Ferroelectrics. Disordered Ferroelectrics

Eugene V. Colla

Physics 403 Fall 2021

Outline

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

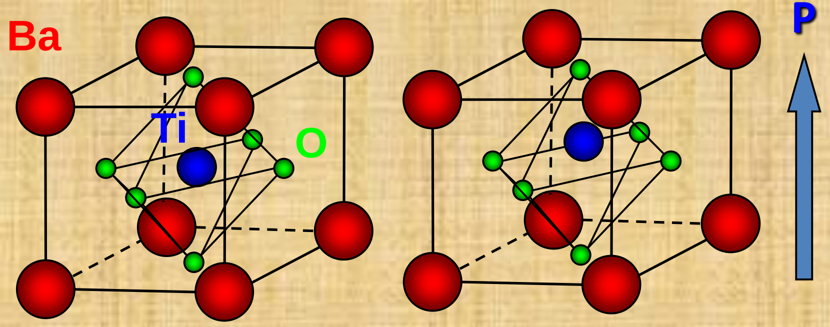
Ferroelectricity. Definition.

- **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

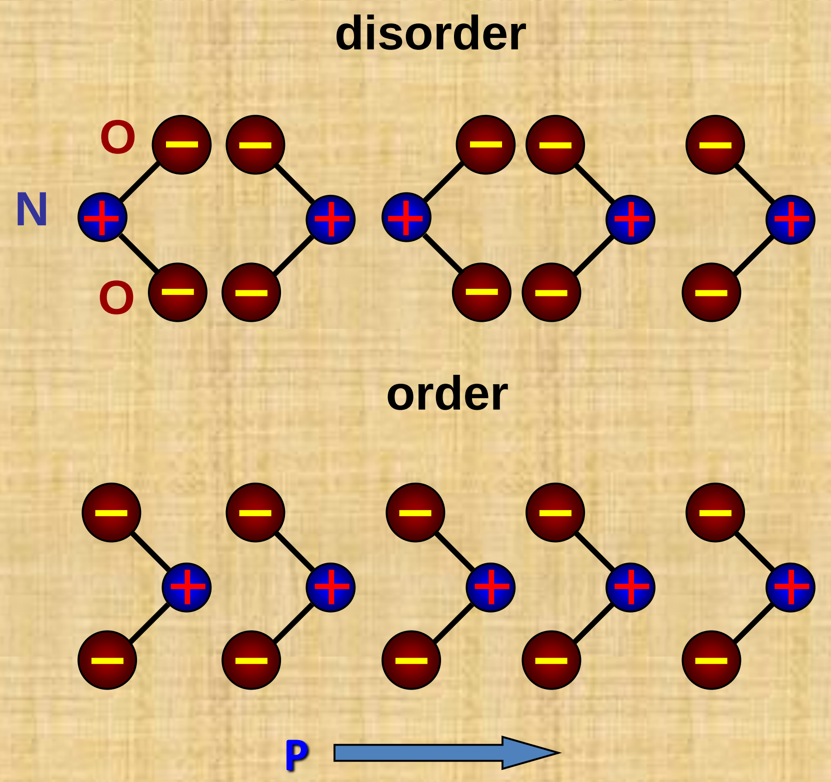
Ferroelectricity: Two classes of ferroelectrics

Displacement type



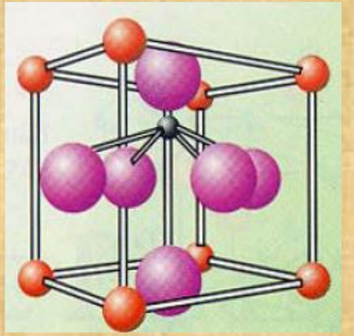
$BaTiO_3$

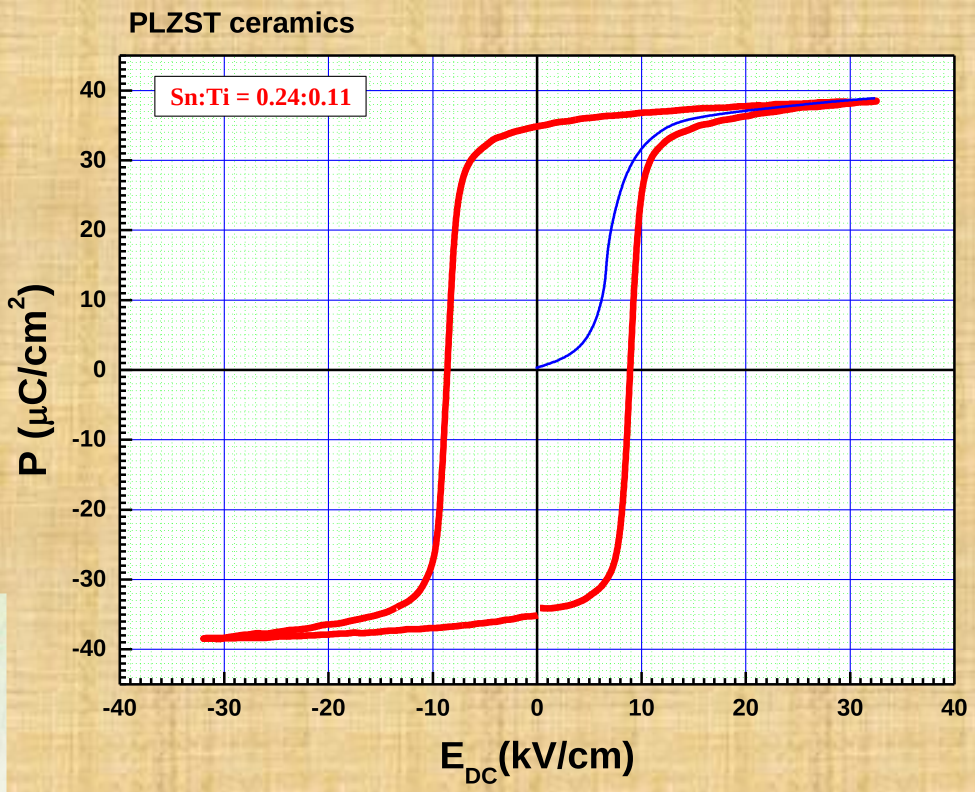
Order-Disorder

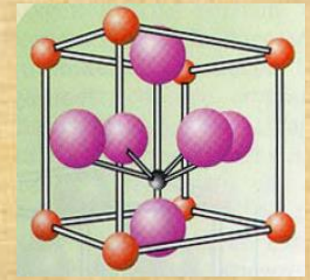


$NaNO_2$

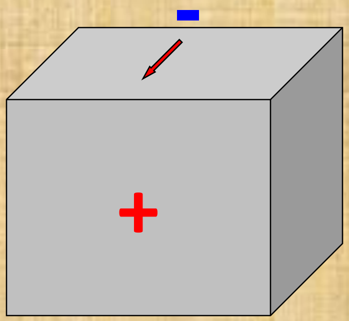
Ferroelectricity: Polarization reversible. (P-E hysteresis)







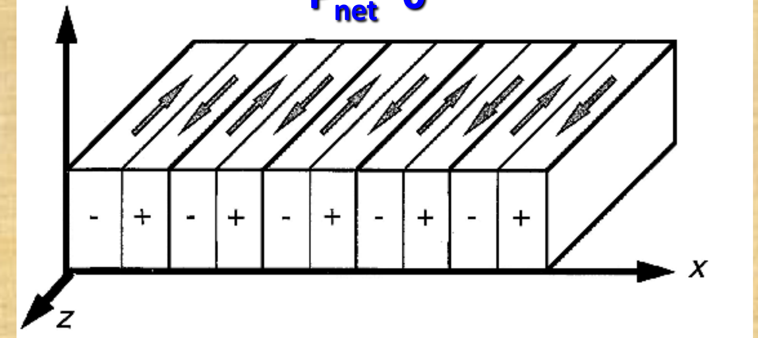
Ferroelectricity: Domains



Single domain state

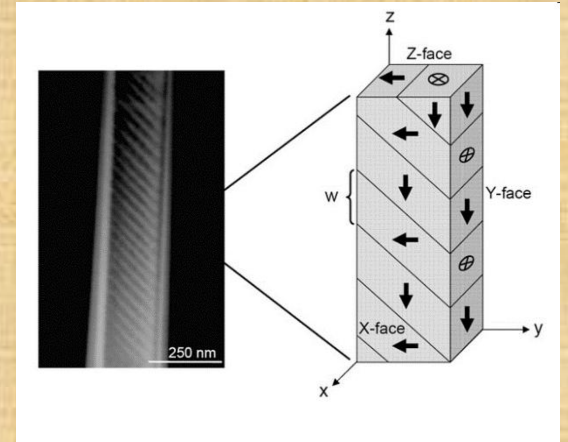
Multi domain state

P_{net}~0



180º domain pattern

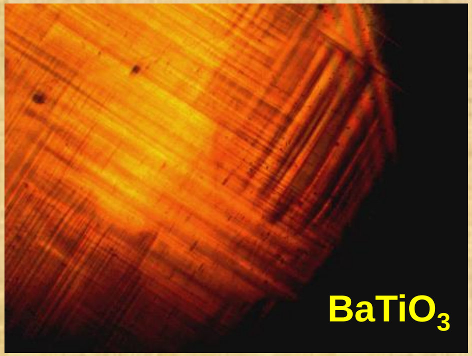
Y Lu et al. Science 1997;276:2004-2006



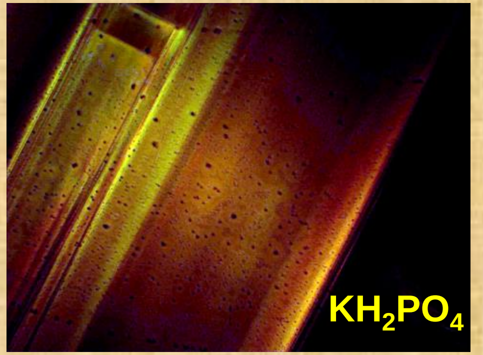
90º domains

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

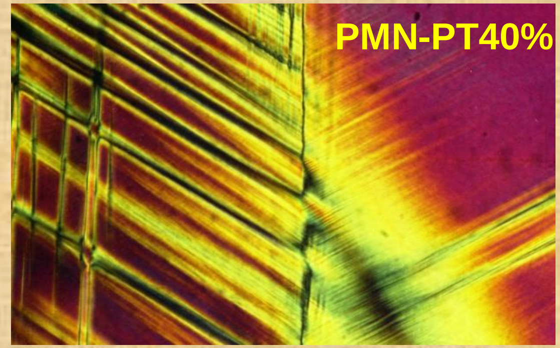
Ferroelectricity: Domains



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

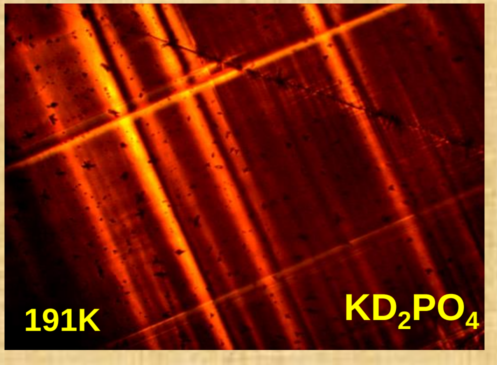


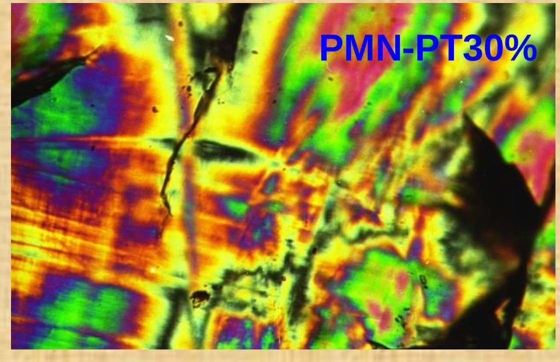
Courtesy of Allison Pohl, P403, Fall2009



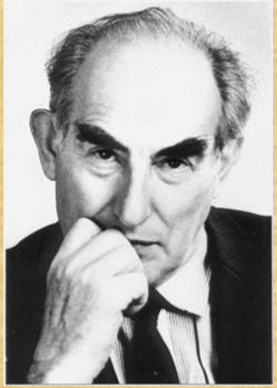
Crystal from Forschungsinstitut für mineralische und metallische

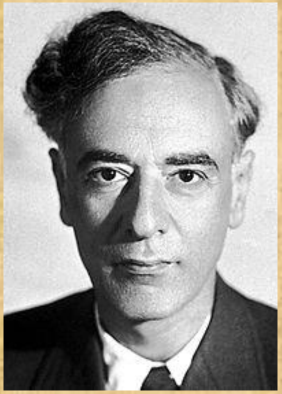
Werkstoffe -Edelsteine/Edelmetalle





Ferroelectricity: Landau-Ginzburg phenomenological theory


Vitaly Ginzburg
1916-2009


Lev Landau
1908-1968

Free energy

Order parameter (polarization)

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

Electric field

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

Ignoring higher terms we can get the linear solution:

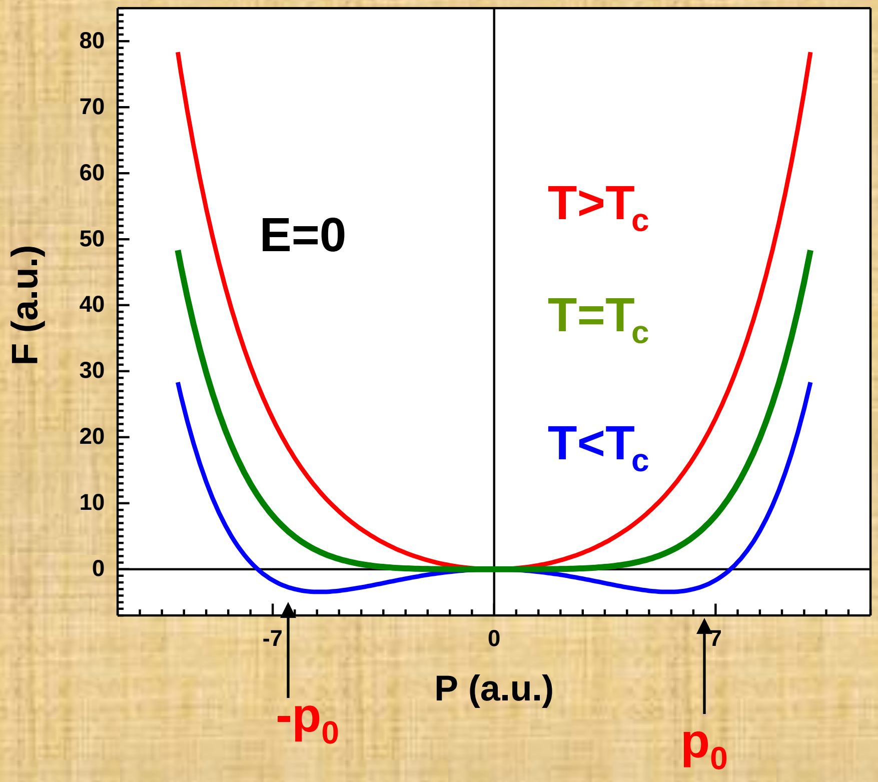
$$\frac{\partial F}{\partial P} = aP - E = 0 \qquad \chi = \frac{\partial P}{\partial E} = \frac{1}{a}$$

Assuming linear dependence of a on temperature we will have:

