

Ferroelectrics. Disordered Ferroelectrics.

Eugene V. Colla

Physics 403 Summer 2022



Outline

- **Ferroelectricity**
 - **Main properties**
 - **History. Discovery. Materials**
 - **Disordered Ferroelectrics Relaxors**
 - **Applications**

Ferroelectricity. Definition.

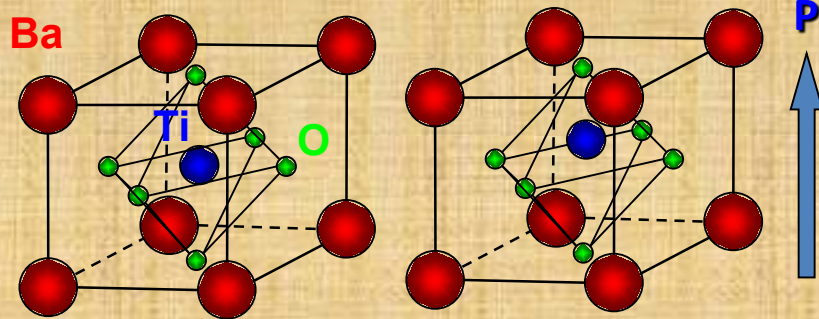
- **Ferroelectric Materials.** A ferroelectric material is a material that exhibits, over some range of temperature, a **spontaneous electric polarization** that can be reversed or reoriented by application of an electric field.

An American National Standard
IEEE Standard Definitions of
Primary Ferroelectric Terms

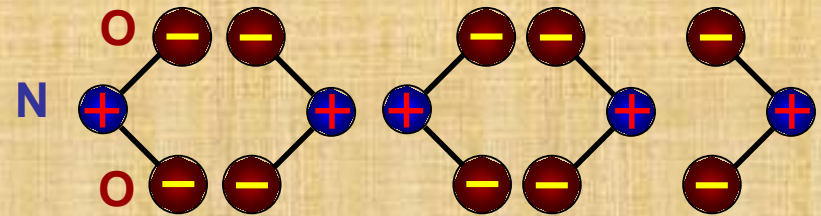
Ferroelectricity: Two classes of ferroelectrics

Order-Disorder

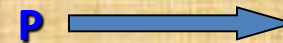
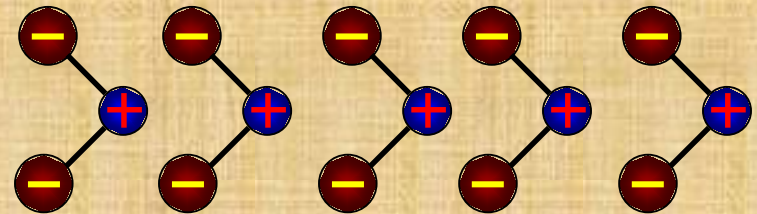
Displacement type



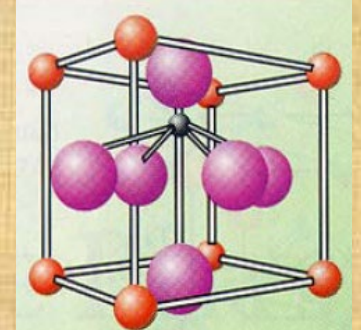
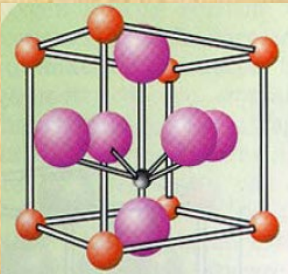
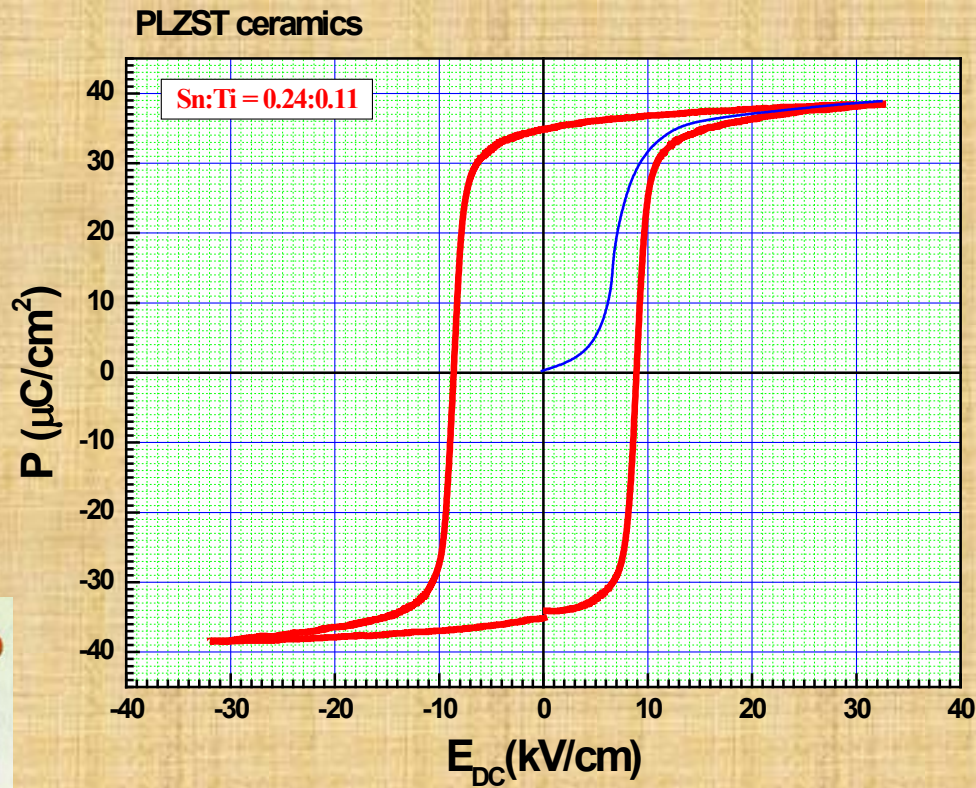
disorder



