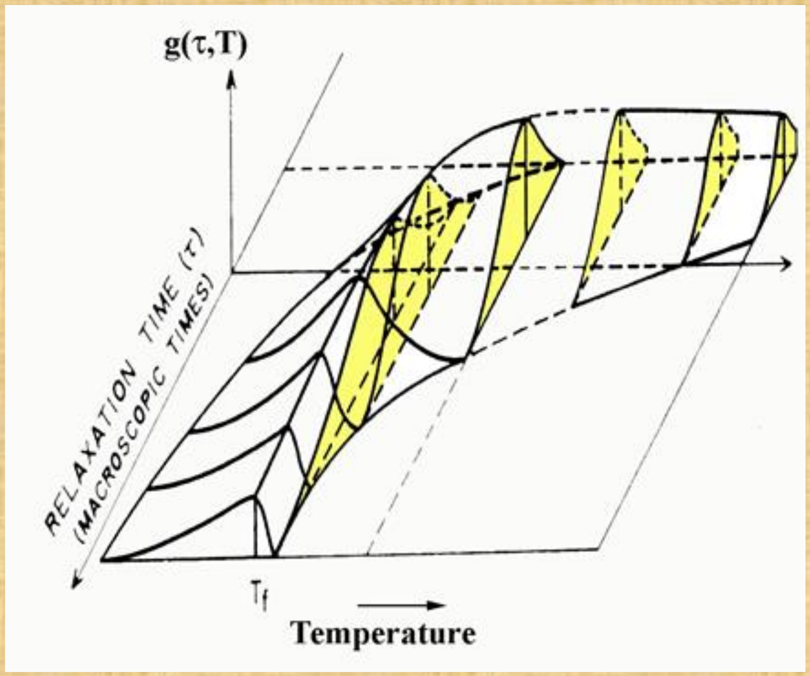
$$f_{max} = f_0 \exp\left[\frac{-E_0}{T - T_{VF}}\right]$$

PMN. Frequency Dispersion.



PMN. Frequency Dispersion.





$$\varepsilon'(\omega,T)=\varepsilon_{\infty}+\Delta\varepsilon\int_{-\infty}^{\infty}\frac{g(\tau,T)\ln\tau}{1+(\omega\tau)^{2}}$$

Relaxors. Nanodomains.