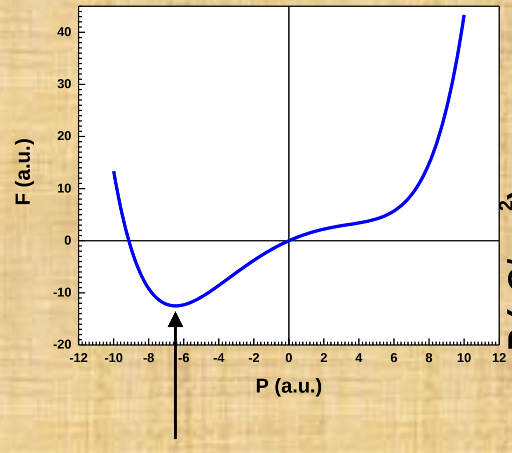
$$\alpha = \frac{1}{C}(T - T_c)$$ and finally we will have Curie-Weiss law $$\boxed{\chi = \frac{C}{(T - T_c)}}$$

Ferroelectricity: Landau-Ginzburg phenomenological theory

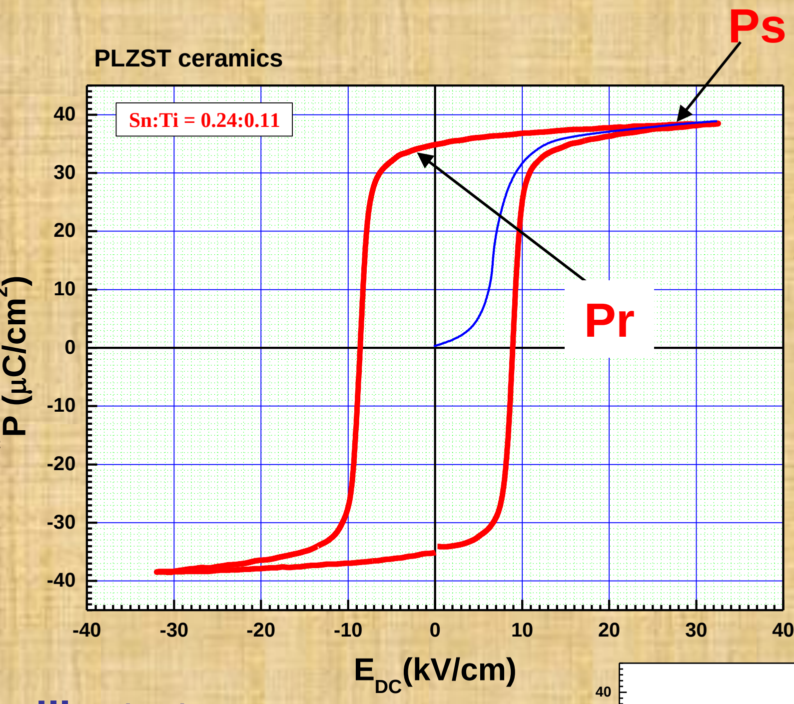
In case of b>) (C>0 also) We will have the solution for second order phase transition with two equilibrium points $-p_0$ and p_0. Both these states are equivalent

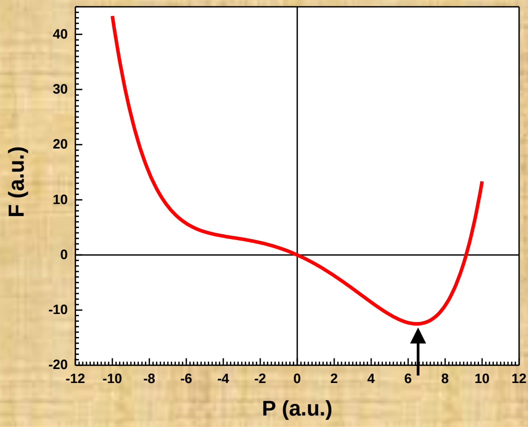


Ferroelectricity: Landau-Ginzburg phenomenological theory



-Ps

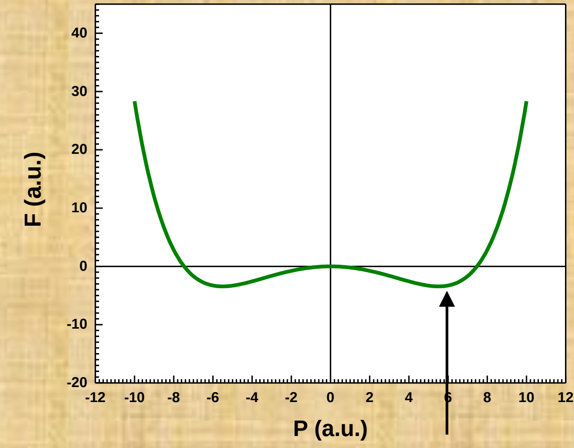




Ps

Including EP term can illustrate the P-E hysteretic behavior

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

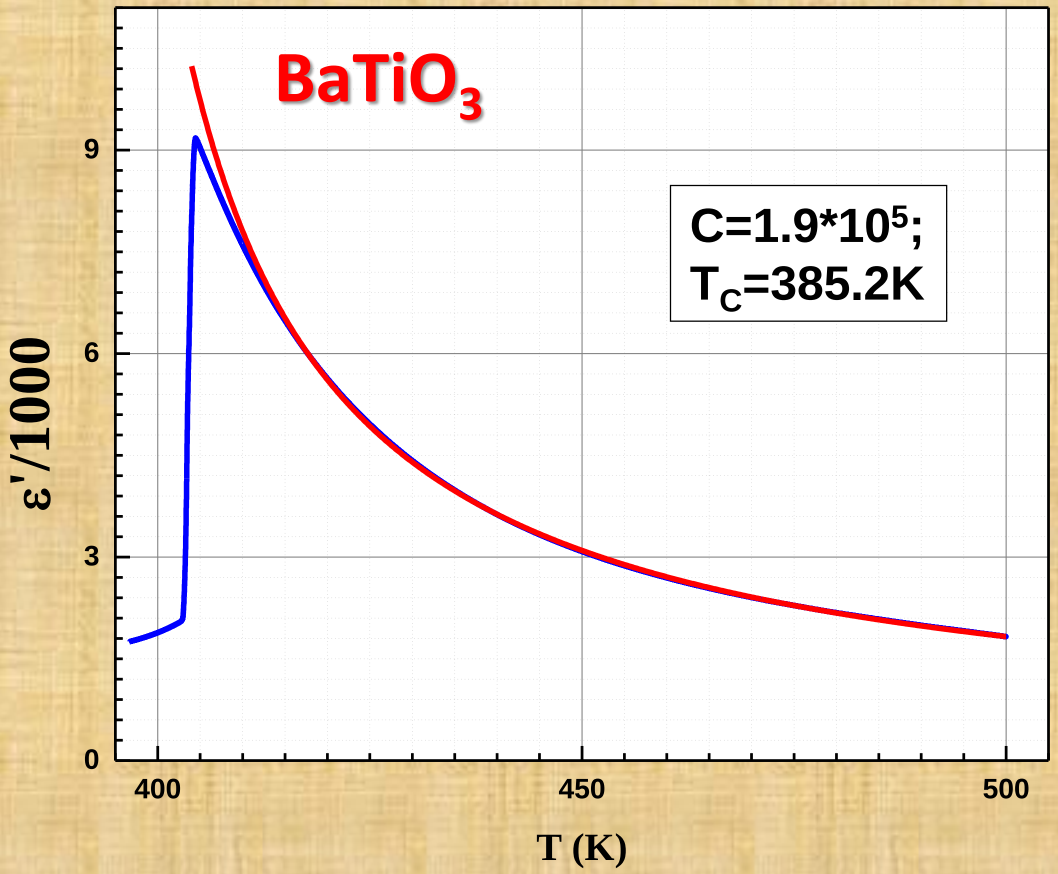


Pr

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 $\varepsilon >> 1$ 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

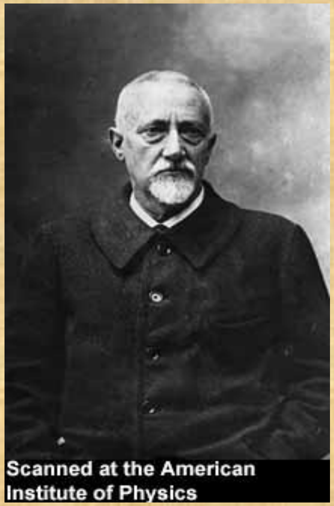
Potassium sodium tartrate discovered (in about 1675) by an apothecary, *Pierre Seignette*

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

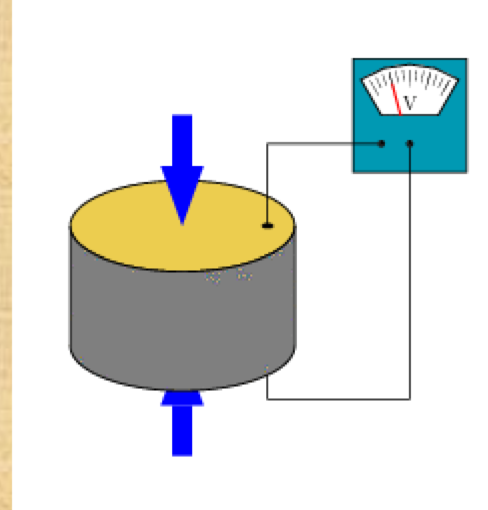
Ferroelectricity: Discovery

Rochelle Salt $KNaC_4H_4O_6*4H_2O$



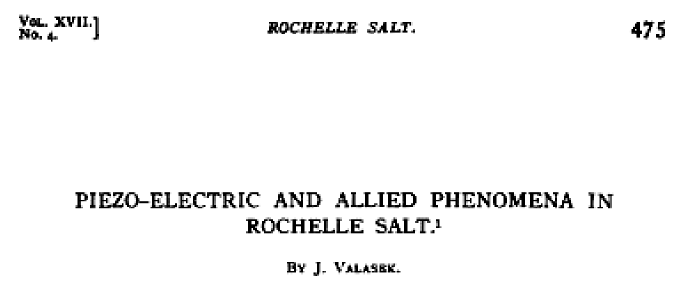
Paul-Jacques Curie
1856 – 1941

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.

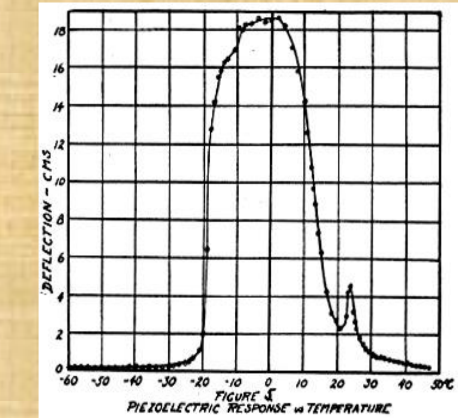


Fig3. Piezoelectric response as a function of temperature [2]

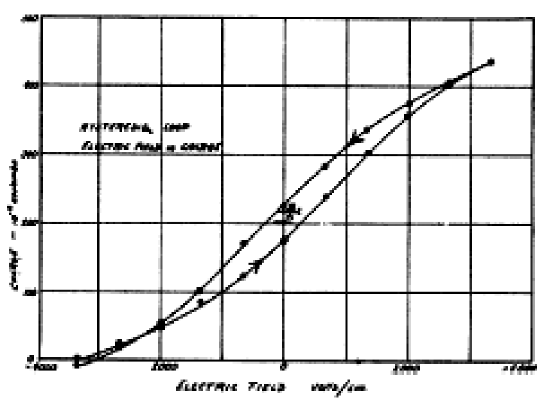


Fig.1. The first published hysteresis loop [1]

1920

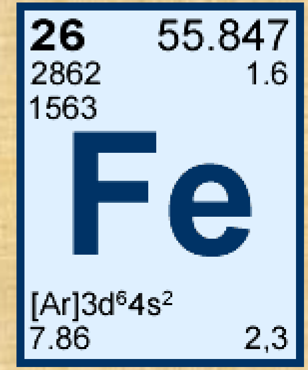
1969

Joseph Valasek (1897-1993)
University of Minnesota

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

Rochelle Salt $KNaC_4H_4O_6*4H_2O$

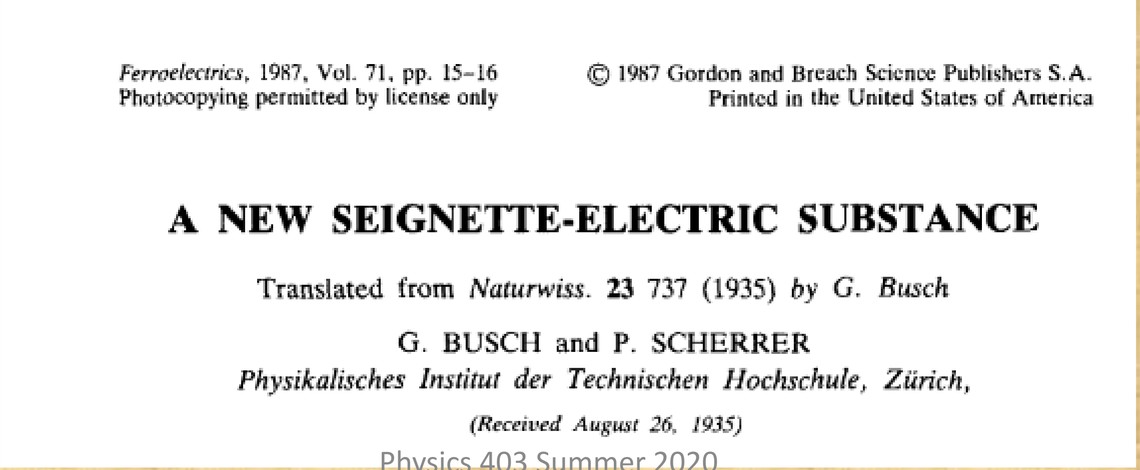
Ferroelectricity. Terminology.



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
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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

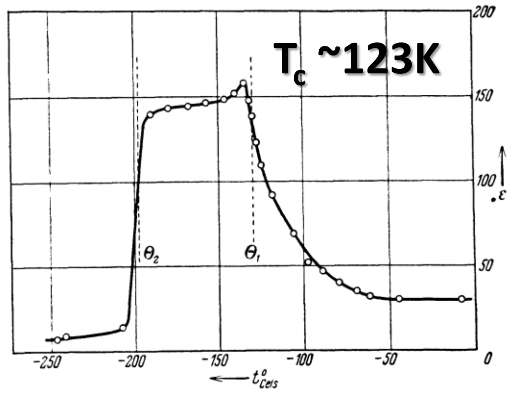


Fig. 1. Temperaturverlauf der Dielektrizitätskonstanten ε_{33} an KH_2PO_4.