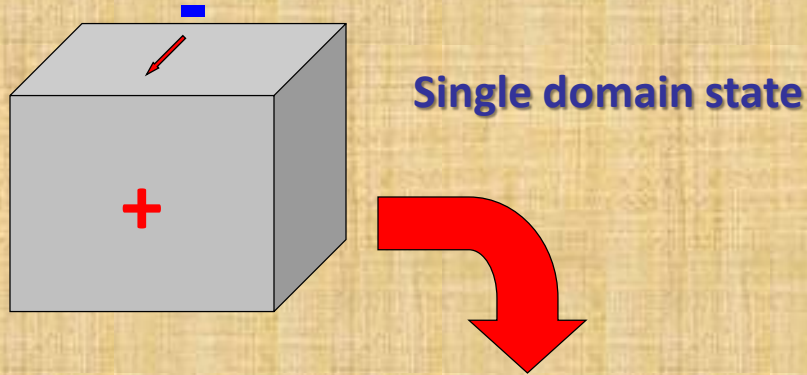
order



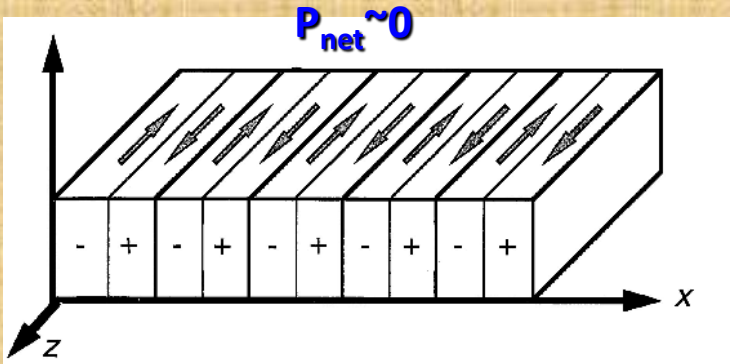
Ferroelectricity: Polarization reversible. (P-E hysteresis)



Ferroelectricity: Domains

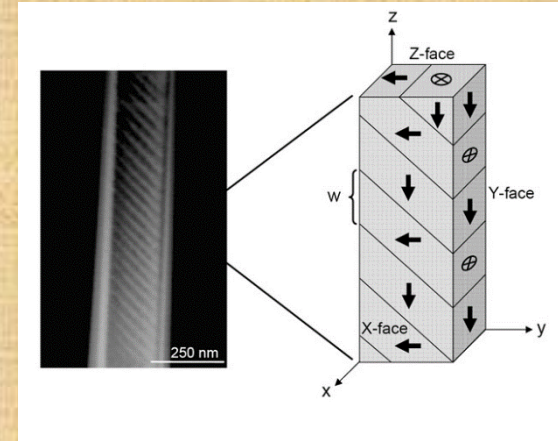


Multi domain state



180° domain pattern

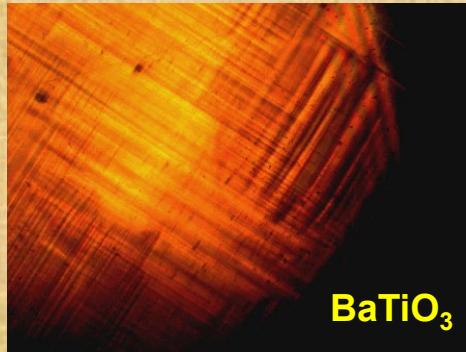
Y Lu et al. Science 1997;276:2004-2006



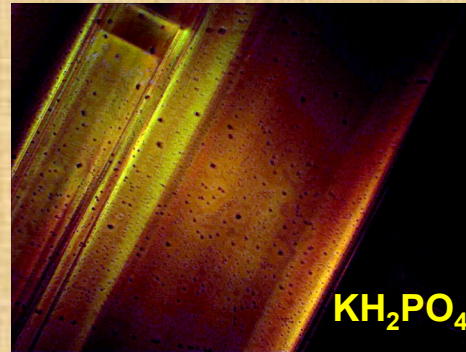
90° domains

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

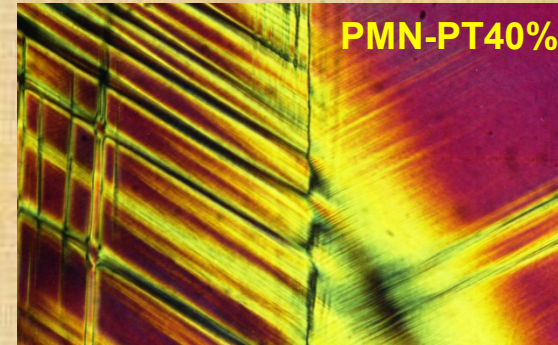
Ferroelectricity: Domains



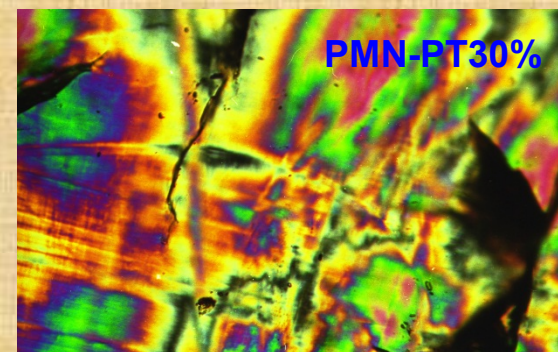
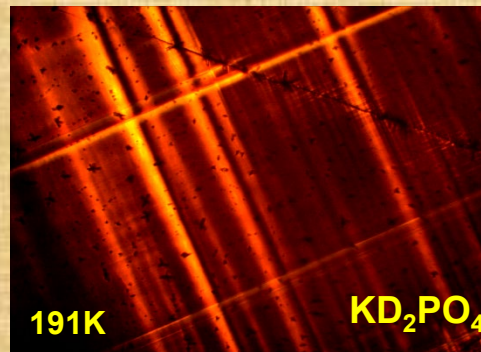
Courtesy of Benjamin Vega-Westhoff and Scott Scharfenberg, P403, Fall2009



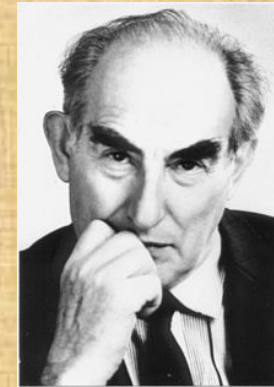
Courtesy of Allison Pohl, P403, Fall2009



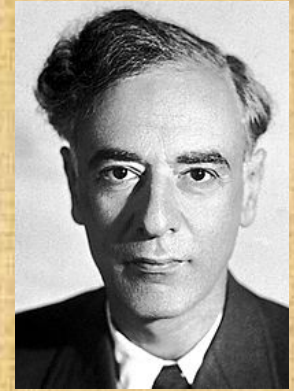
Crystal from Forschungsinstitut für mineralische und metallische Werkstoffe -Edelsteine/Edelmetalle



Ferroelectricity: Landau-Ginzburg phenomenological theory



Vitaly Ginzburg
1916-2009



Lev Landau
1908-1968

Free energy

Order parameter (polarization)

$$F_P = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \dots - EP$$

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

Electric field

Ignoring higher terms we can get the linear solution:

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

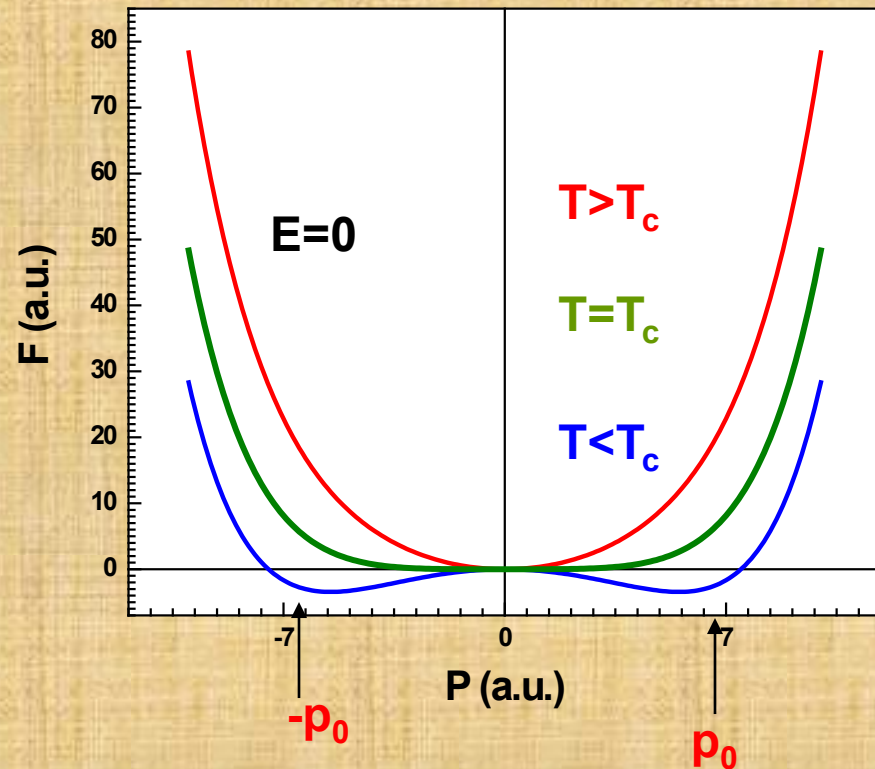
Assuming linear dependence of **a** on temperature we will have:

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

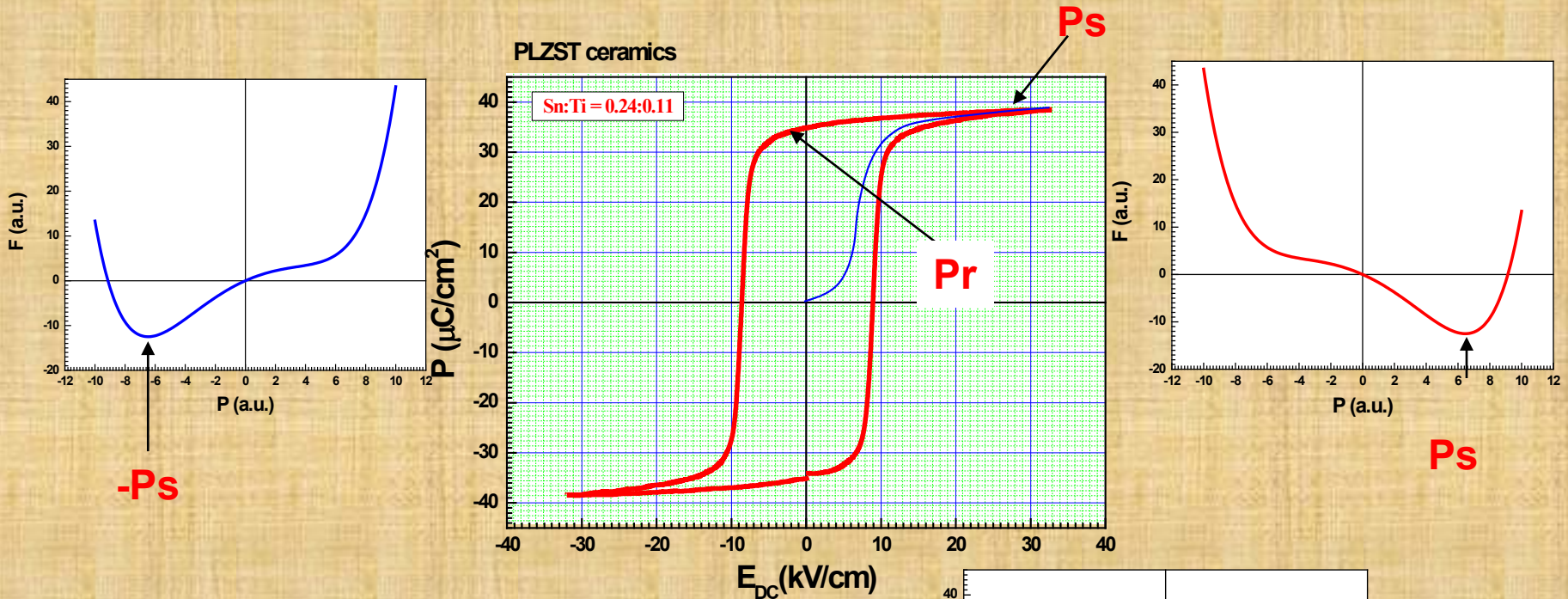
$$\chi = \frac{C}{(T - T_c)}$$

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

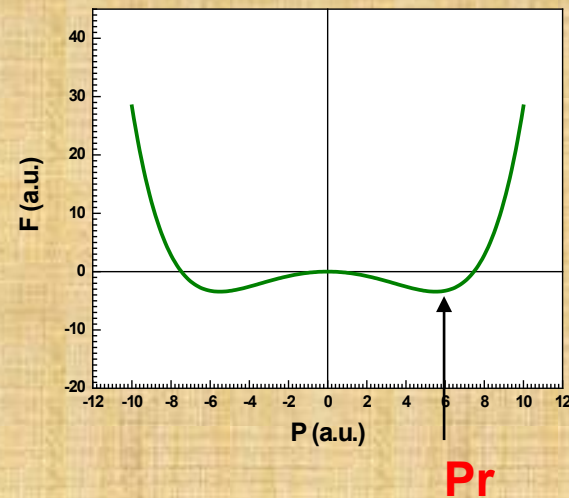


Ferroelectricity: Landau-Ginzburg phenomenological theory



Including EP term can illustrate the P-E hysteretic behavior

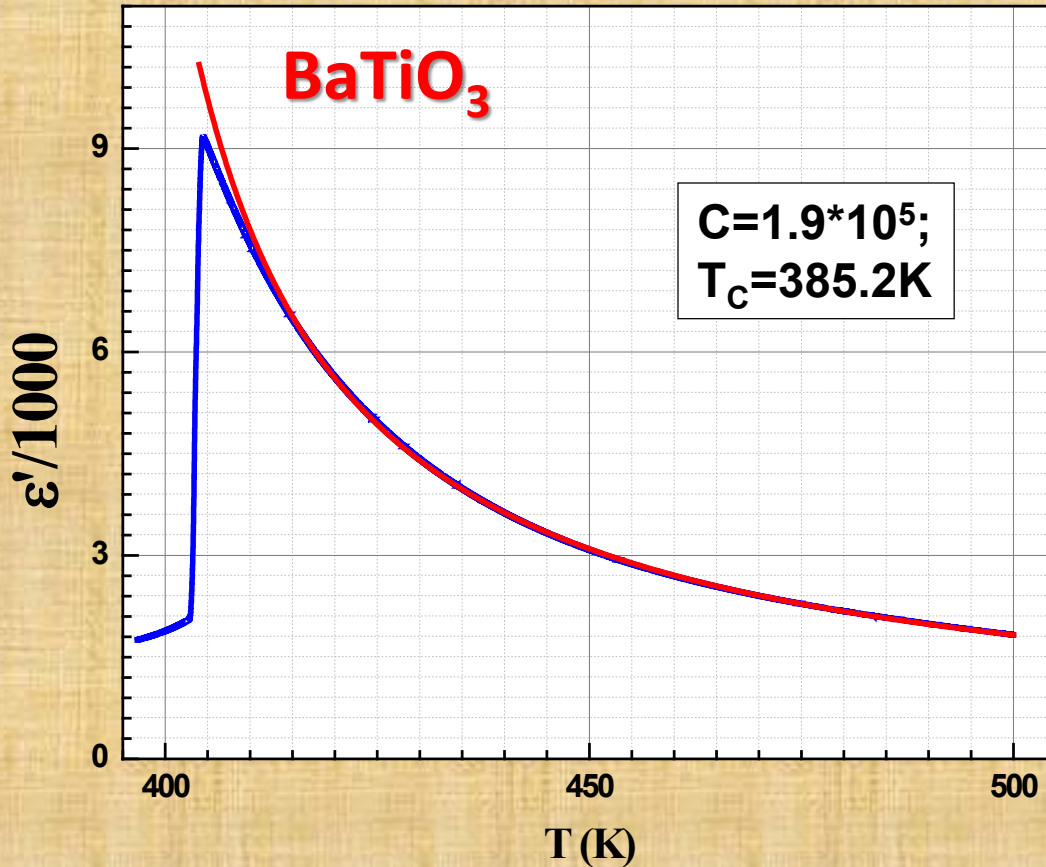
$$F_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots - EP$$



Ferroelectricity: Susceptibility

$$\vec{P} = \epsilon_0 \chi \vec{E} \quad \vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \vec{E} + \epsilon_0 \chi \vec{E} = \epsilon_0 (1 + \chi) \vec{E} = \epsilon_0 \epsilon \vec{E}$$

For ferroelectrics $\epsilon \gg 1$ and $\epsilon \approx \chi$



Curie-Weiss law:

$$\epsilon = \frac{C}{(T - T_{CW})} + \epsilon_{00}$$

Ferroelectricity: Discovery

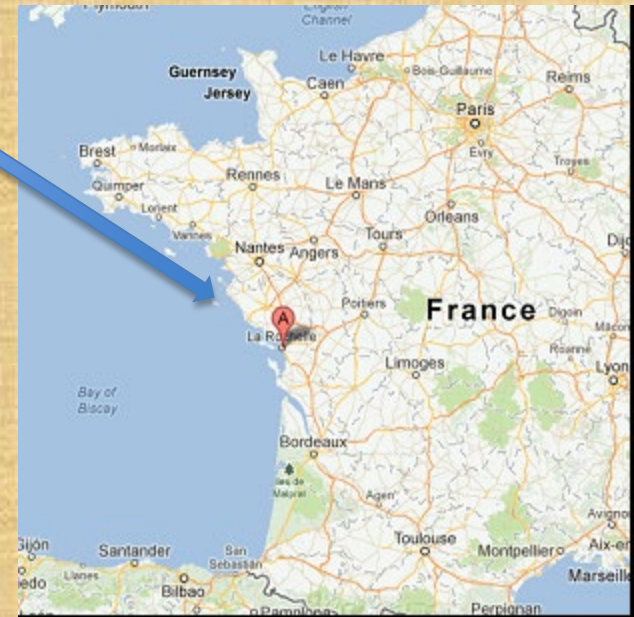
Rochelle Salt $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$



Elie Seignette

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

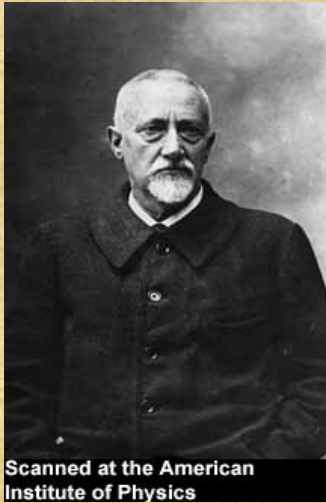
Rochelle Salt originates from French city of La Rochelle where it was produced by ***Pierre Seignette*** another name of this material is Seignette salt



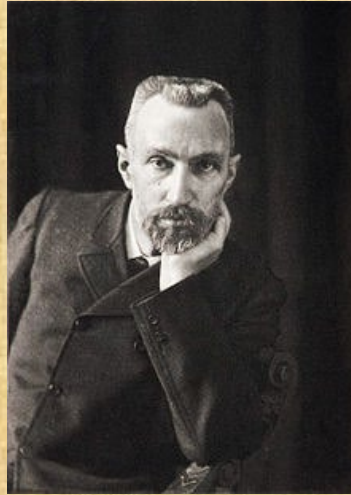
Rochelle Salt was used in medicine and food industry

Ferroelectricity: Discovery

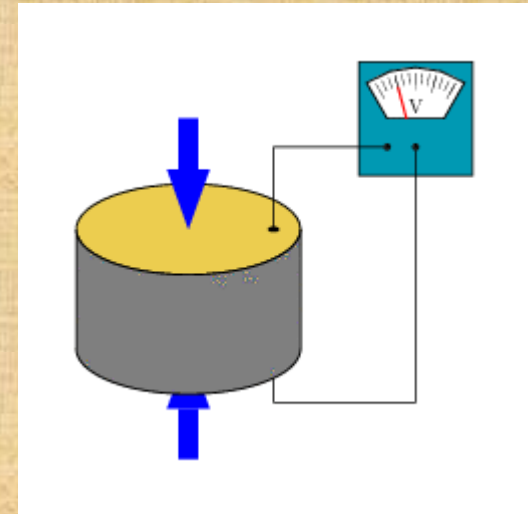
Rochelle Salt $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$



Paul-Jacques Curie
1856 – 1941



Pierre Curie
1859-1906



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

Ferroelectricity: Discovery

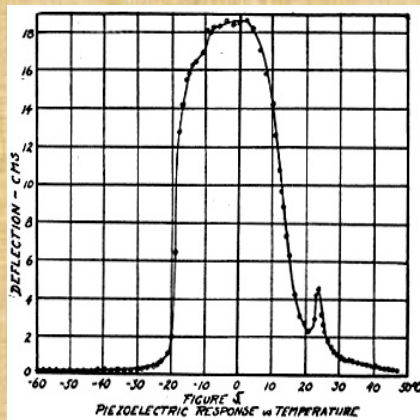
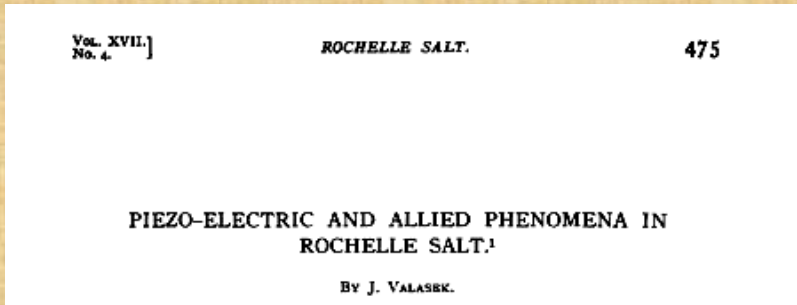