PNR – polar nanodomains
COR – chemically ordered regions

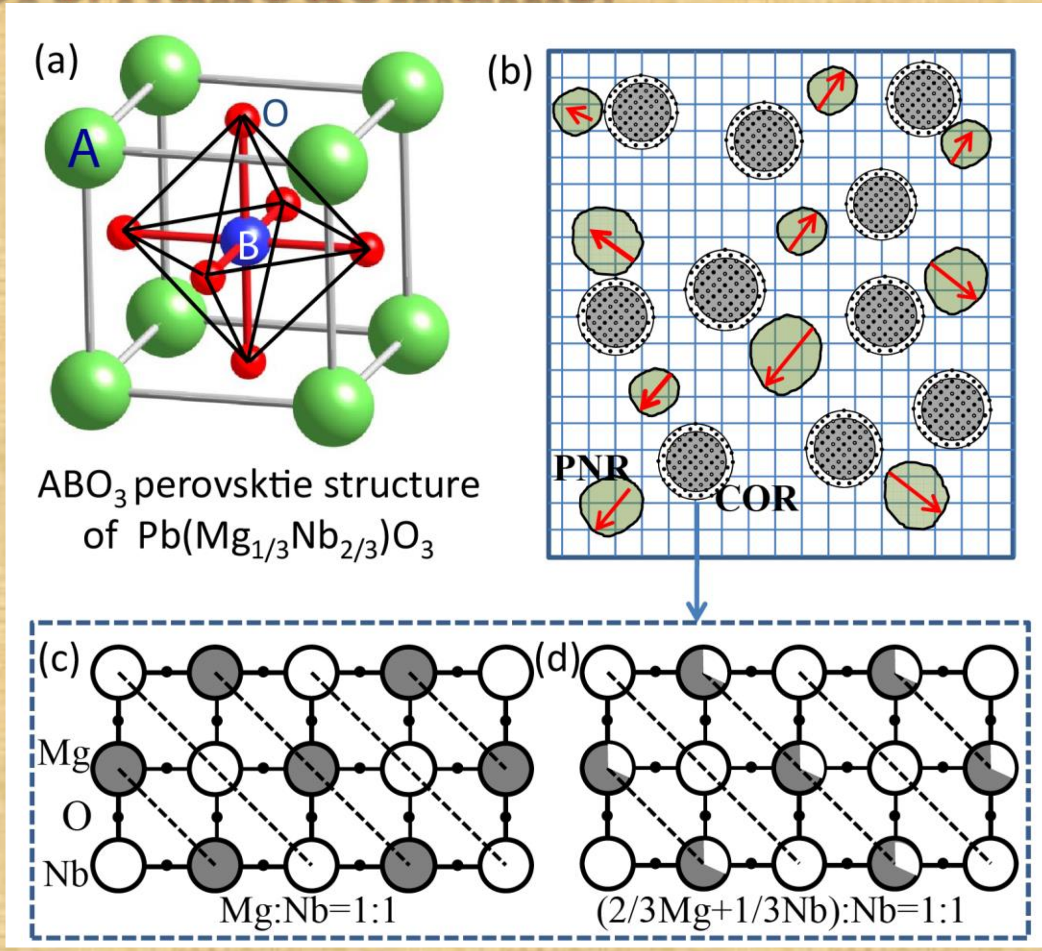
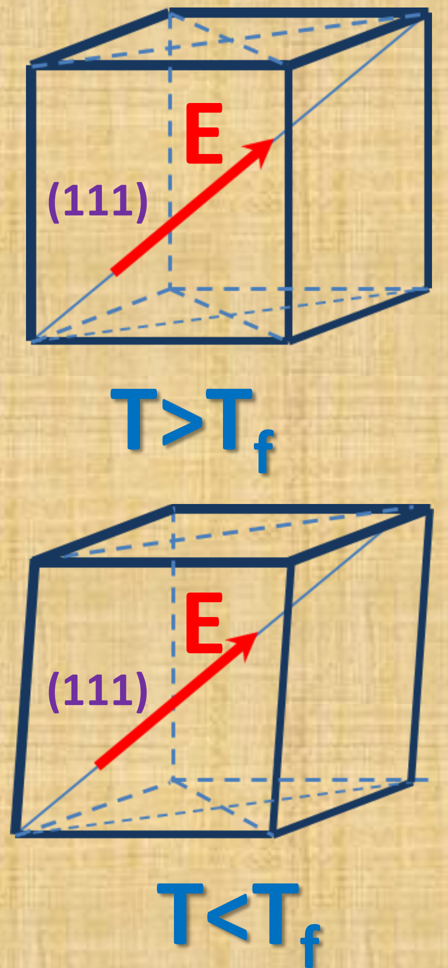
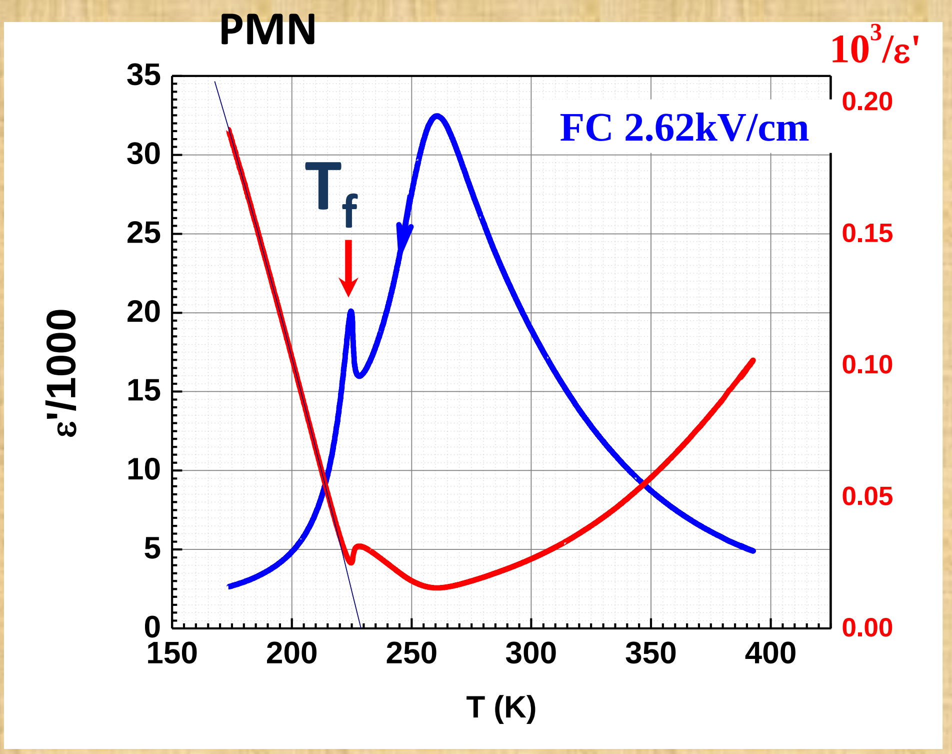


Figure 3.
(a) ABO_3perovskite structure. (b) Model for relaxor structure. PNR and COR represent the polar nano-region and chemically order region, respectively. (c) &(d) show two models of atom arrangement for COR. To maintain the electric neutrality, a Nb-rich layer is required for case (c).