DIE NATURWISSENSCHAFTEN

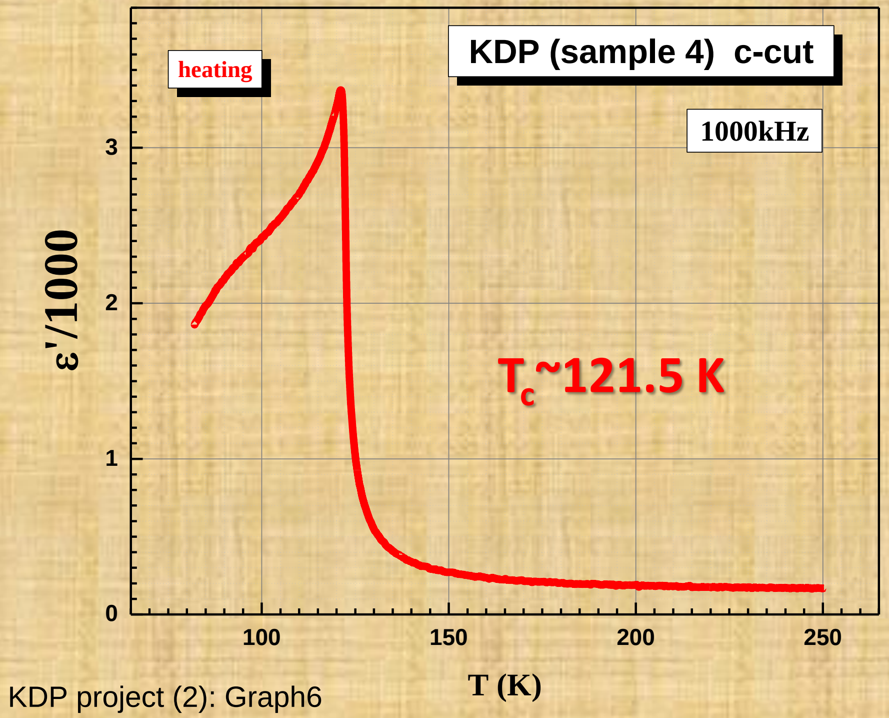
23. Jahrgang 25. Oktober 1935 Heft 43

Eine neue seignette-elektrische Substanz.

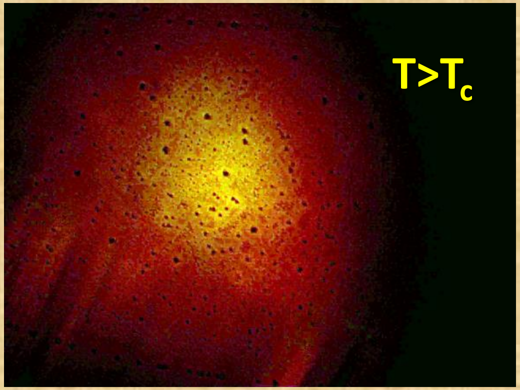
Materials. KDP

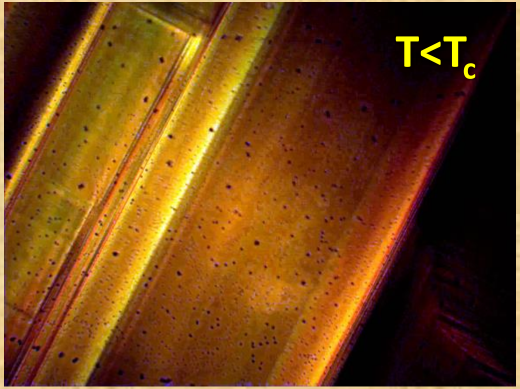
KDP (KH_2PO_4) - potassium dihidrophosphate

T_c ~121-123 K



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



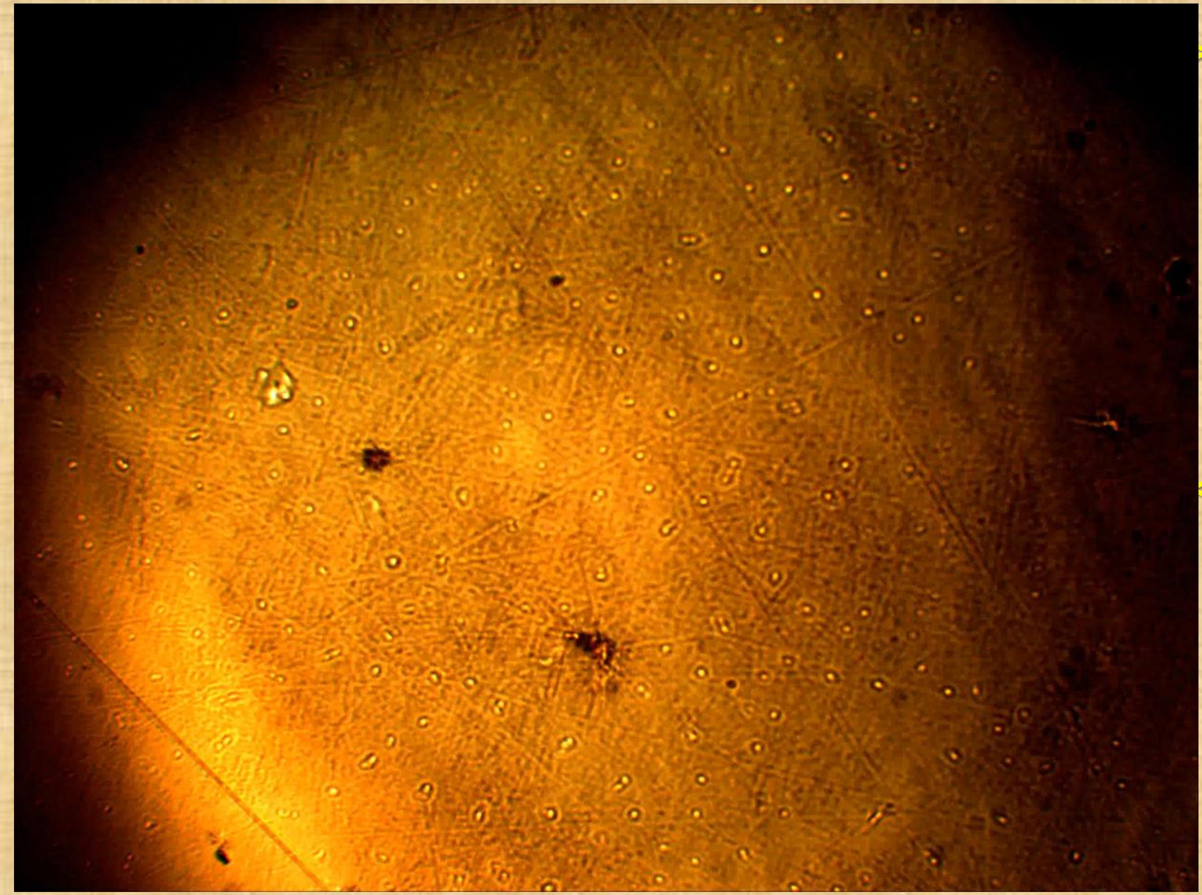


Courtesy of Alison Pohl, Physics 403, Spring 2009

Materials. DKDP

DKDP (KD_2PO_4) – deuterated potassium dihidrophosphate

T_c ~230K



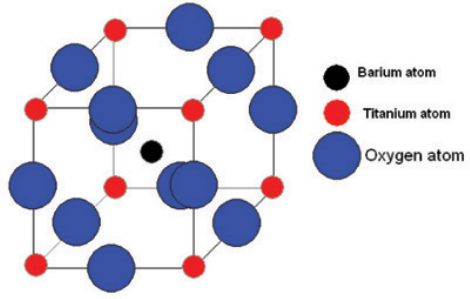
$>T_c$

$<T_c$

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 BaTiO3 A. von Hippel (USA); Wul, Goldman (USSR))



T_c ~400K

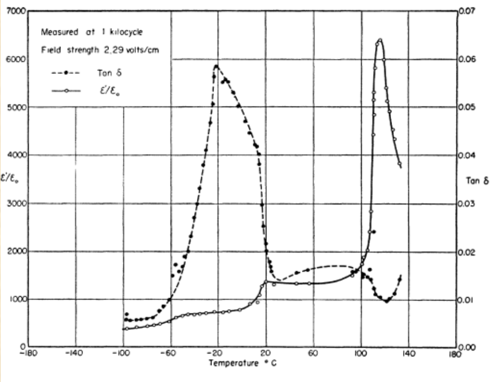


FIG. 6. Dielectric constant and loss of barium titanate ceramic.

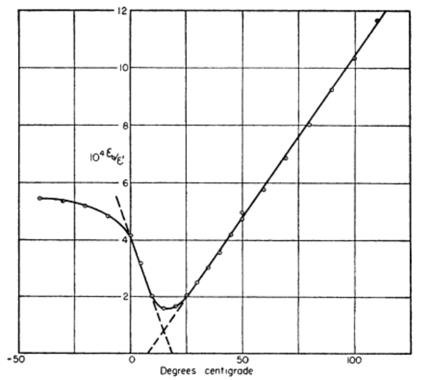
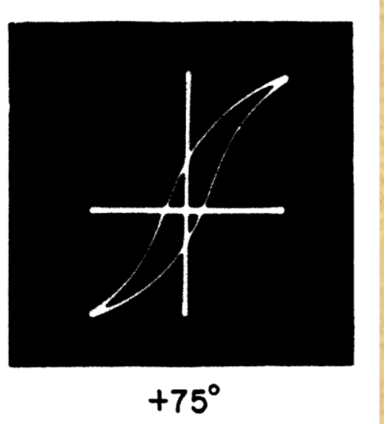
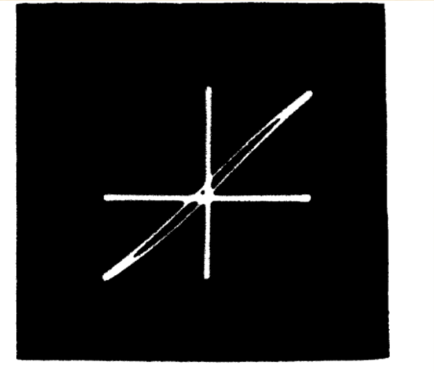


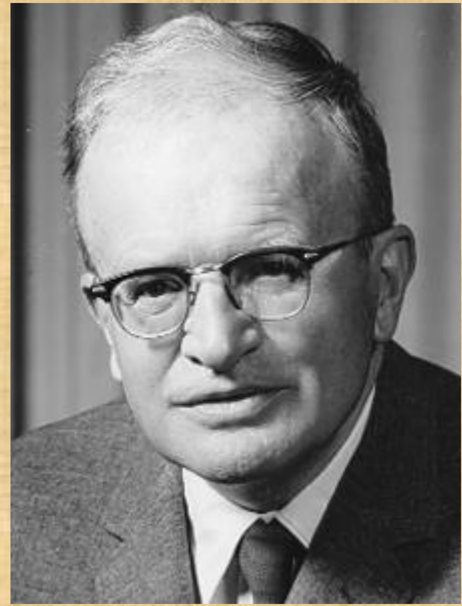
FIG. 15. Confirmation of Curie-Weiss laws in (Ba-Sr)TiO_3 (400 kc).



+75°



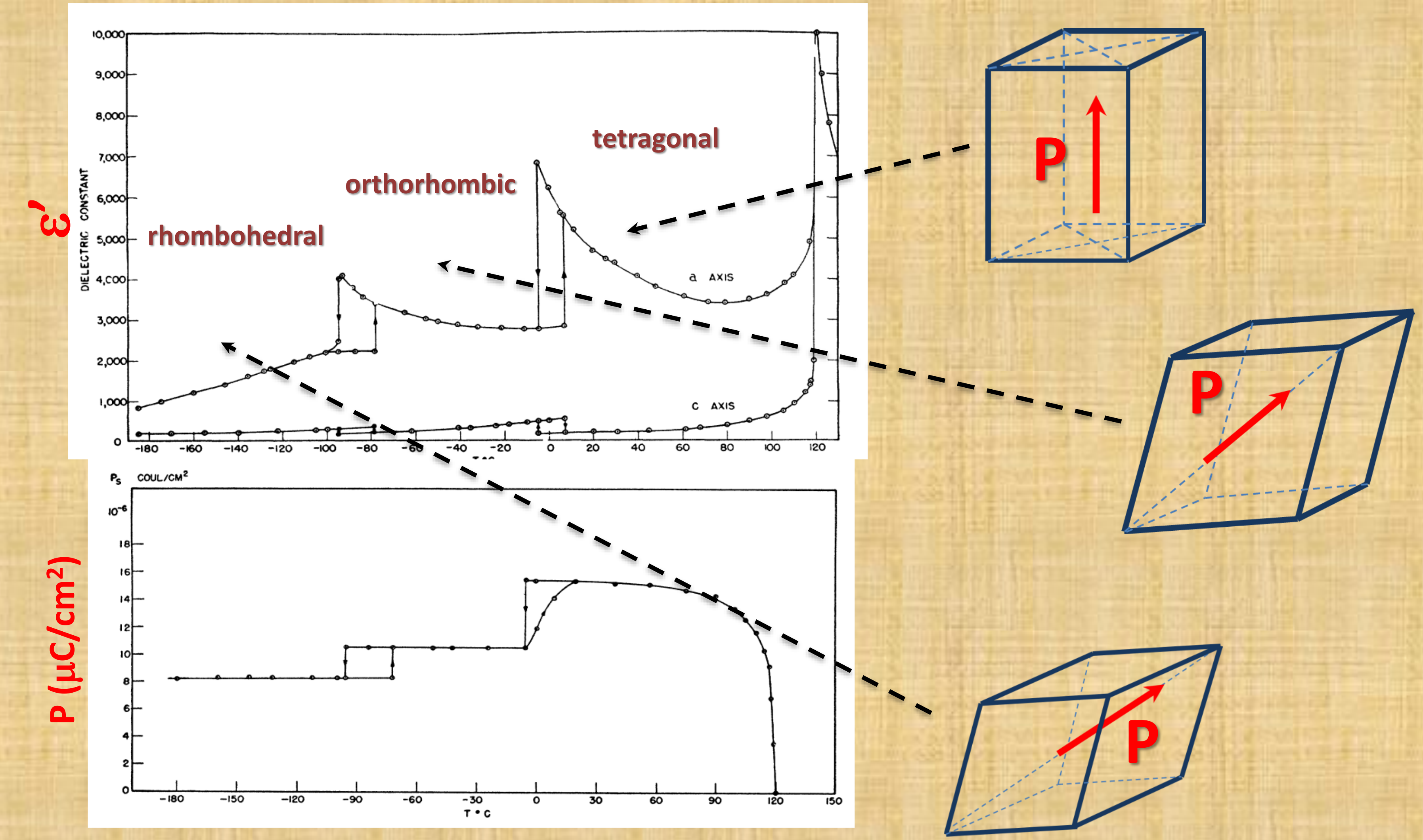
+125°



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.