Fig3. Piezoelectric response as a function of temperature [2]

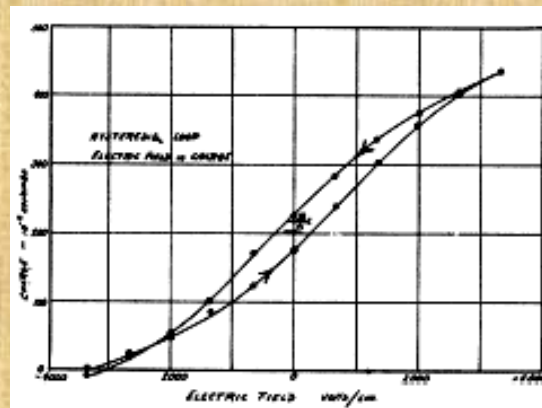


Fig.1. The first published hysteresis loop [1]

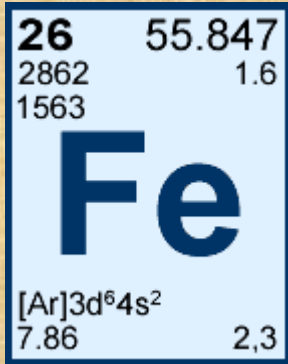


Joseph Valasek (1897-1993)
University of Minnesota

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

Rochelle Salt $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$

Ferroelectricity. Terminology.



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

Fe has no relation to the phenomenon of *ferroelectricity* but because of a lot of common features of *ferroelectric* phase transition to *ferromagnetic* the “new” class of dielectrics was named as *ferroelectrics*.

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)

Physics 403 Spring 2022

Materials. KDP

KDP (KH_2PO_4) - potassium dihydrophosphate

1935

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



Georg Busch
1908-2000



Paul Scherrer
1890-1969

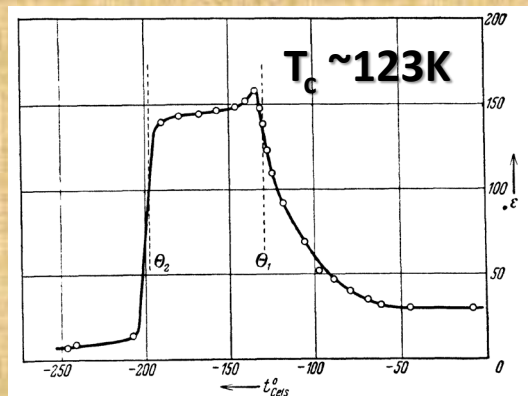


Fig. 1. Temperaturverlauf der Dielektrizitätskonstanten ϵ_{33} an KH_2PO_4 .



DIE NATURWISSENSCHAFTEN

23. Jahrgang

25. Oktober 1935

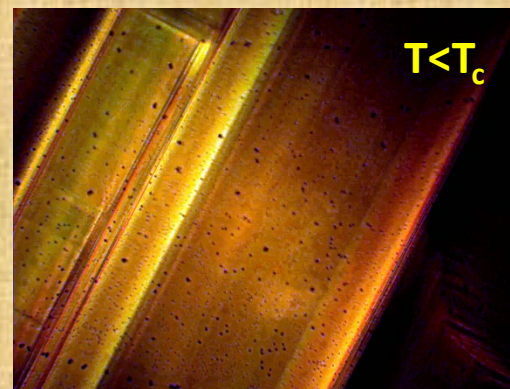
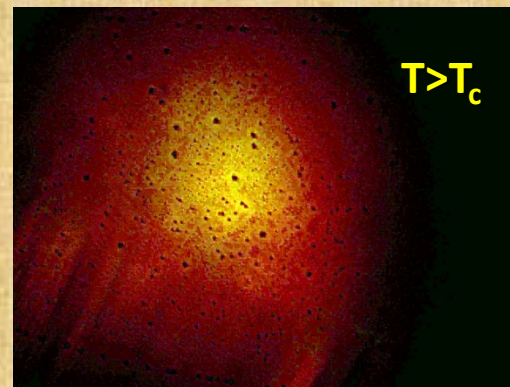
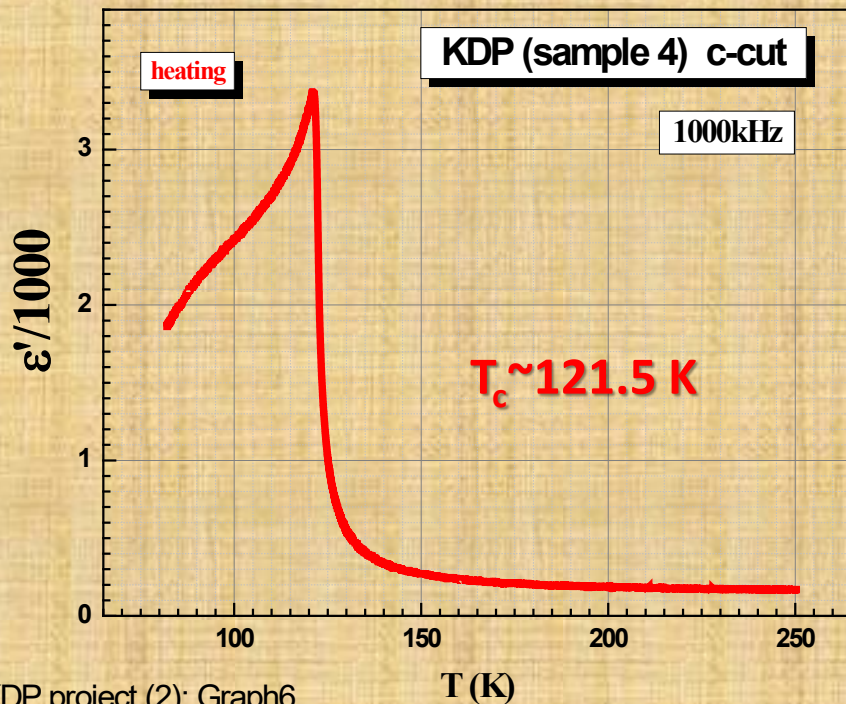
Heft 43

Eine neue seignette-elektrische Substanz.