D. Fu, et all in "Advances in Ferroelectrics", ISBN 978-953-51-0885-6, November 19, 2012

Relaxors. Field Induced Ferroelectric Transition. .

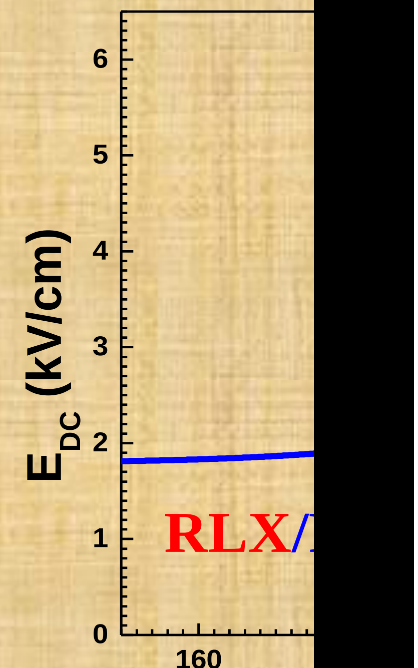


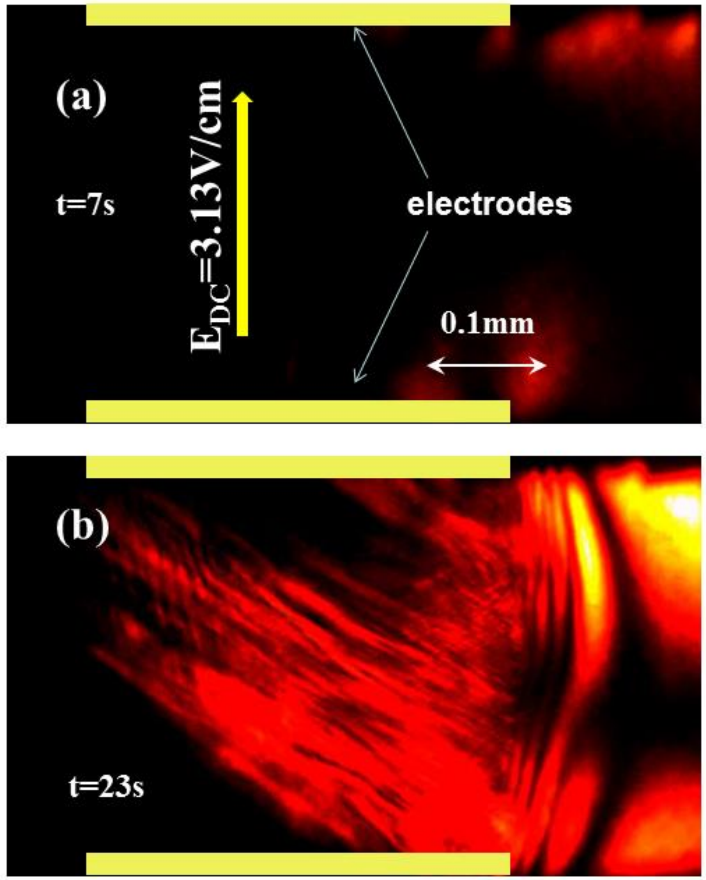


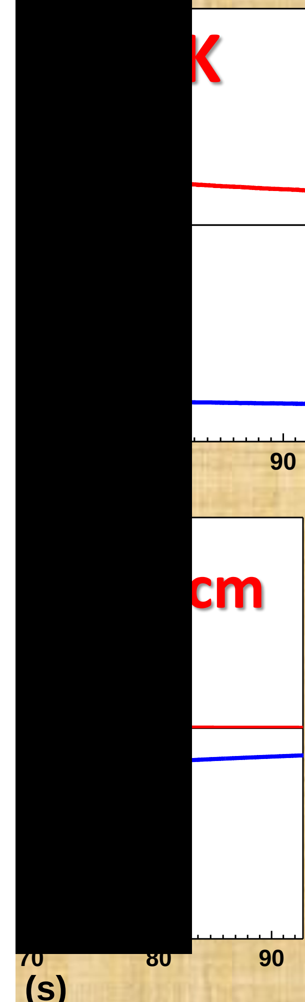
E_{DC} is applied in (111) direction
T_f – temperature of the induced relaxor – ferroelectric transition

Rhombohedral distortion

PMN. Field Induced. Ferroelectric Transition.