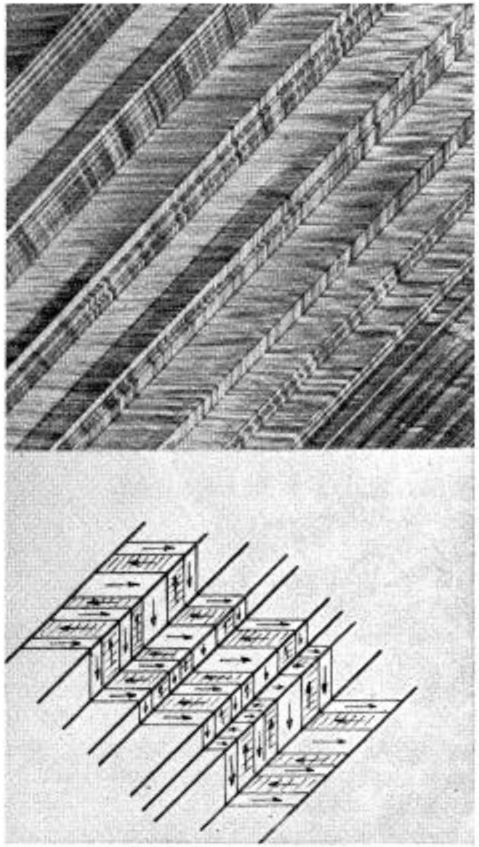
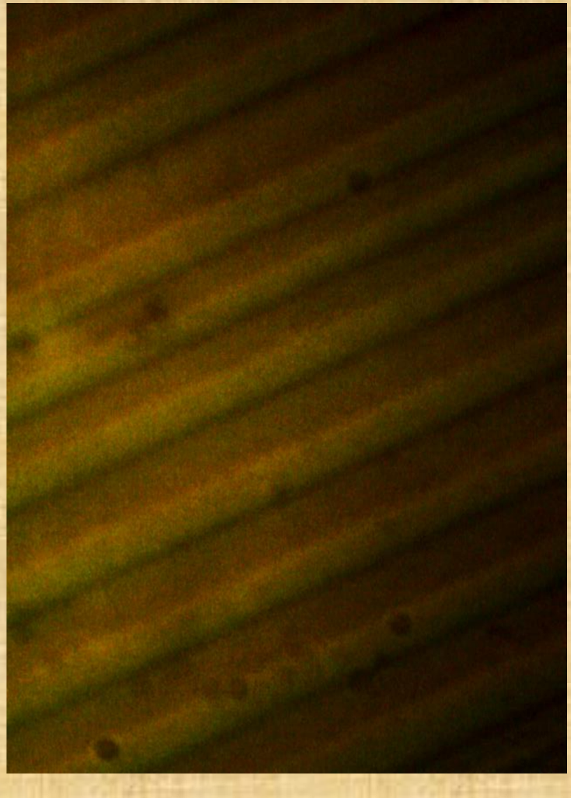


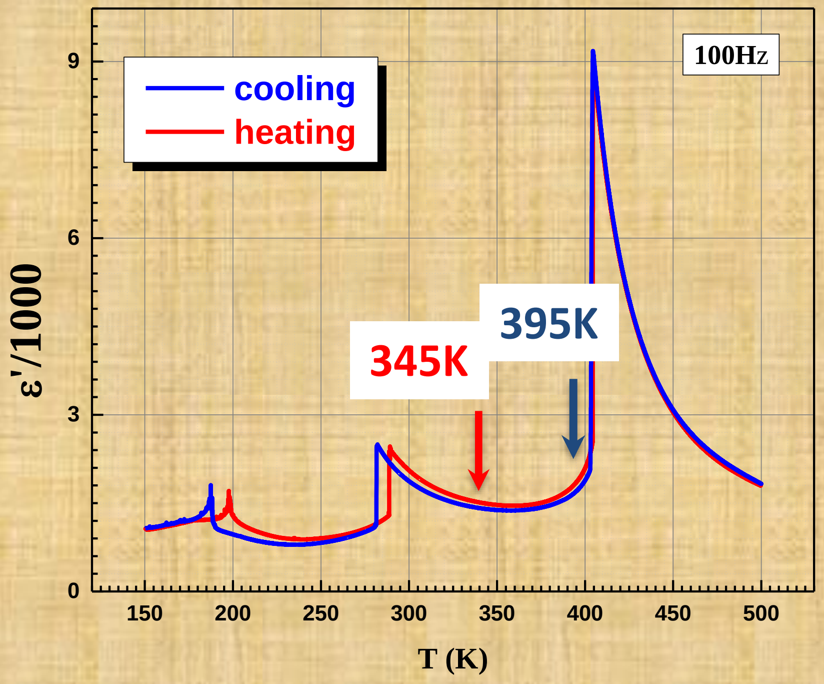
FIG. 4. Surface of an *a*-domain crystal showing 90° walls and antiparallel domains.

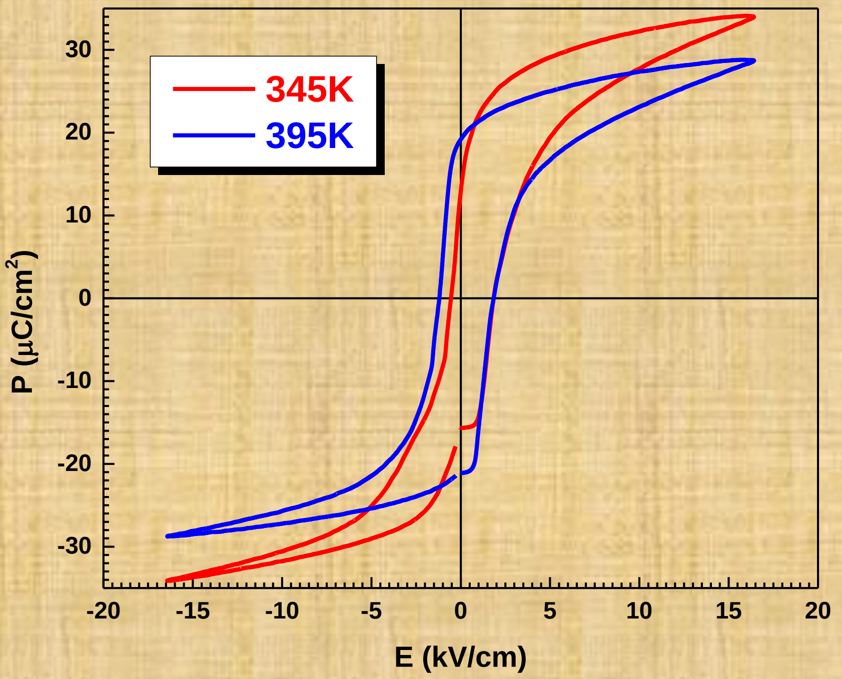
John A. Hooton, Walter J. Merz, Phys. Rev. 98, 409,1955



Physics 403 Lab, August 2011

Materials. $BaTiO_3$. P-E hysteresis.





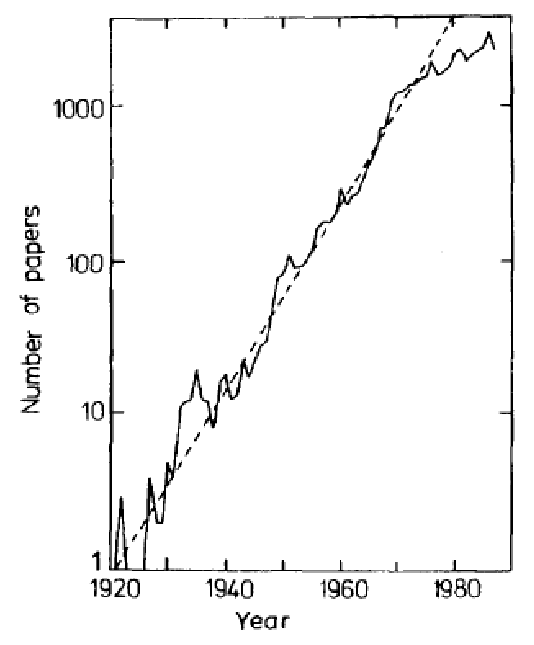
Courtesy of Liu M. & Lopez P,
Physics 403, Spring 2013

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

ABO_3

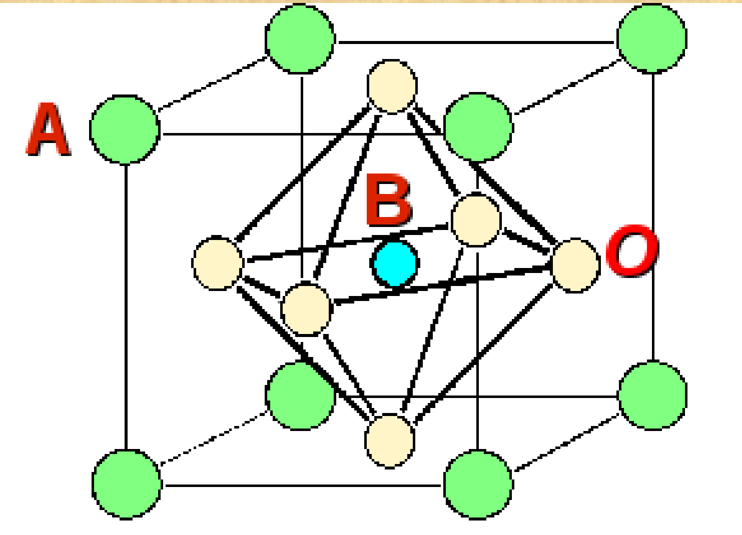
Springer Handbook of Condensed Matter and Materials Data



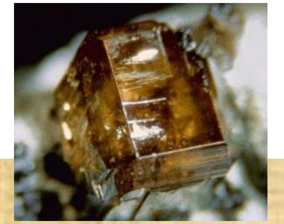
Number of publications concerning ferroelectricity. From Jan Fousek *"Joseph Valasek and the Discovery of Ferroelectricity"*

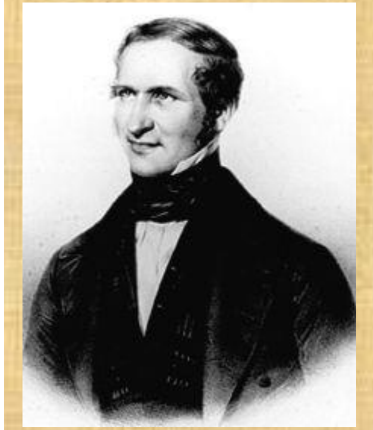
Perovskite Structure

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.



ABO_3





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

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)

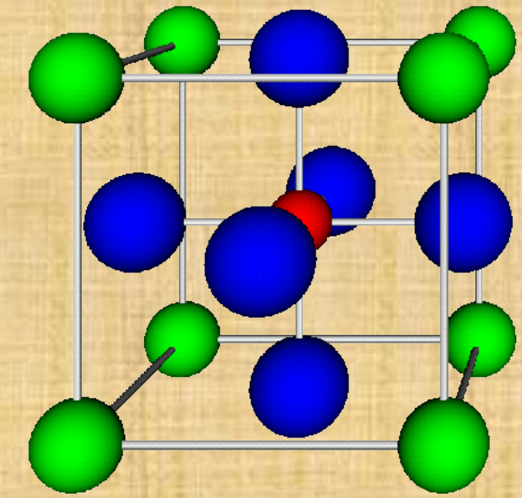
Smolenskii G.A.[2]
(1910 – 1986)

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

Relaxors

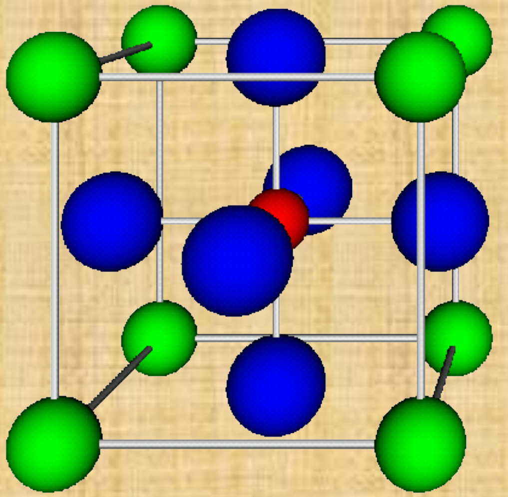
Regular ferroelectric $BaTiO_3$



$T > T_c$ (cubic)

🟢 Ba 🔵 O 🔴 Ti

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

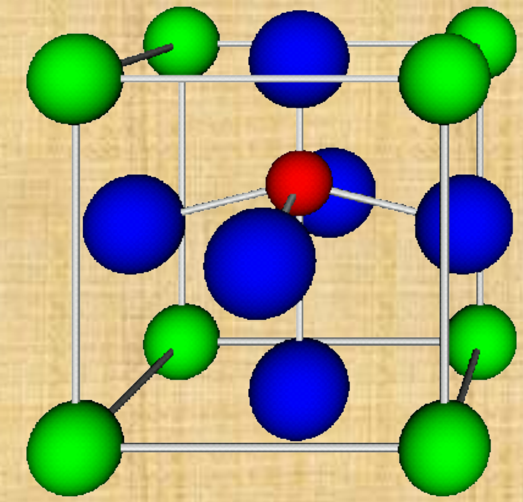


(cubic)

🟢 Pb 🔵 O 🔴 Mg^{+2} or Nb^{+5}

Relaxors

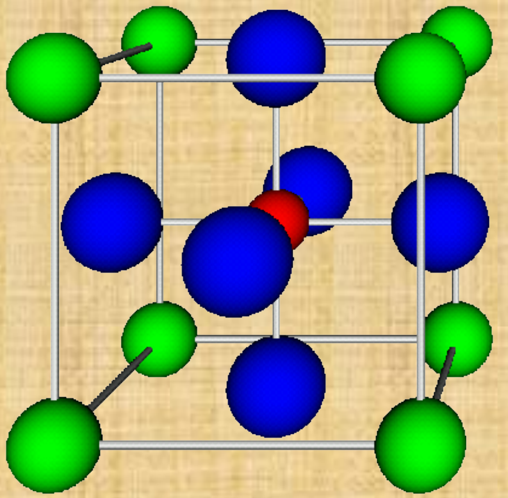
Regular ferroelectric $BaTiO_3$



$T < T_c$ (tetragonal)

● Ba ● O ● Ti

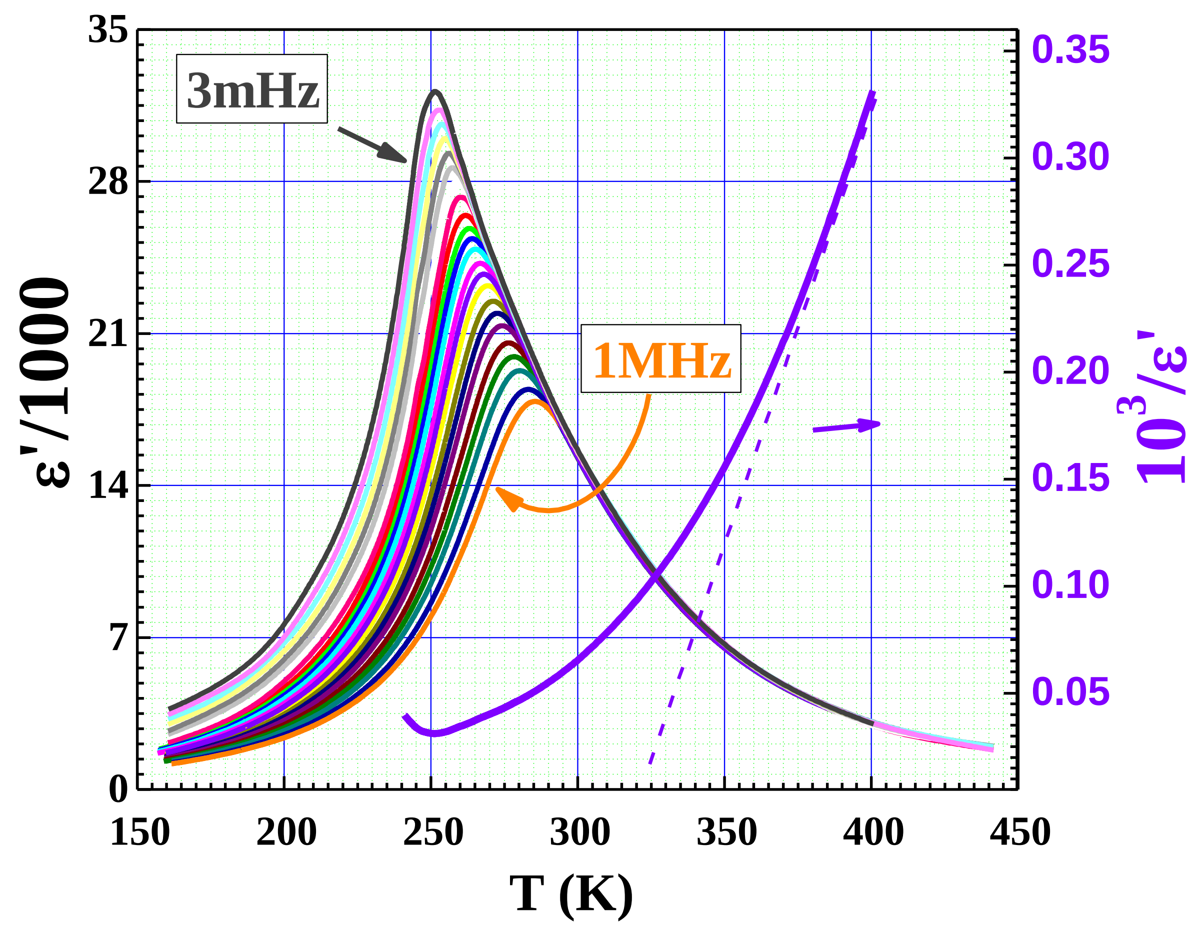
Relaxor - PMN $Pb(Mg_{1/3} Nb_{2/3})O_3$