Materials. KDP

KDP (KH_2PO_4) - potassium dihydrophosphate

$T_c \sim 121-123 \text{ K}$

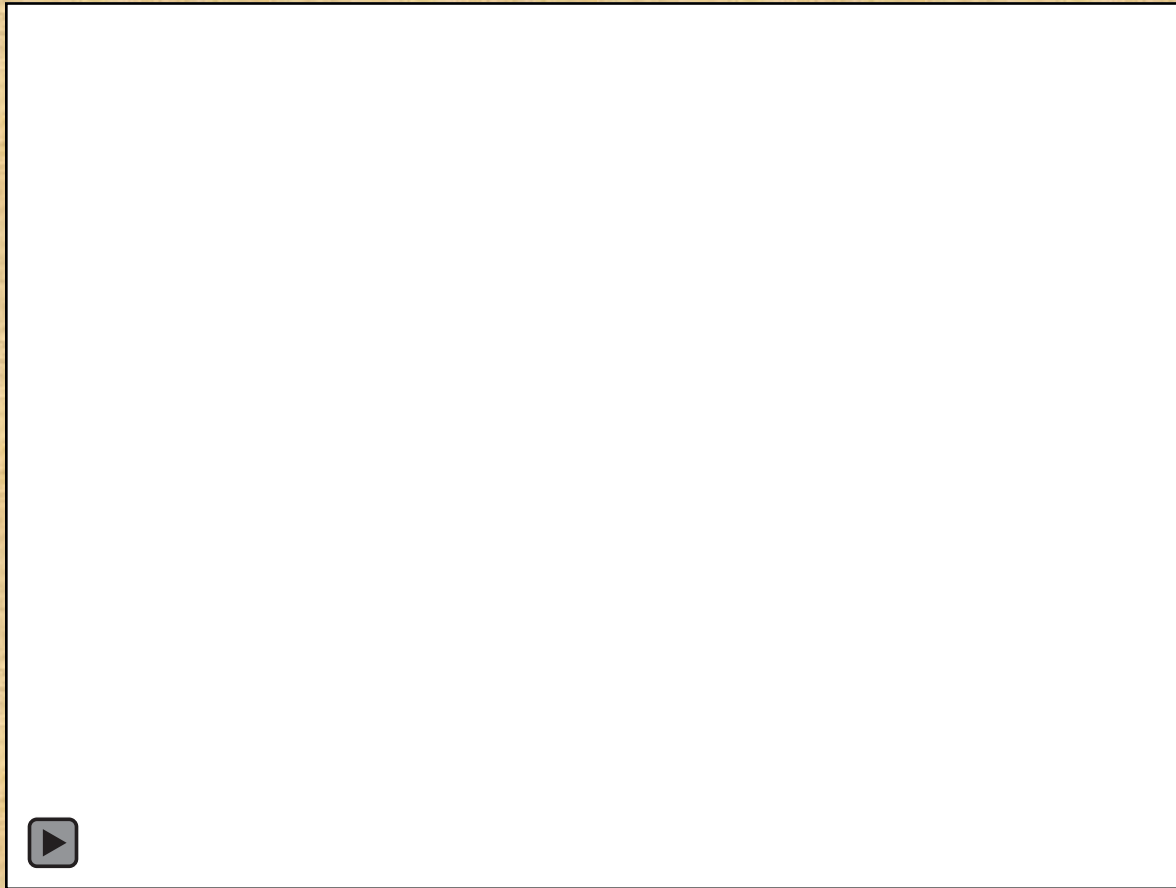


Courtesy of Tim S. Thorp, Zhangji Zhao, Physics 403, Spring 2013

Courtesy of Alison Pohl, Physics 403, Spring 2009

Materials. DKDP

DKDP (KD_2PO_4) – deuterated potassium dihydrophosphate $T_m = 230\text{K}$



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))

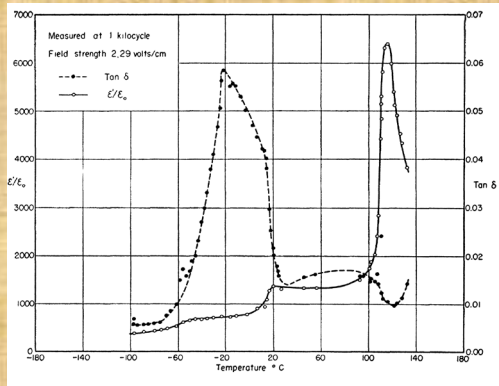
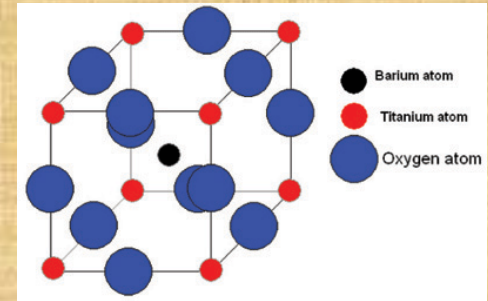


FIG. 6. Dielectric constant and loss of barium titanate ceramic.

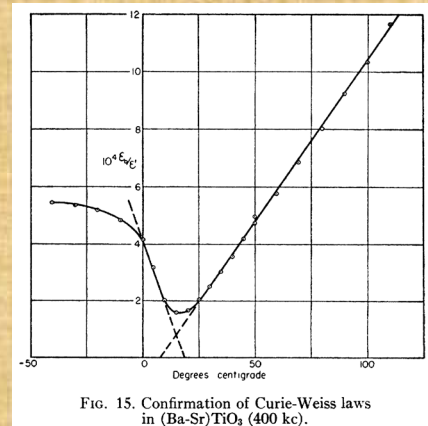
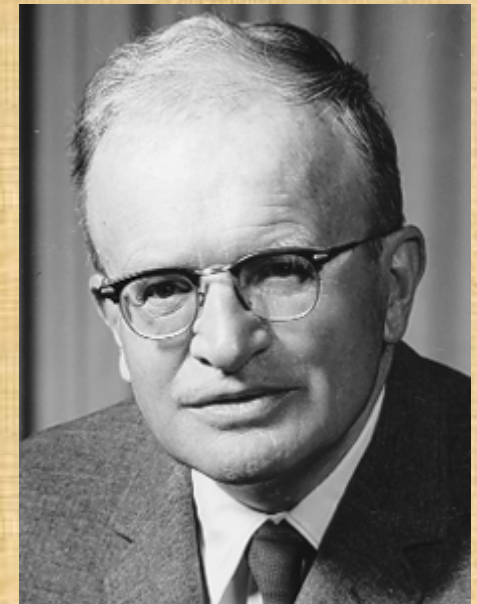
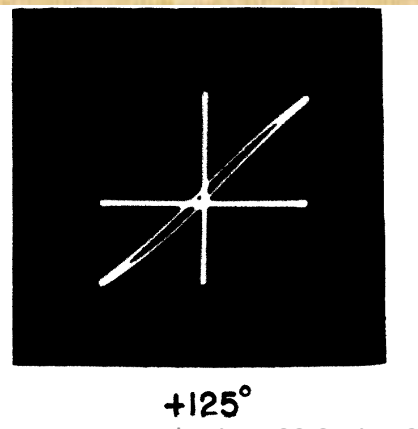
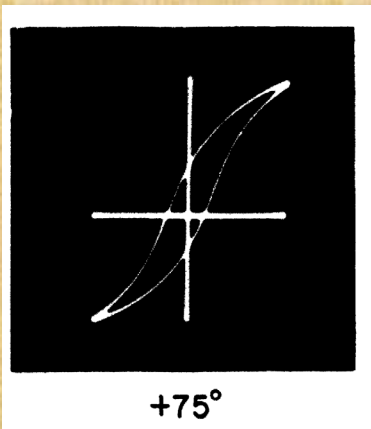


FIG. 15. Confirmation of Curie-Weiss laws in $(\text{Ba-Sr})\text{TiO}_3$ (400 kc).