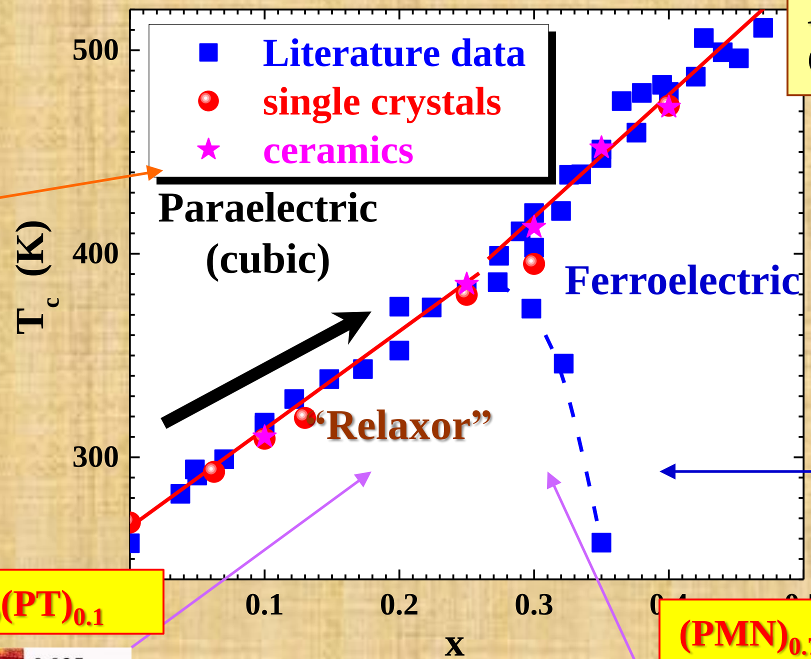


E-T phas
in (111) c

Solid solution relaxor-regular ferroelectric.

$(PMN)_{0.97}(PT)_{0.03}$

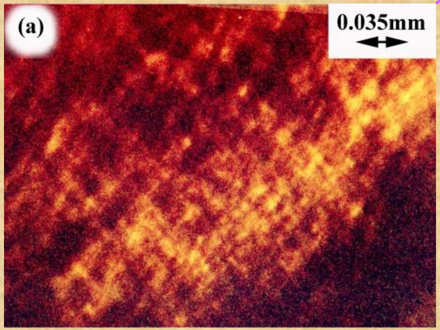
$(PMN)_{(1-x)}(PT)_{(x)}$ phase diagram



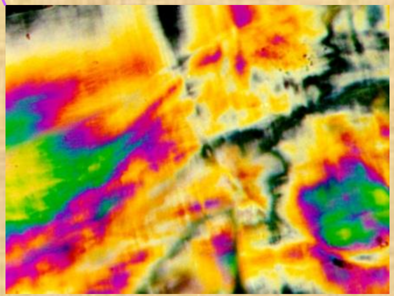
PT: $PbTiO_3$, ferroelectric with Curie temperature 763K