(cubic)

● Pb ● O ● Mg^{+2} or Nb^{+5}

Relaxor. Frequency dispersion

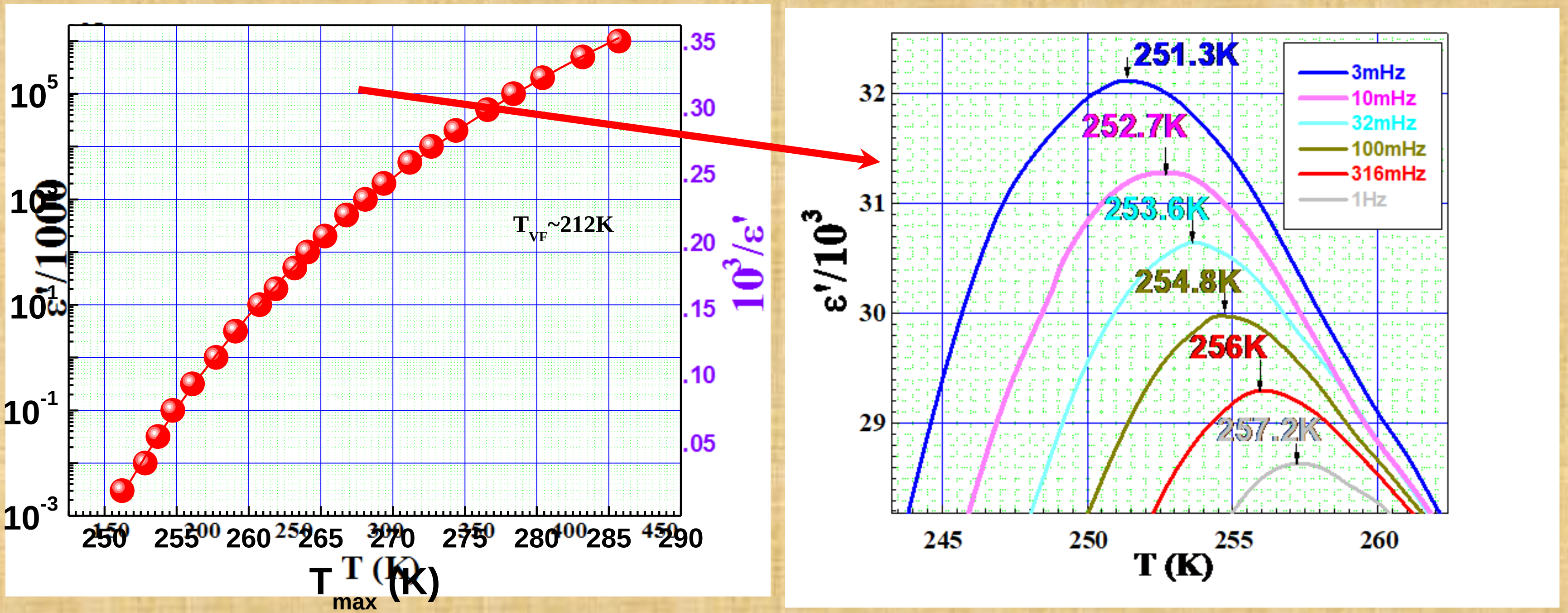


ε'_{max} and T_{max} depend o
the measuring frequenc

ε' does not follow Curie-Weiss law

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

PMN. *Vogel – Fulcher* dependence



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

Relaxors. Nanodomains.

PNR – polar nanodomains
COR – chemically ordered regions

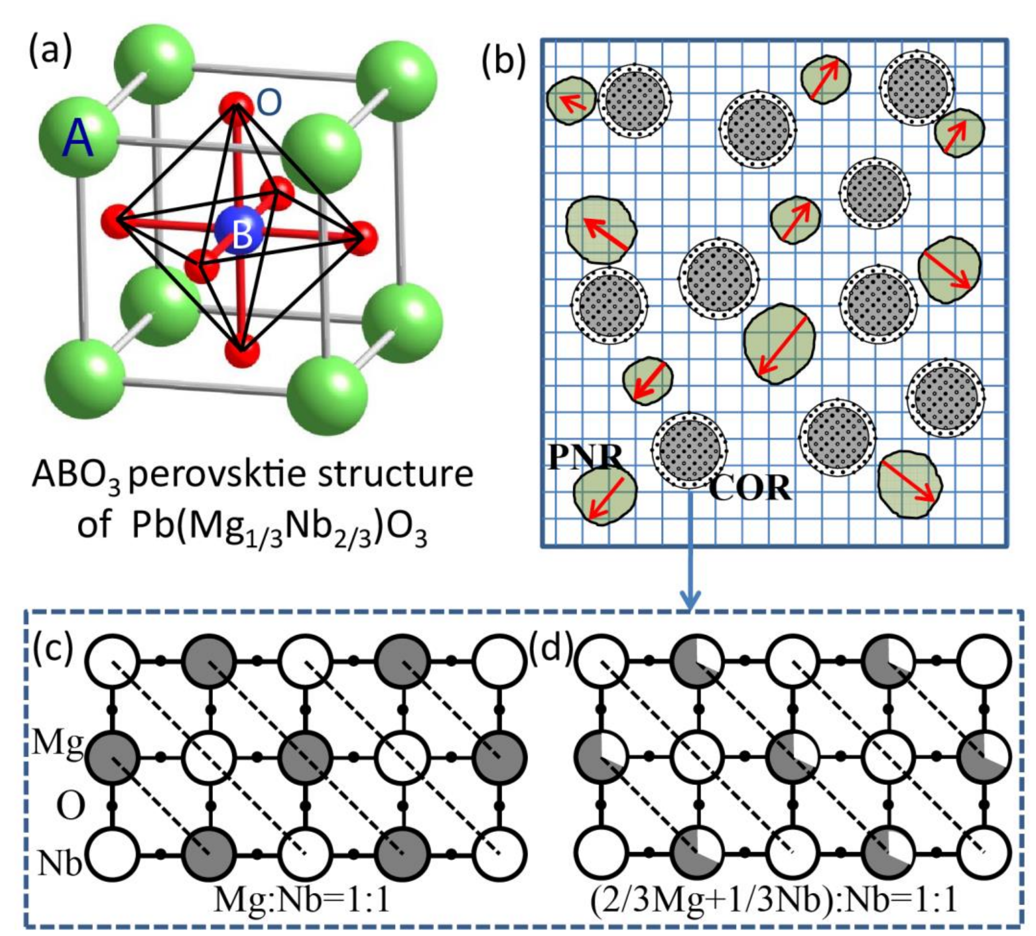
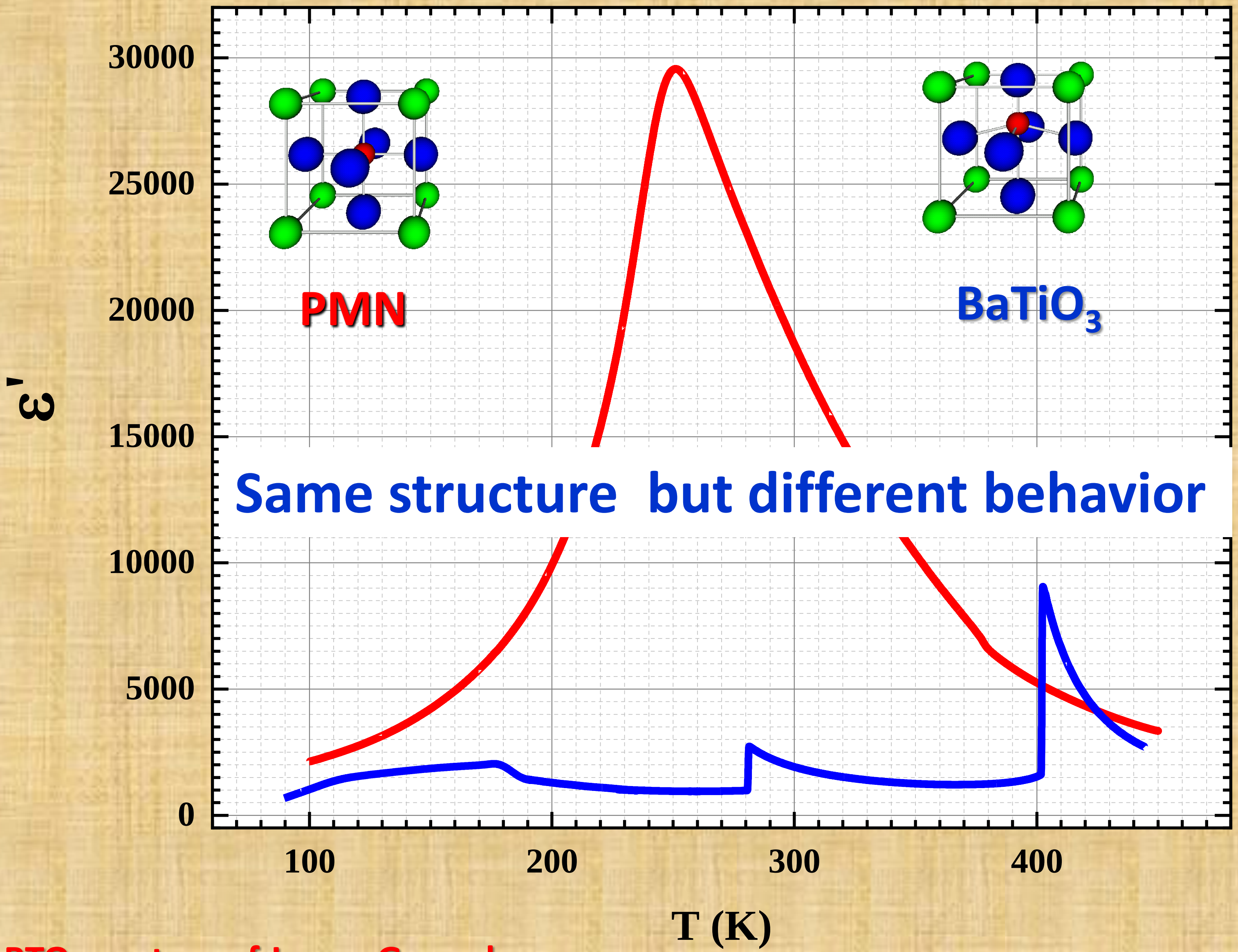


Figure 3.
(a) ABO$_3$perovskite structure. (b) Model for relaxor structure. PNR and COR represent the polar nano-region and chemically order region, respectively. (c) &(d) show two models of atom arrangement for COR. To maintain the electric neutrality, a Nb-rich layer is required for case (c).

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

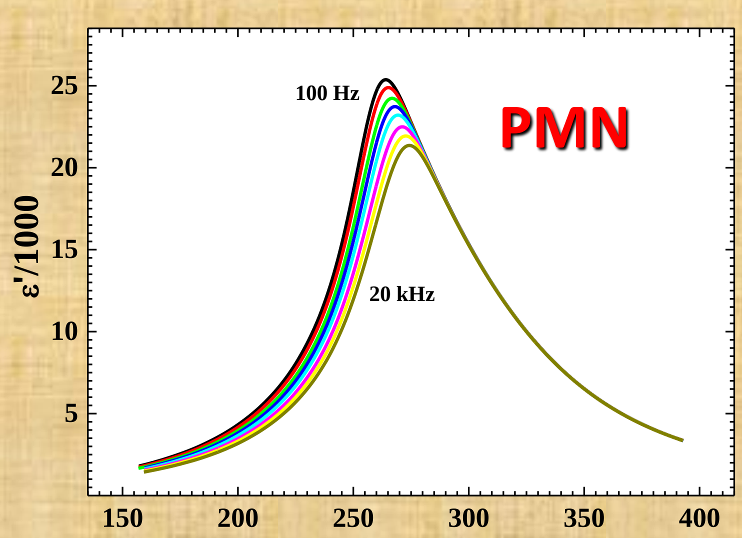
Regular Ferroelectrics - Relaxors

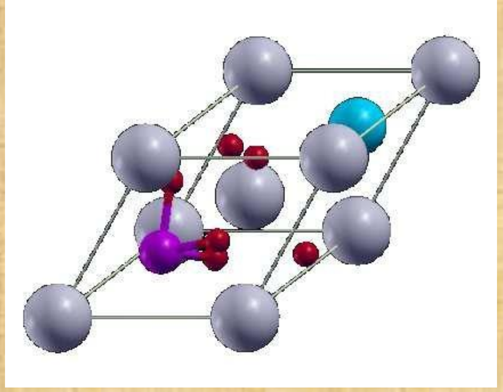


Same structure but different behavior

BTO courtesy of James Graessle

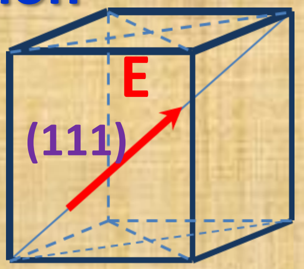
Disorder in Regular Ferroelectrics

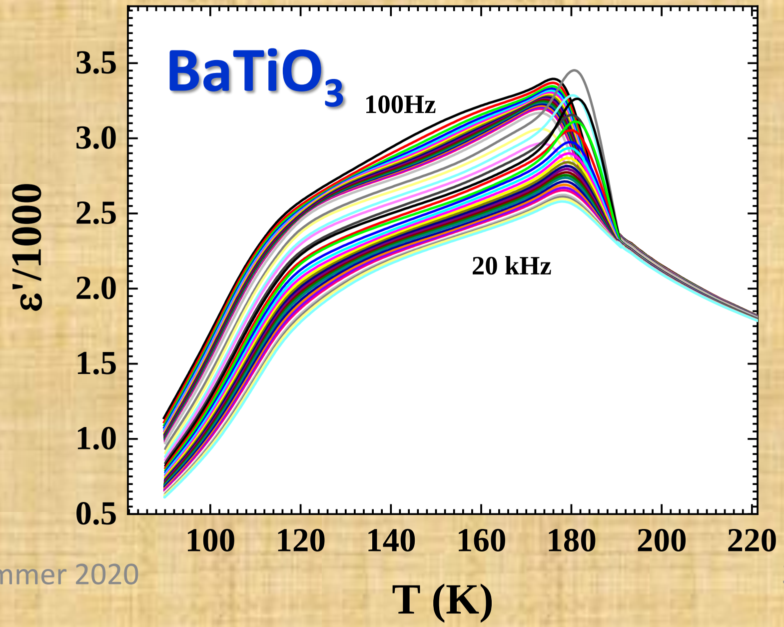




BaTiO$_3$ Rhombohedral phase

PMN remains in cubic phase but it is easy to move it in rhombohedral phase by application of the DC field in (111) direction