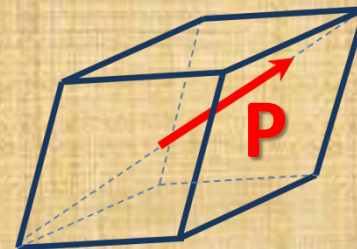
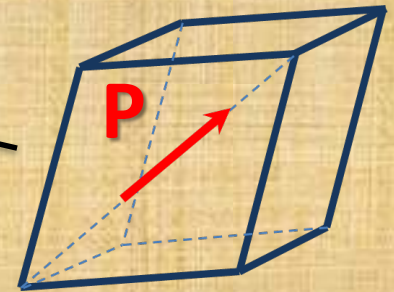
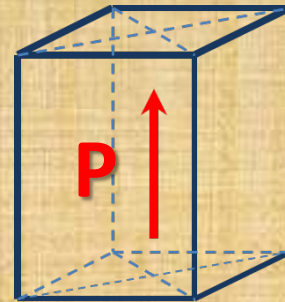
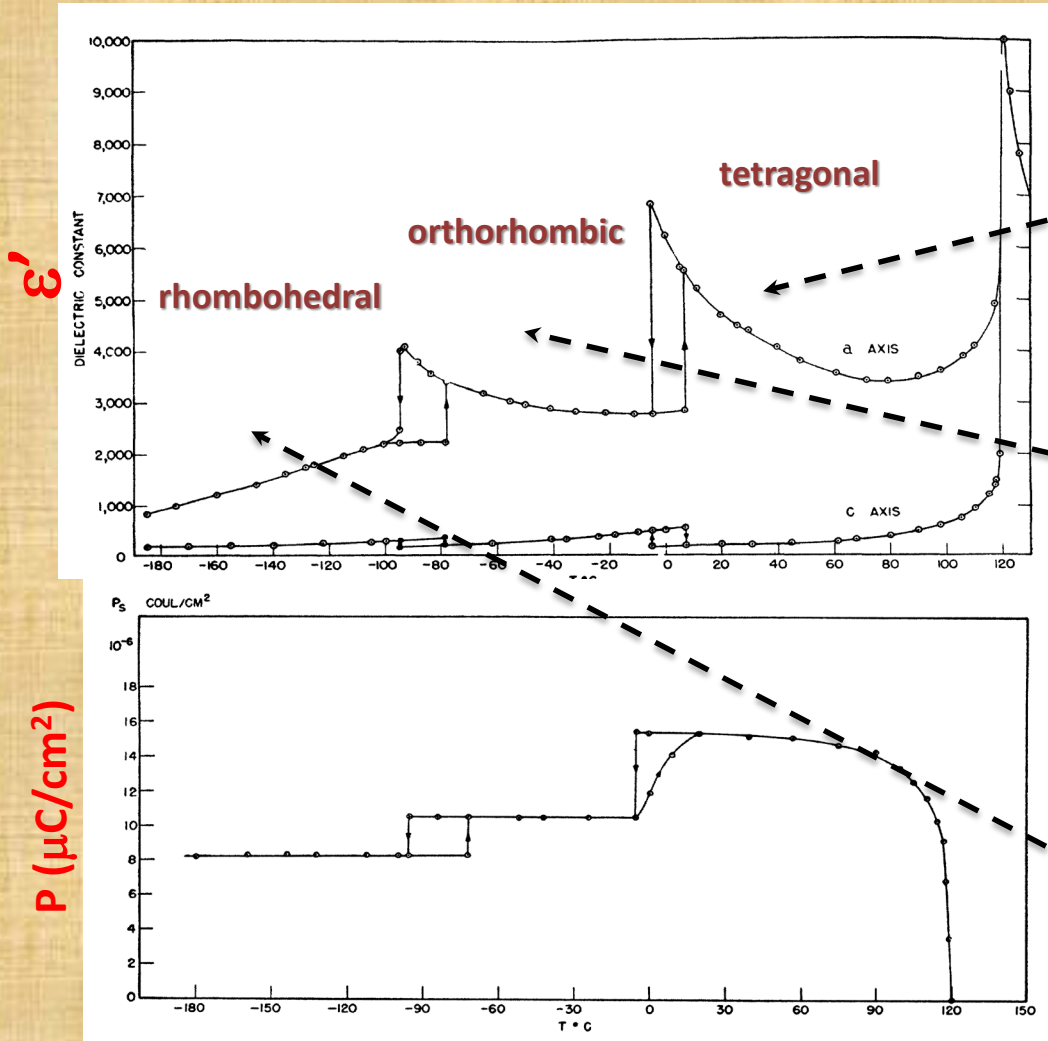
$T_c \sim 400\text{K}$



Arthur R. von Hippel
1898-2003



Materials. Barium Titanate.



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

Materials. BaTiO₃. Domains.

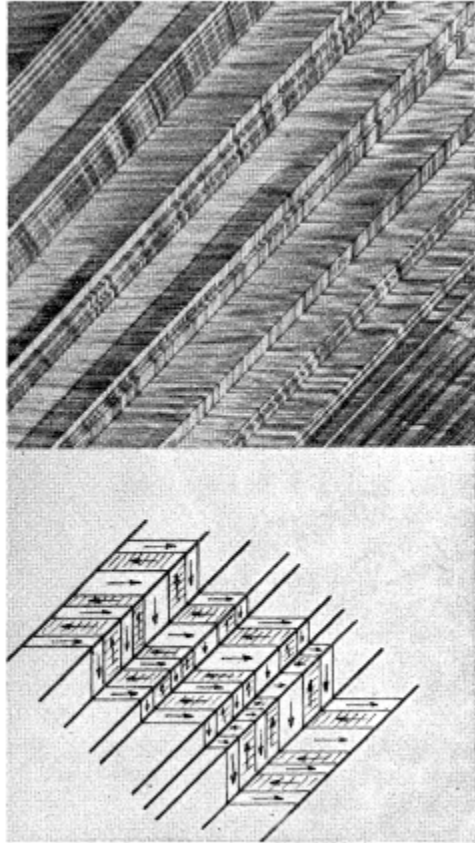
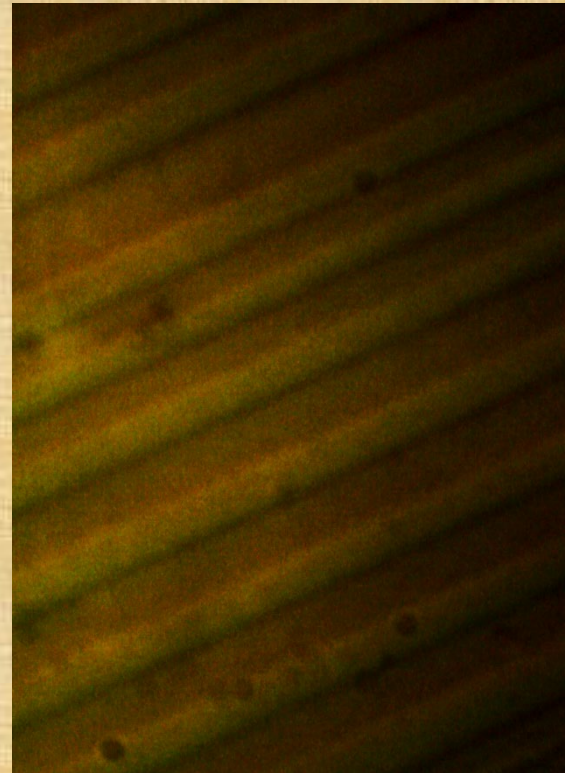