$(PMN)_{0.6}(PT)_{0.4}$

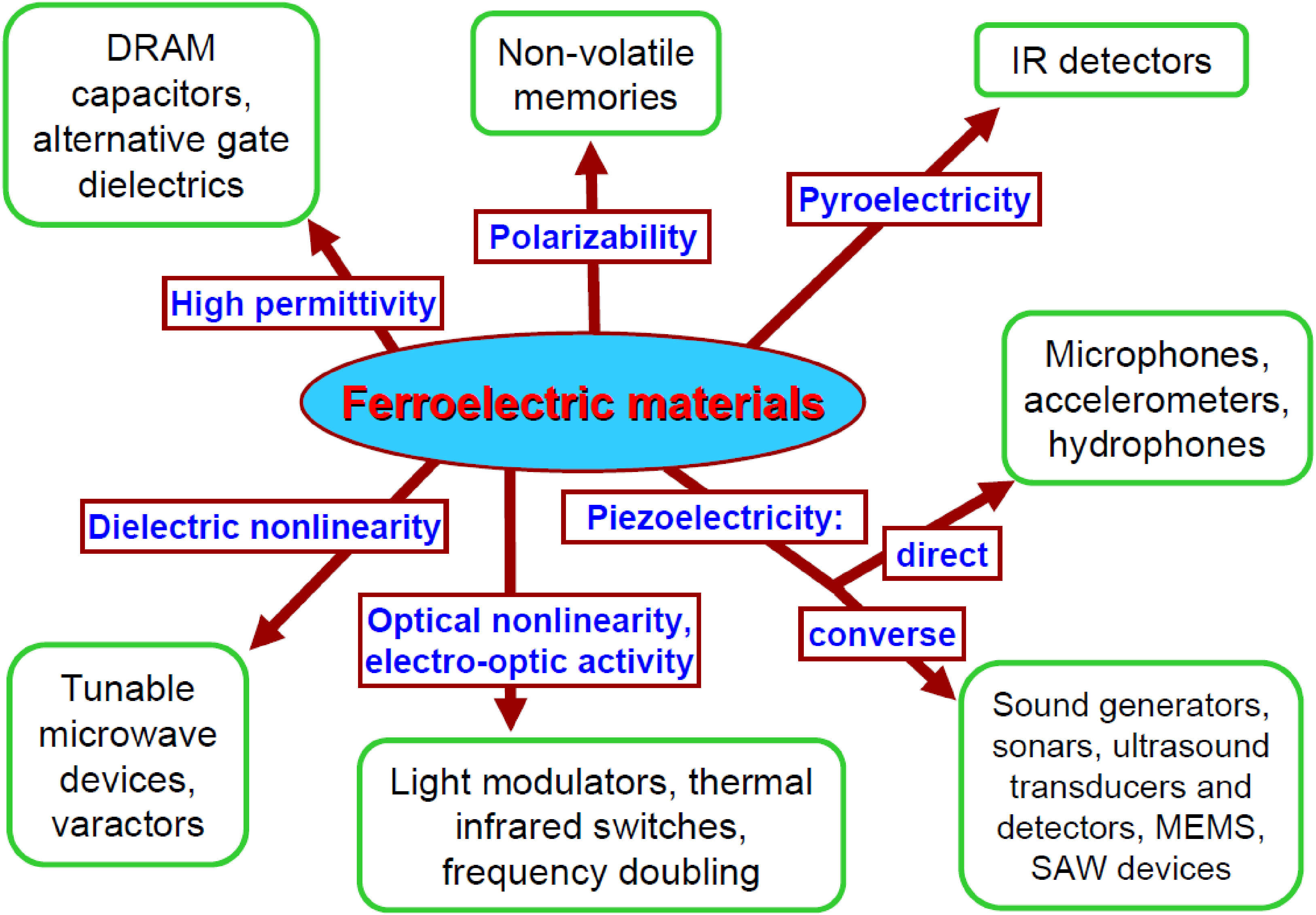
$(PMN)_{0.9}(PT)_{0.1}$



$(PMN)_{0.7}(PT)_{0.3}$



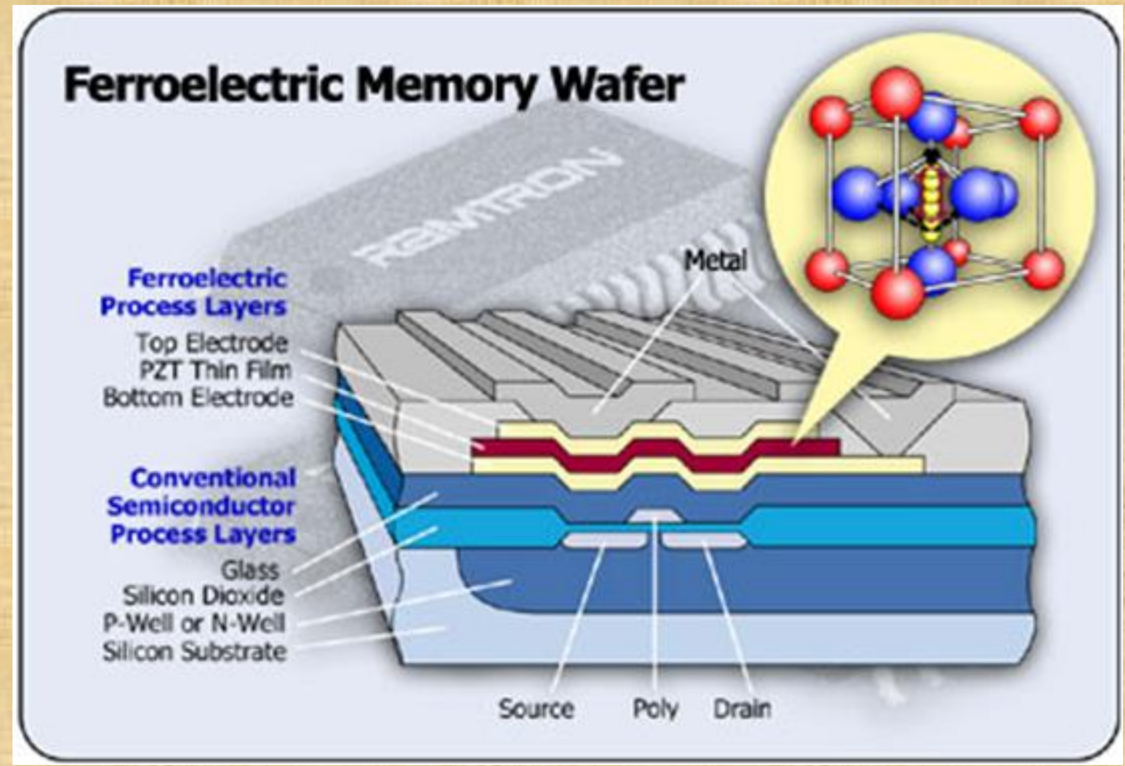
Applications of ferroelectrics



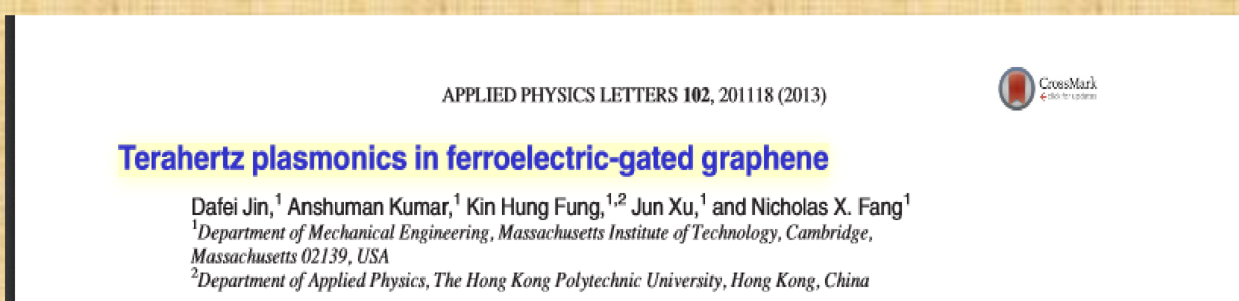
Courtesy of D. Tenne, Boise State University

Applications. Nonvolatile Memory

RAMTRON



Fast write speed (65-70ns)
High endurance (10^{14} cycles)
Low power consumption



APPLIED PHYSICS LETTERS 102, 201118 (2013)