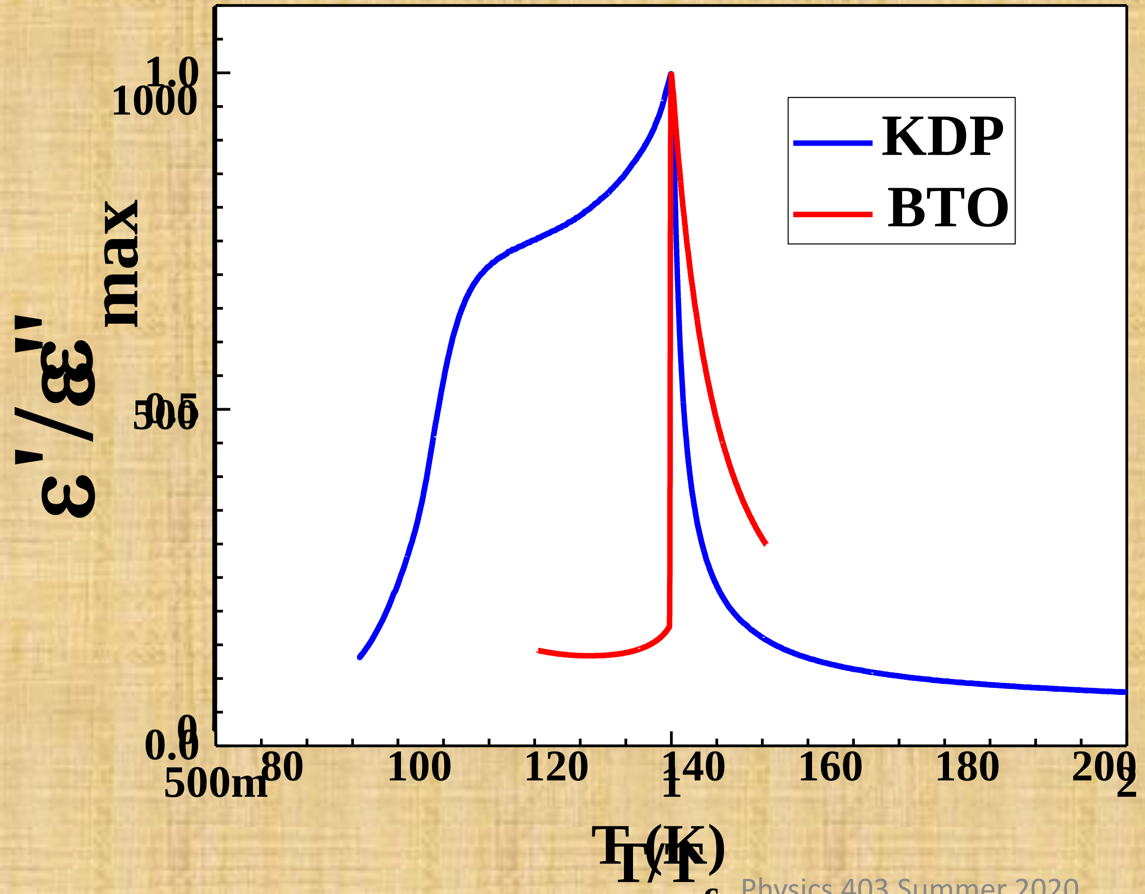


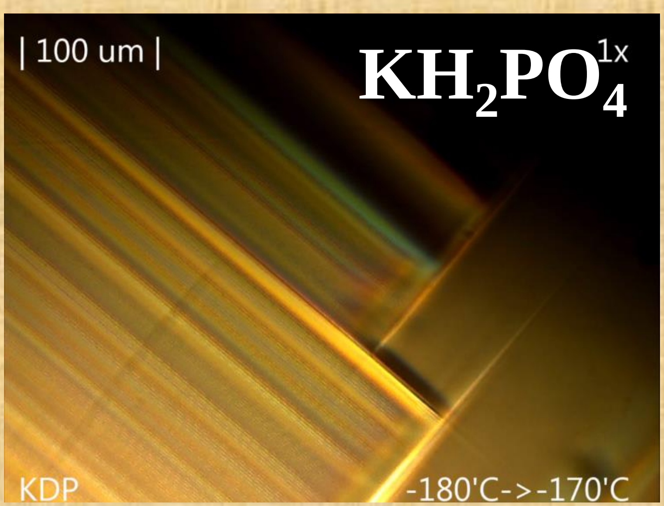
BTO courtesy of James Graessle

Disorder in Regular Ferroelectrics. KDP family

KH_2PO_4 KDP - T_c ~ 120 K

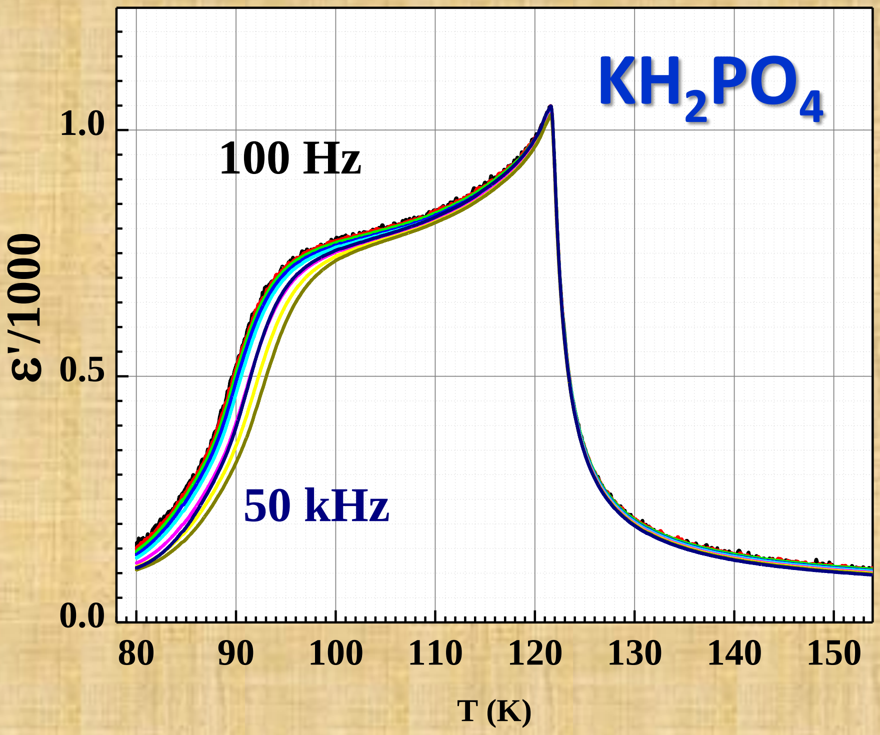
KD_2PO_4 Deuterated analog DKDP T_c~230K

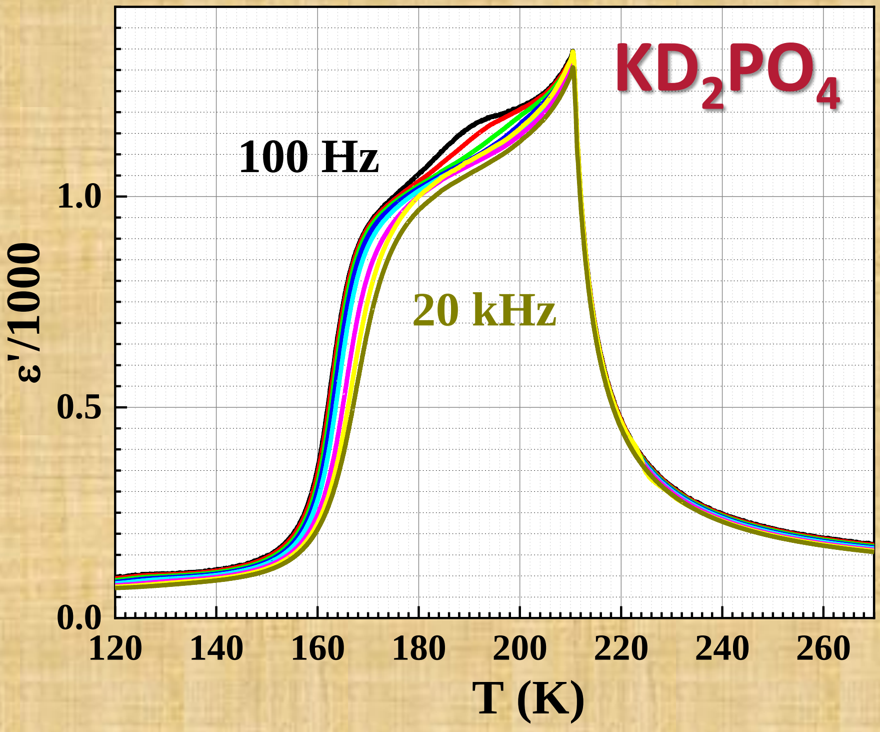




Disorder in Regular Ferroelectrics. KDP family

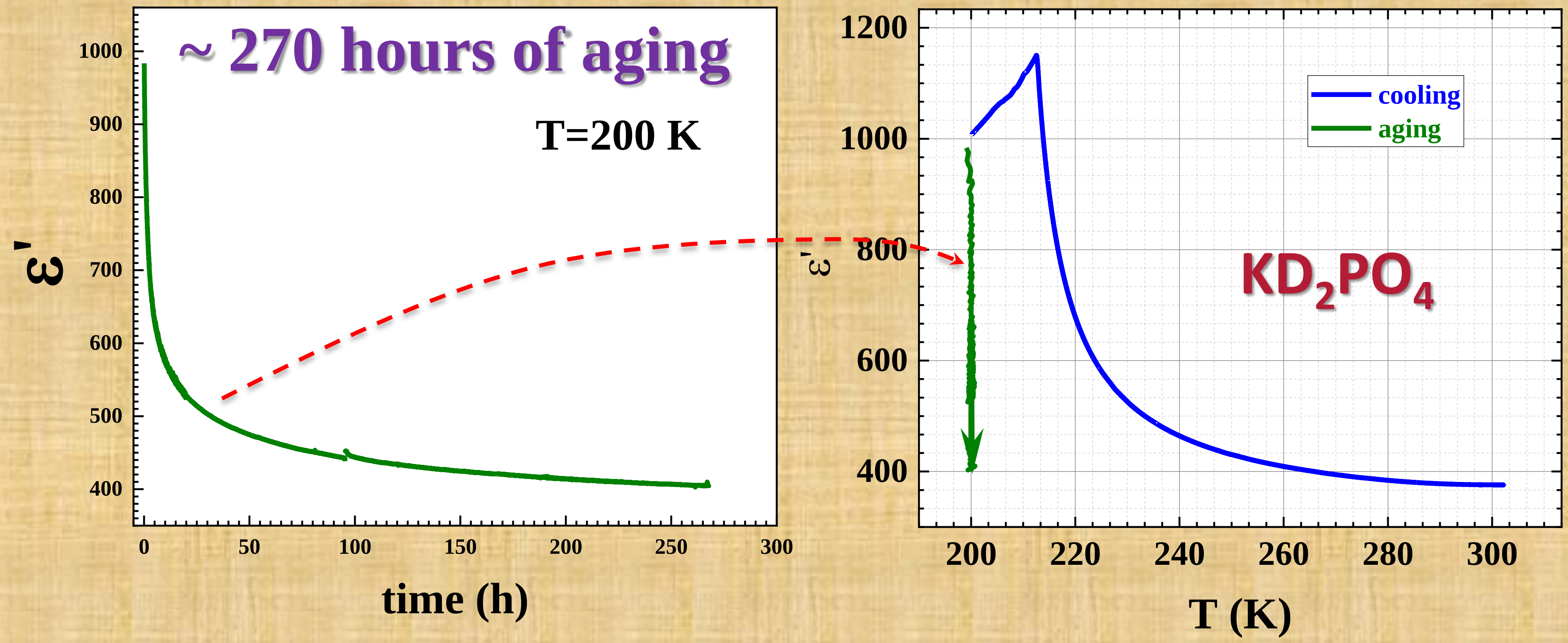
Below Tc KDP and DKDP show wide (> 30 K) plateau. This state is not equilibrium and has a trend to decrease the susceptibility in time (aging)





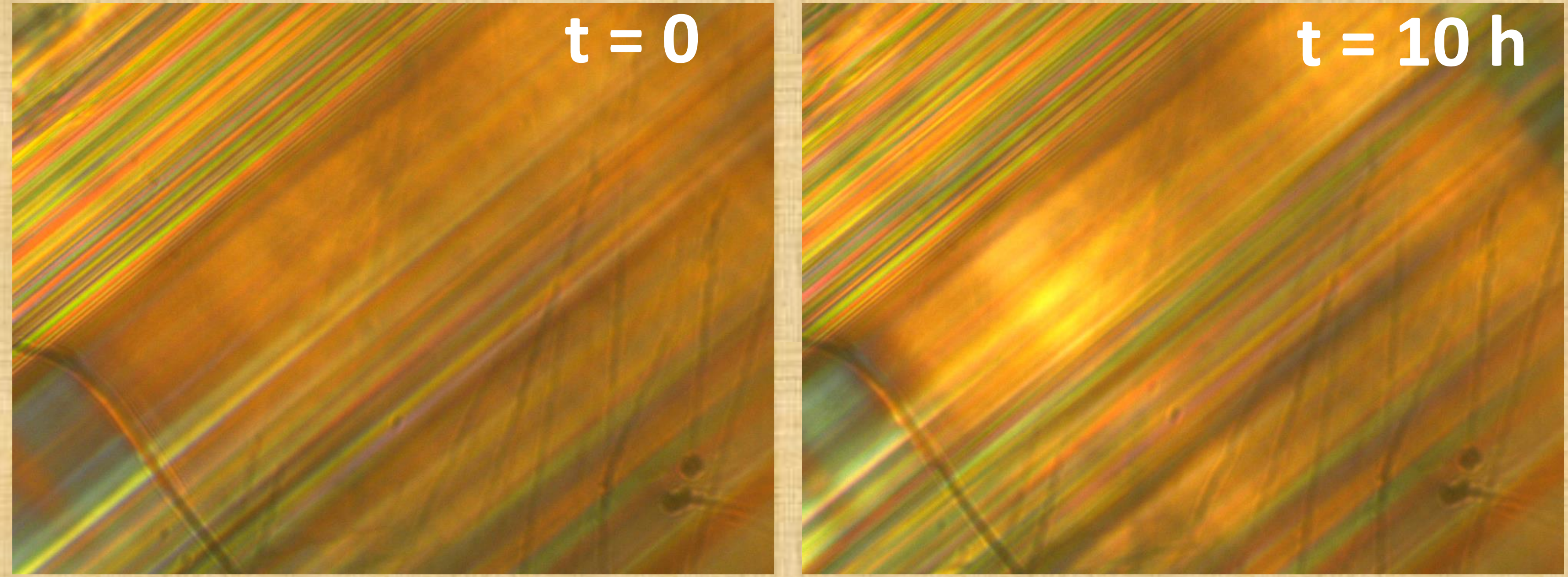
Disorder in Regular Ferroelectrics. KDP family

Aging depends on the concentration of deuterium in $(KH_2PO_4)_{(1-x)}(KD_2PO_4)_x$ composition