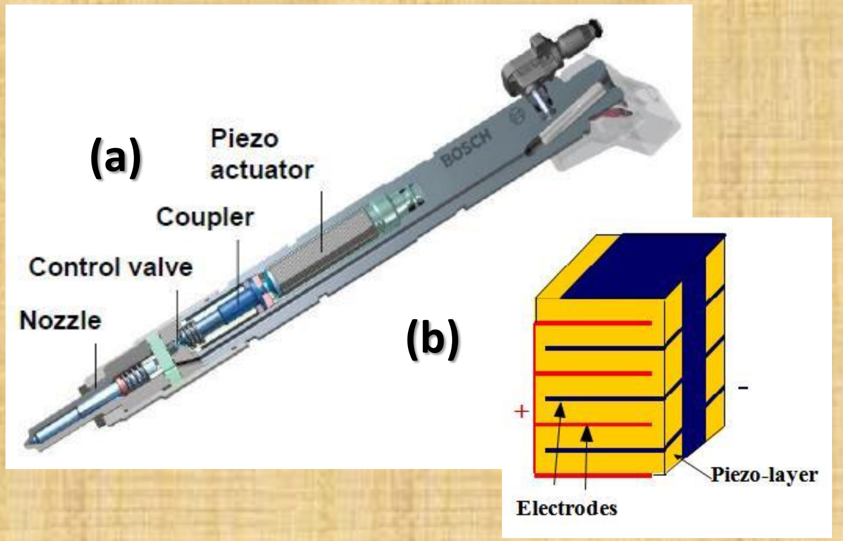
CrossMark

Terahertz plasmonics in ferroelectric-gated graphene

Dafei Jin,[1] Anshuman Kumar,[1] Kin Hung Fung,[1,2] Jun Xu,[1] and Nicholas X. Fang[1]
[1]*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[2]*Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China*

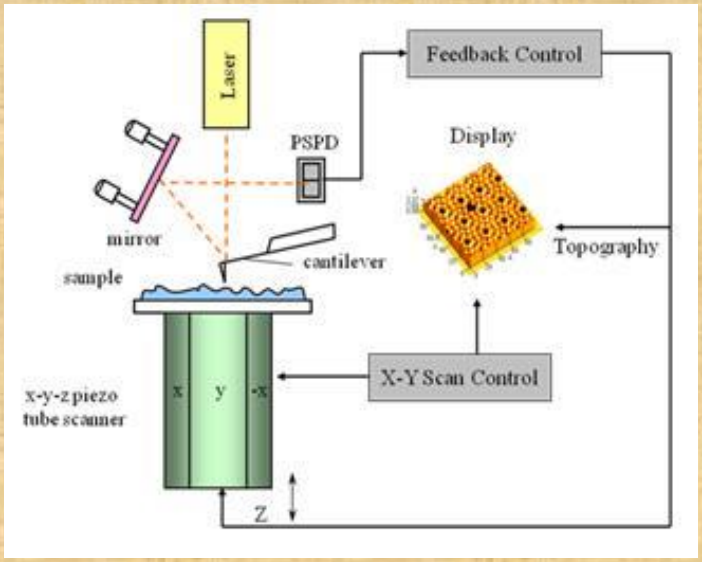
Applications. Actuators

Atomic Force Microscope



Piezo-injector for diesel engines, (b) Multilayer piezoelectric actuator scheme.