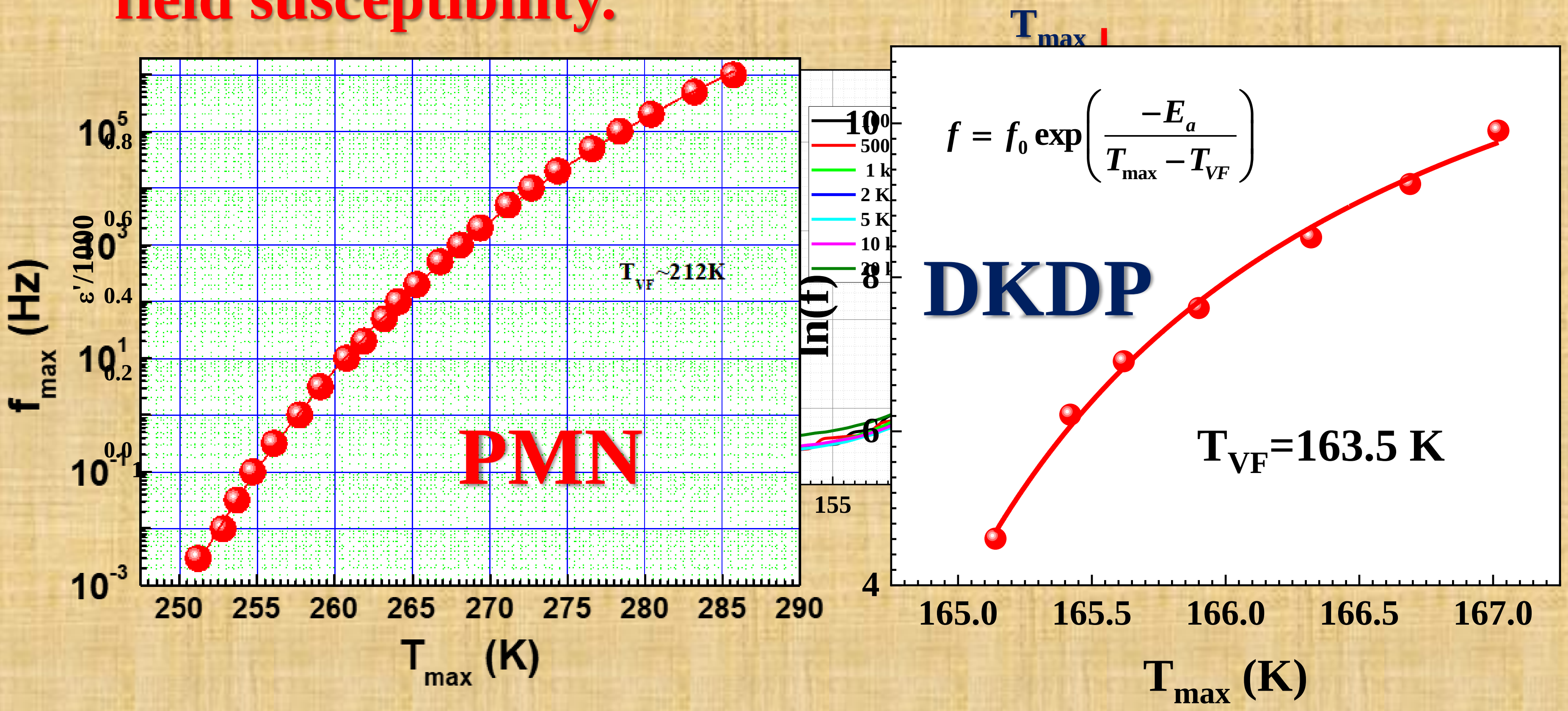
Disorder in Regular Ferroelectrics. KDP family

Aging does not significantly change the domain pattern of the KDP-DKDP ferroelectric. The rearrangements in domain walls are responsible for the decrease of the susceptibility.



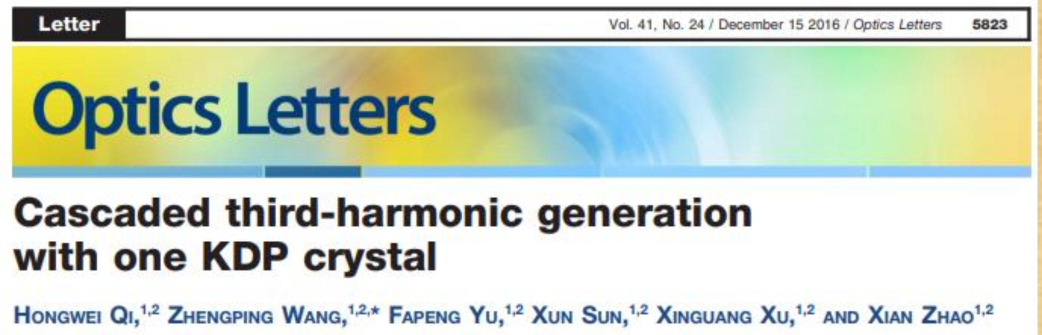
Disorder in Regular Ferroelectrics. KDP family

Finally, at low T these nanoscale polarized regions becomes frozen and do not more contribute low field susceptibility.



Applications of Ferroelectrics

KDP single crystals are mostly used as nonlinear optical materials



Letter Vol. 41, No. 24 / December 15 2016 / *Optics Letters* **5823**

Optics Letters

Cascaded third-harmonic generation with one KDP crystal

Hongwei Qi,[1,2] Zhengping Wang,[1,2,*] Fapeng Yu,[1,2] Xun Sun,[1,2] Xinguang Xu,[1,2] and Xian Zhao[1,2]

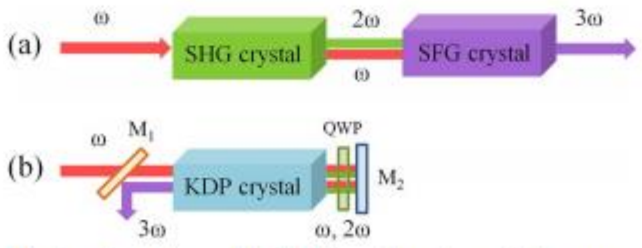


Fig. 1. Comparison of the THG configurations: (a) the conventional configuration that includes two NLO crystals and (b) the suggested configuration which uses only one KDP crystal.

KDP powder is widely used as fertilizer

1bag potassium dihydrogen phosphate Potash Ferti

$1.79

Free Shipping

Get it by Thu, Apr 2 -

China

- New condition
- 30 day returns - Bu

" 【Structure or Molecu

Read full description

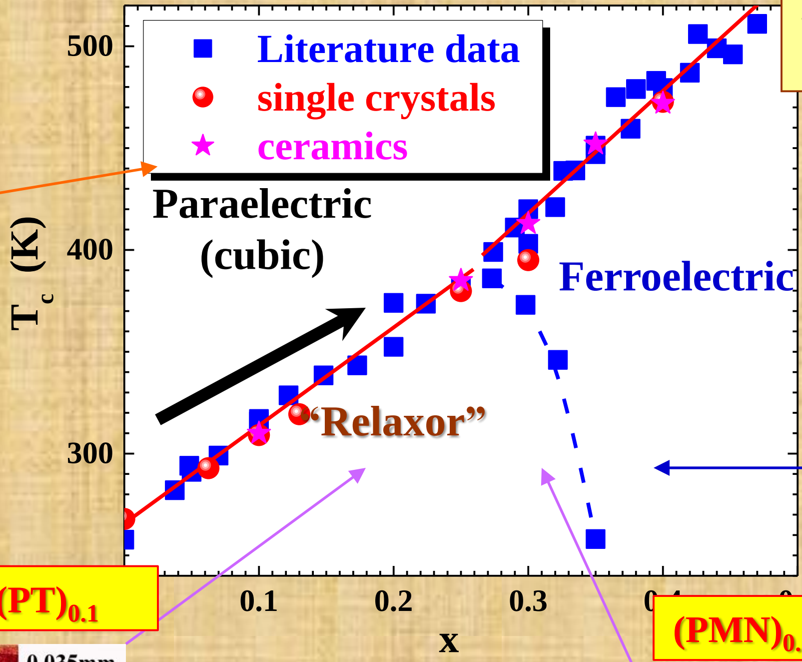
See details

Solid solution relaxor-regular ferroelectric.

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

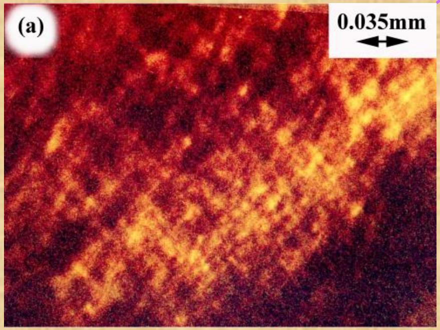
$(PMN)_{(1-x)}(PT)_{(x)}$ phase diagram

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

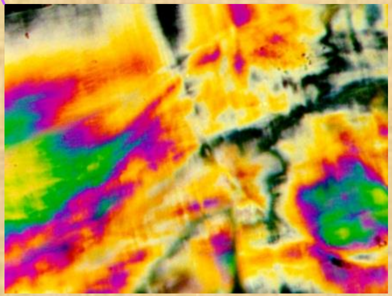


$(PMN)_{0.6}(PT)_{0.4}$

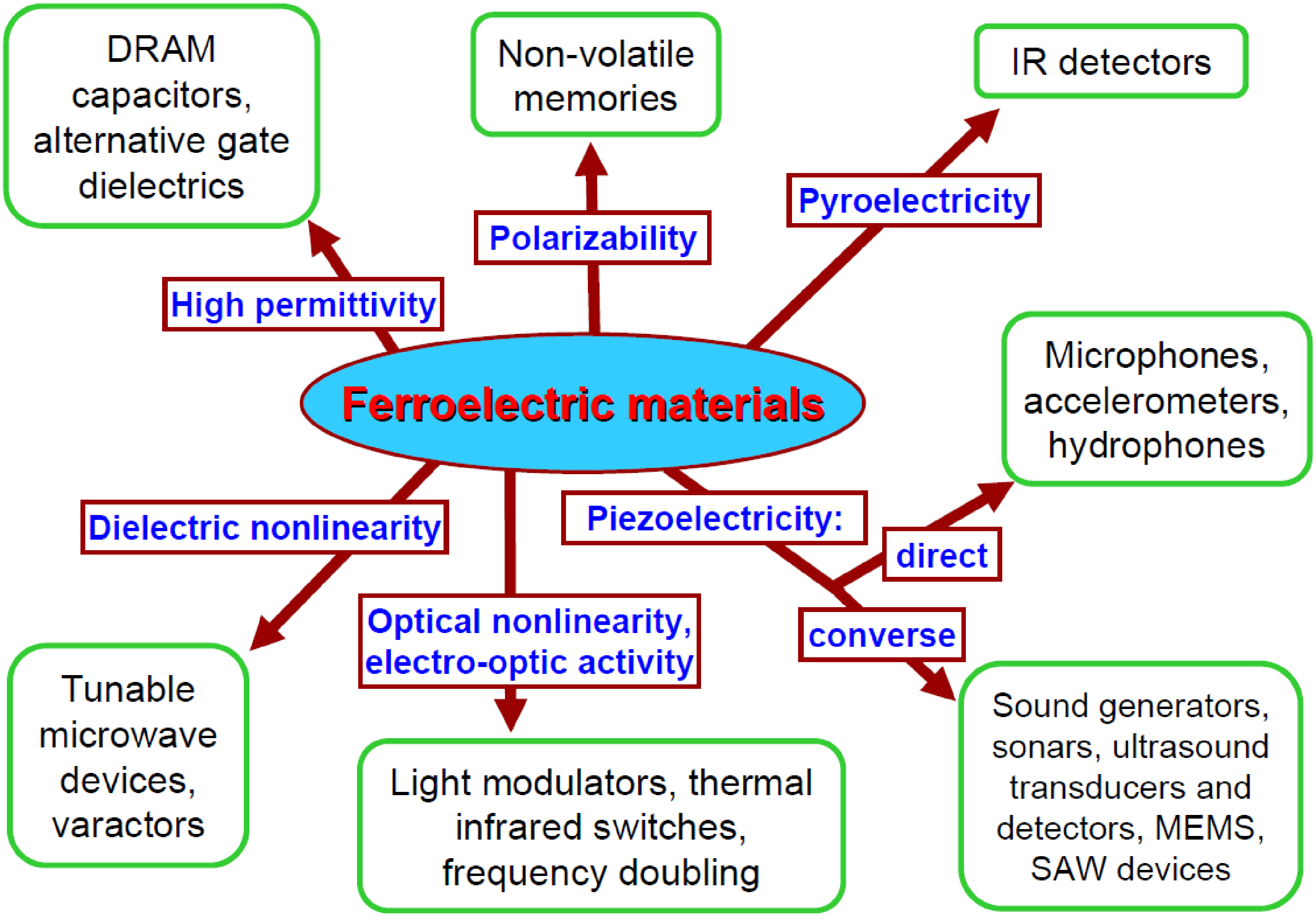
$(PMN)_{0.9}(PT)_{0.1}$



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



Applications of ferroelectrics



Ferroelectric materials

High permittivity → DRAM capacitors, alternative gate dielectrics

Polarizability → Non-volatile memories

Pyroelectricity → IR detectors

Piezoelectricity:

direct → Microphones, accelerometers, hydrophones

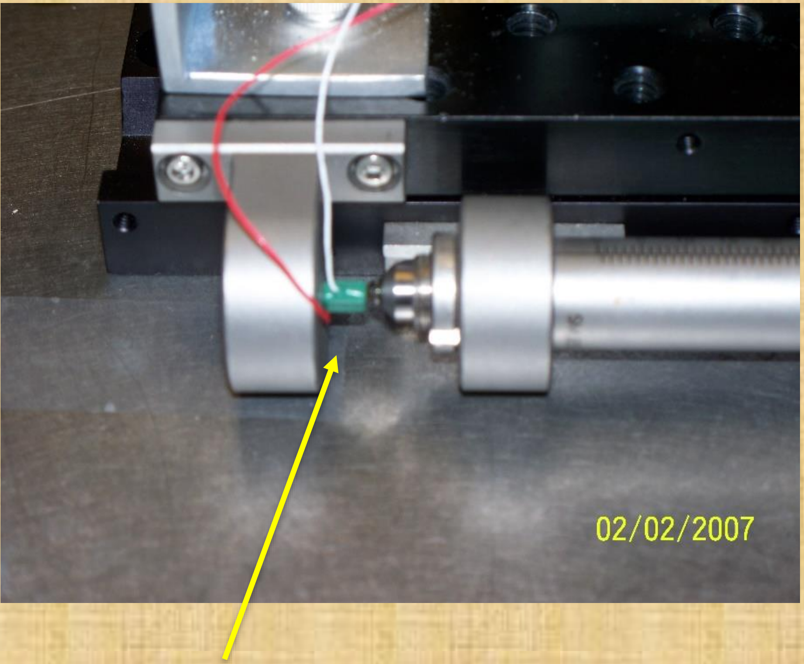
converse → Sound generators, sonars, ultrasound transducers and detectors, MEMS, SAW devices

Optical nonlinearity, electro-optic activity → Light modulators, thermal infrared switches, frequency doubling