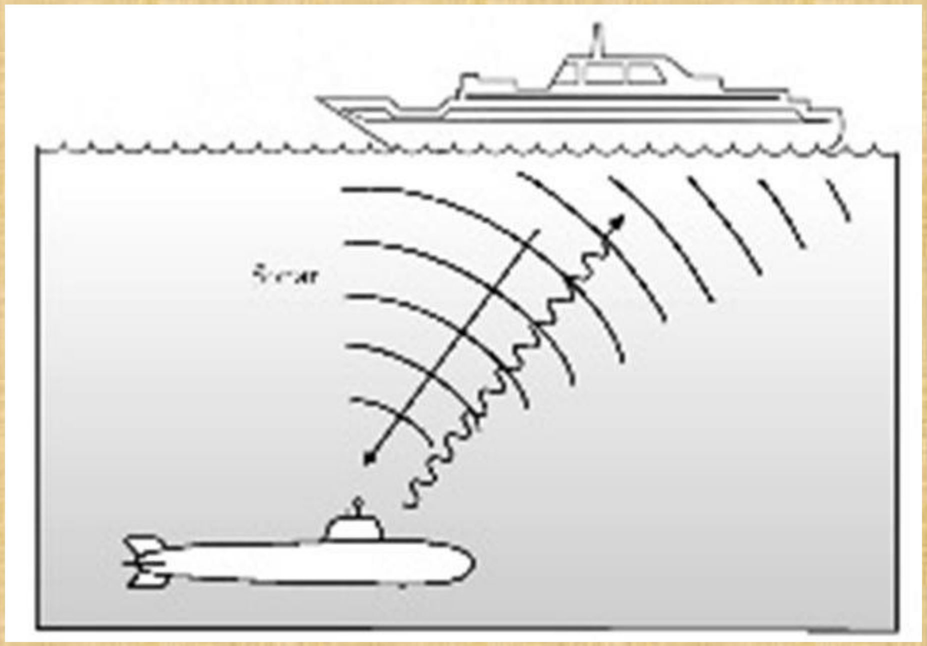
Courtesy Technische Universität Darmstadt



Lead Zirconium Titanate piezo scanner

PI (www.pi.ws)

Applications. Sonars
Military Applications

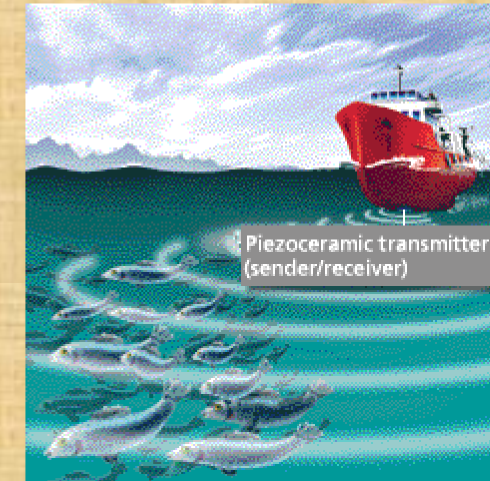


APPLICATIONS:

- MINE HUNTING
- WEAPONS SONAR
- COUTERMEASURES
- ACOUSTIC COMMUNICATIONS
- PROJECTOR ARRAYS
- HYDROPHONE ARRAYS
- VIBRATION CONTROL

Piezocomposite materials have been tested by the United States military since 1992.