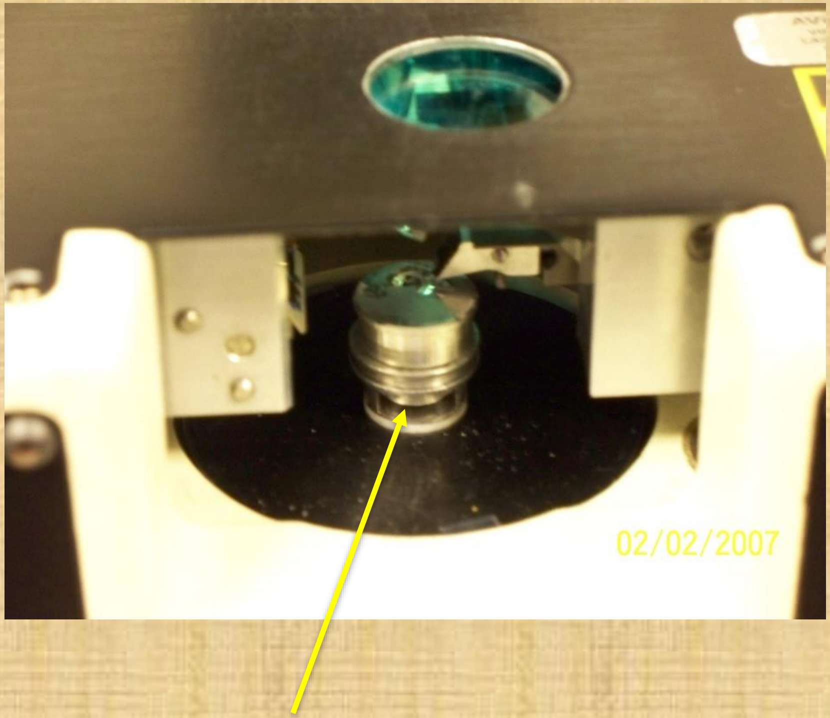
Dielectric nonlinearity → Tunable microwave devices, varactors

Courtesy of D. Tenne, Boise State University

Applications of Ferroelectrics. Physics 403 Lab



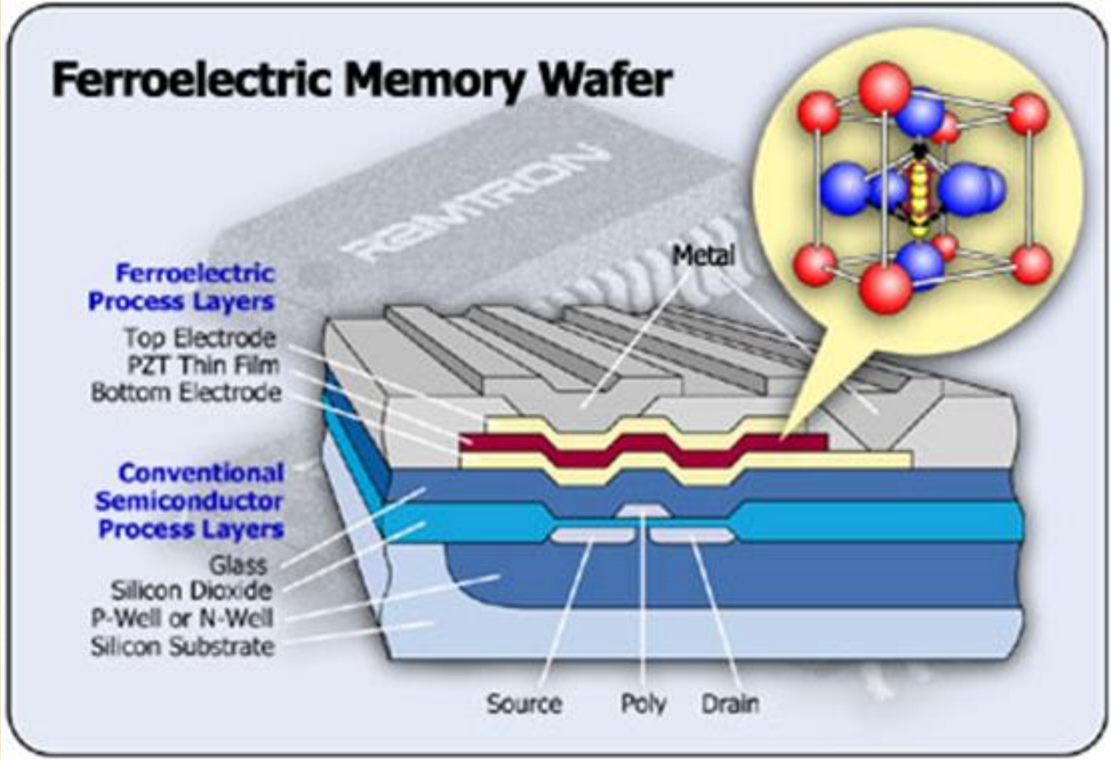
Quantum Optics



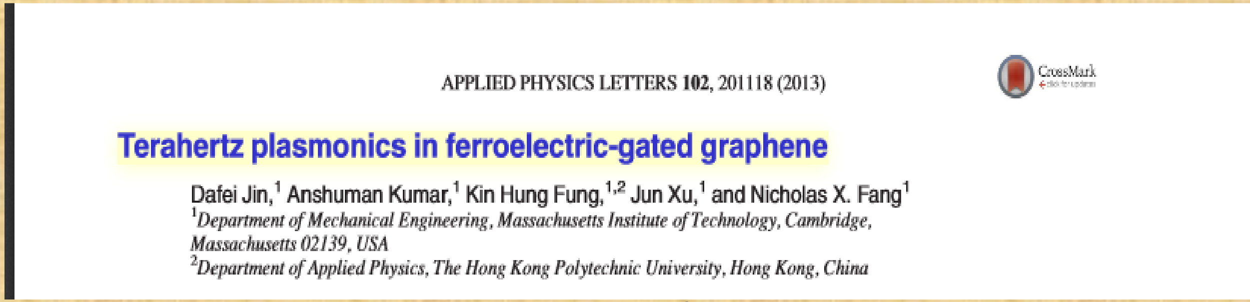
AFM experiment

Courtesy of D. Tenne, Boise State University

Applications. Nonvolatile Memory



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

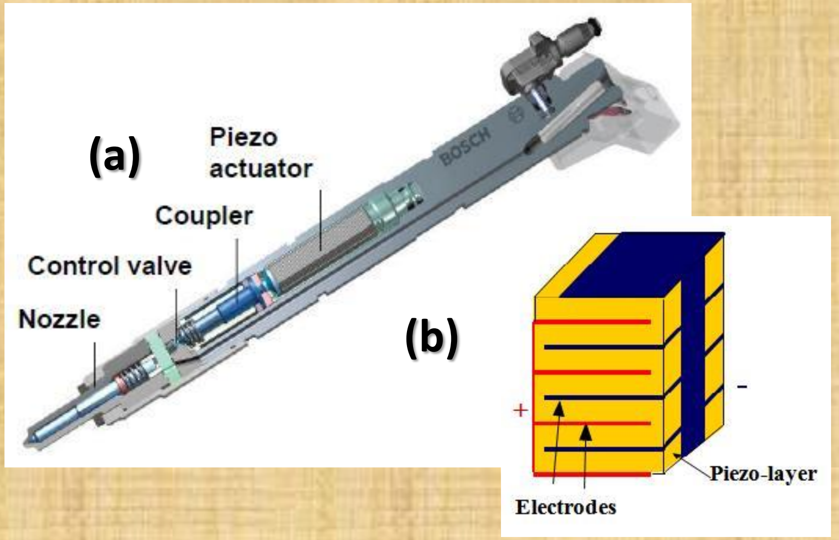


APPLIED PHYSICS LETTERS **102**, 201118 (2013)

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*

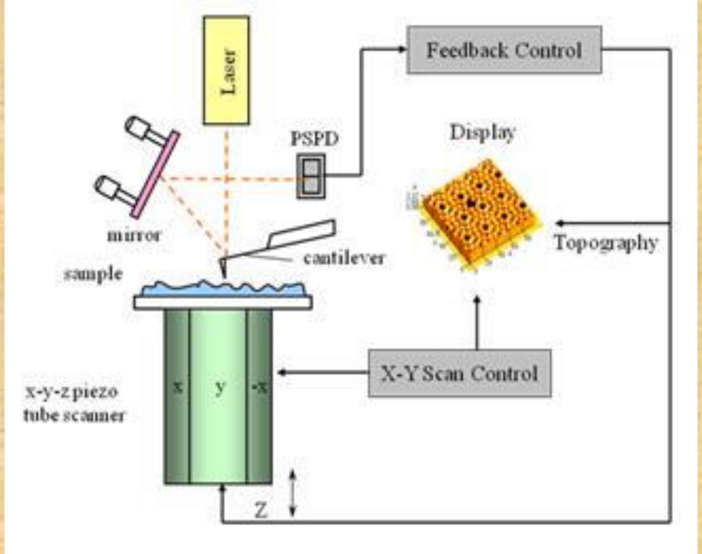
Applications. Actuators



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

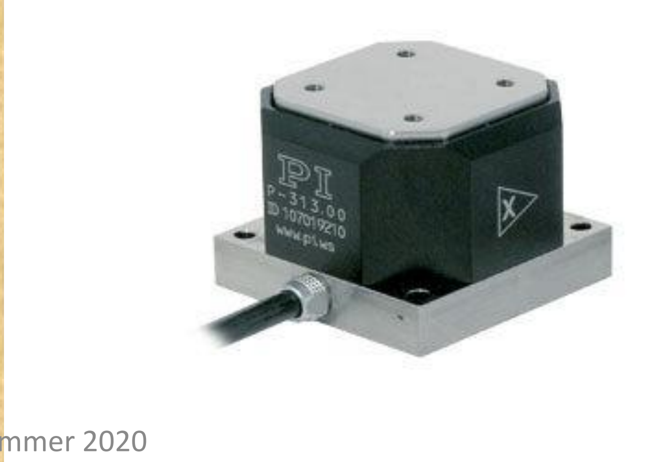
Courtesy Technische Universität Darmstadt

Atomic Force Microscope

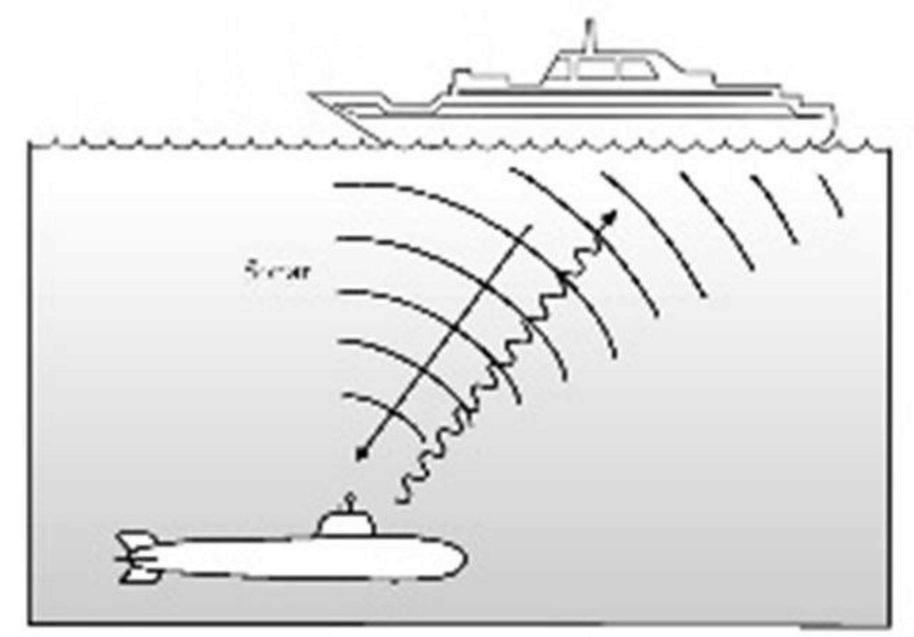


Lead Zirconium Titanate piezo scanner

PI (www.pi.ws)



Applications. Sonars
Military Applications



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

APPLICATIONS:

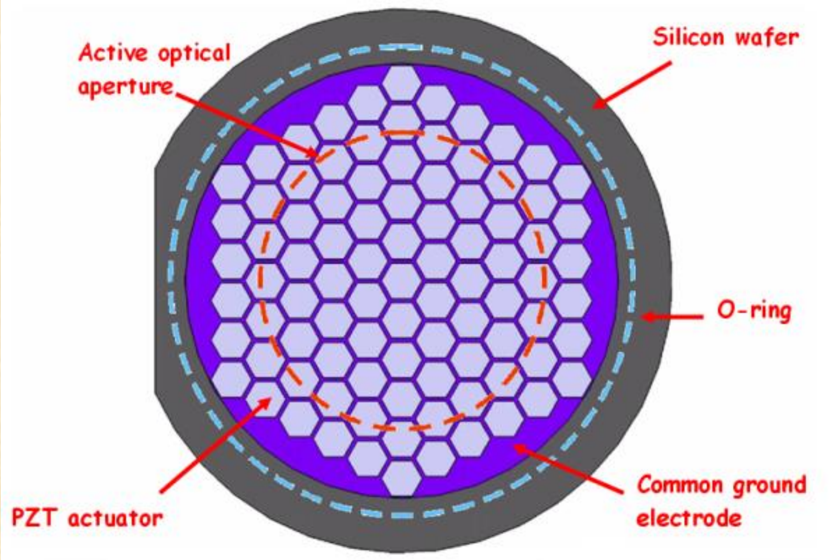
- MINE HUNTING
- WEAPONS SONAR
- COUTERMEASURES
- ACOUSTIC COMMUNICATIONS
- PROJECTOR ARRAYS
- HYDROPHONE ARRAYS
- VIBRATION CONTROL

Applications. Sonars
Civil Applications

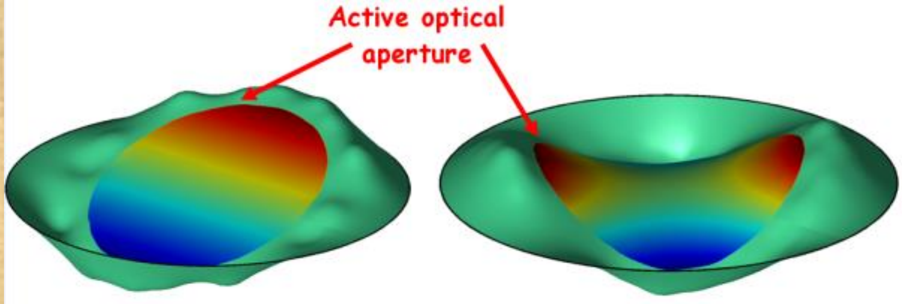
Courtesy FURUNO

Fish Finder

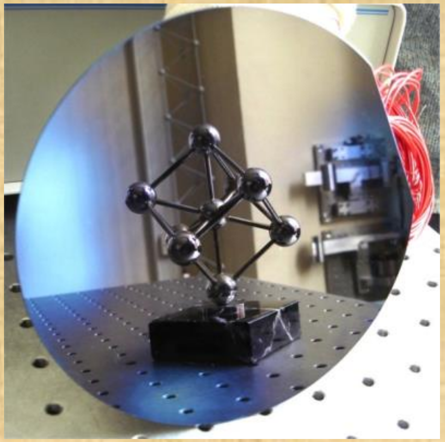
Applications. Adaptive Optics



PZT – Lead Zirconium Titanate $Pb[Zr_xTi_{1-x}]O_3$



Soldered control and mass wires

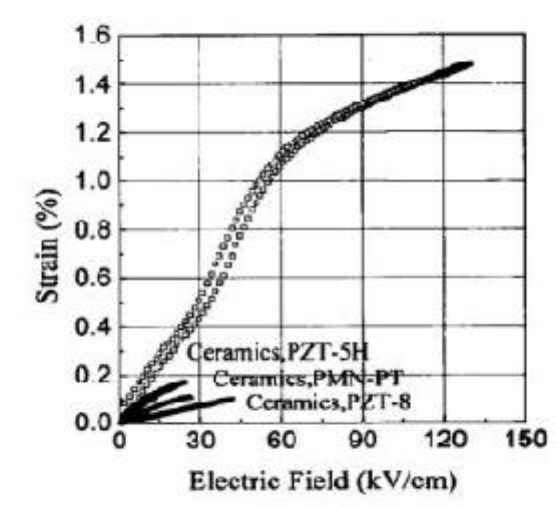


Reflecting surface

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