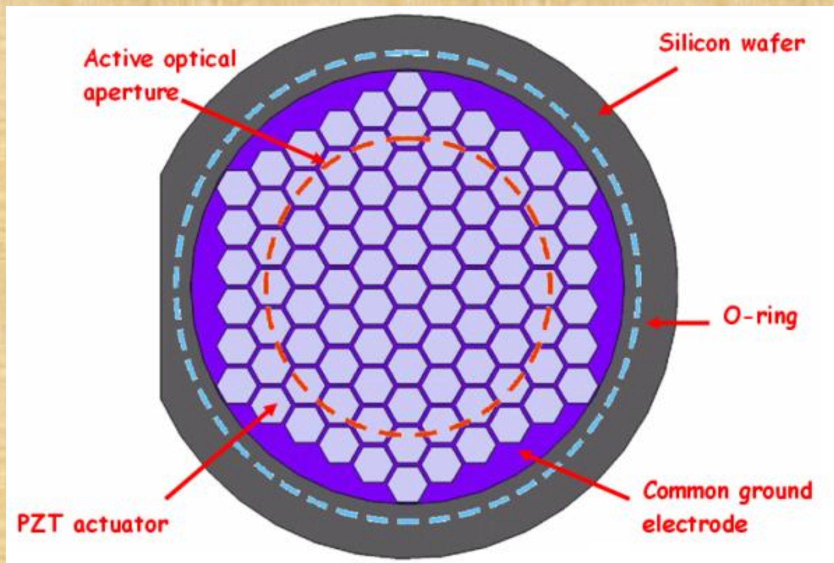
Applications. Sonars
Civil Applications



Fish Finder

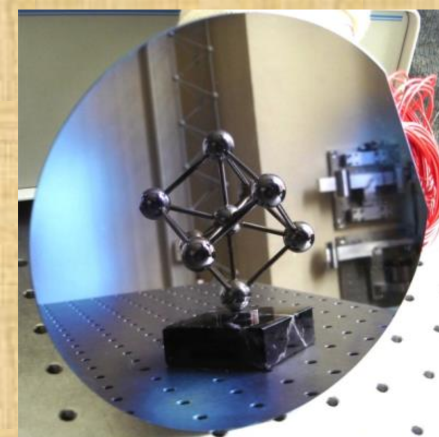
Courtesy FURUNO

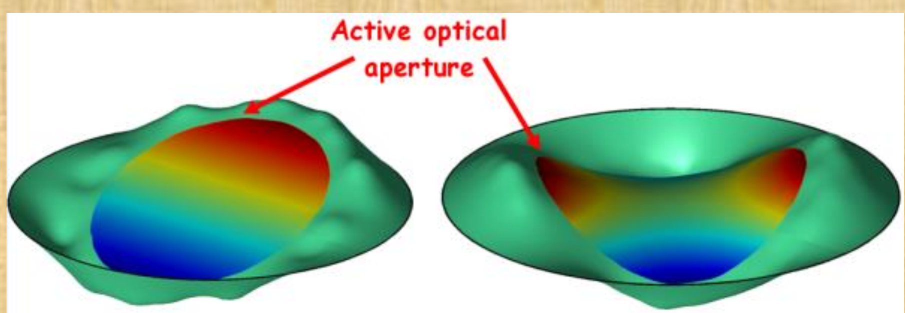
Applications. Adaptive Optics



Soldered control and mass wires

PZT – Lead Zirconium Titanate Pb[Zr$_x$Ti$_{1-x}$]O$_3$



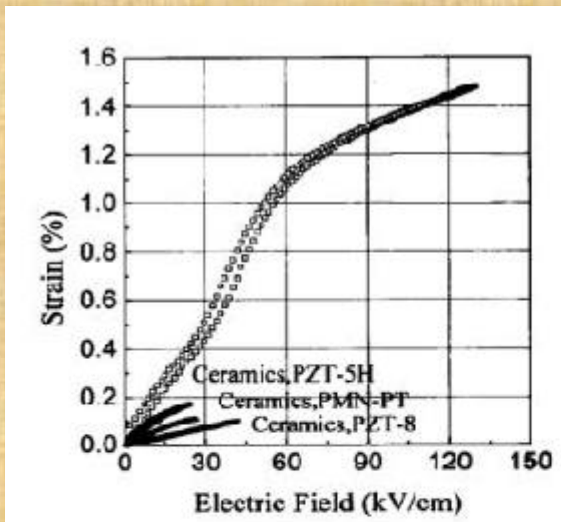


Reflecting surface

Courtesy of Active Structures Laboratory

http://scmero.ulb.ac.be

Ferroelectricity: Relaxors - aplications



DARPA PIEZOCRYSTALS

TRS Ceramics

Actuators

Transducers

Adaptive optics

Capacitors

Line motors for SFM

Transducer stack for ultrasonic sonar application (TRS Ceramics)

Material	Dielectric constant	Piezoelectric coefficient, (pC/n)	Electromechanical coupling factor
Quartz	4.5	2.3	0.1
Rochelle salt (30C)	9.2	27	0.3
Barium titanate ceramic	1700	190	0.52
Lead zirconate titanate PZT 45/55	450	140	060
PMN-PT (sc)	4200	2200	0.92-0.94
PZN-PT (sc)	2500	2400	0.91-0.93

Piezoelectric properties of different materials