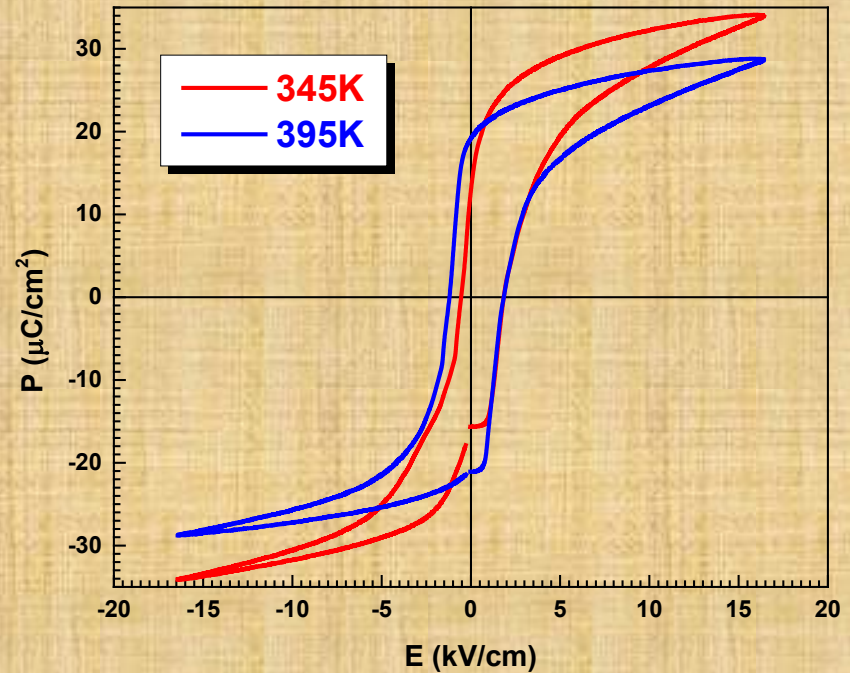
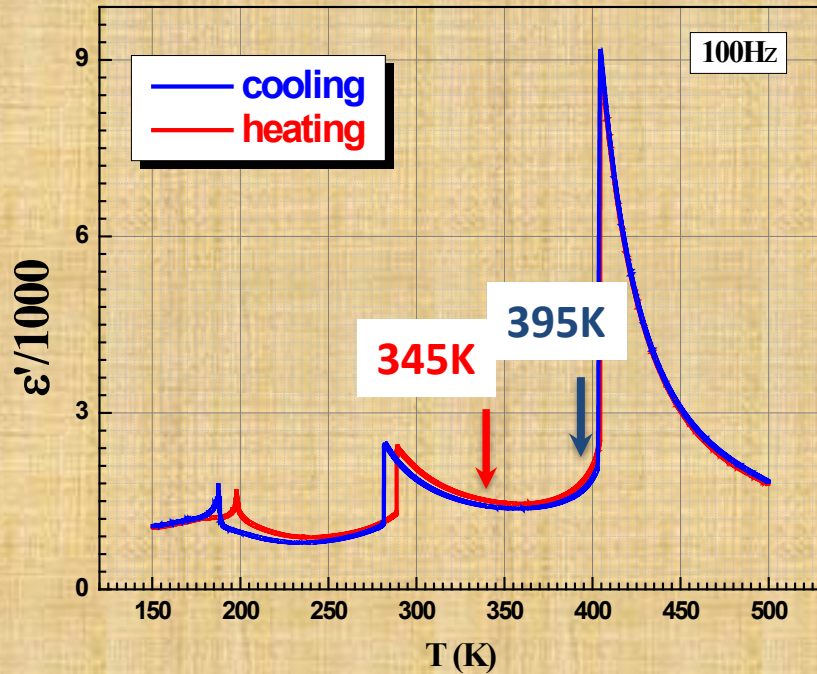
FIG. 4. Surface of an a -domain crystal showing 90° walls and antiparallel domains.



Physics 403 Lab, August 2011

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

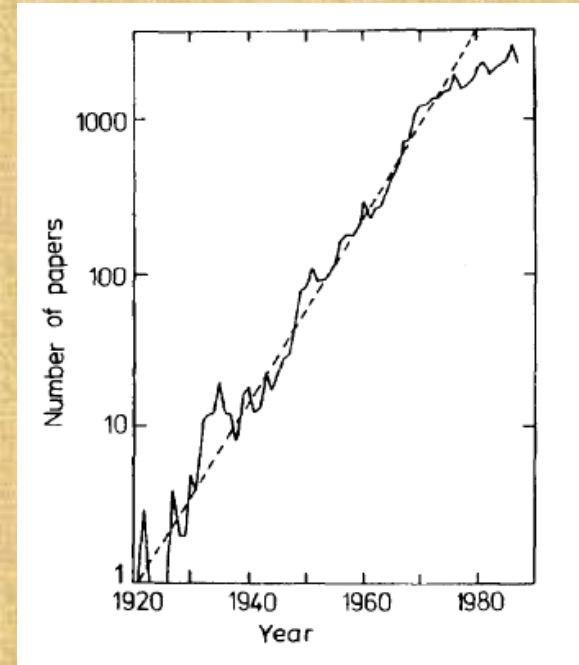
Materials. BaTiO₃. P-E hysteresis.



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

Ferroelectricity: Typical ferroelectric materials

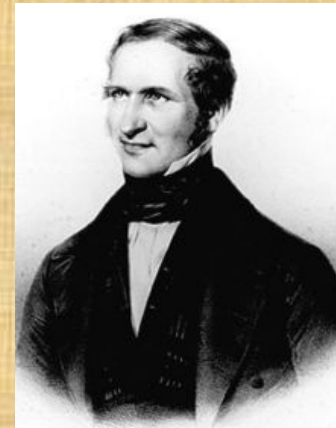
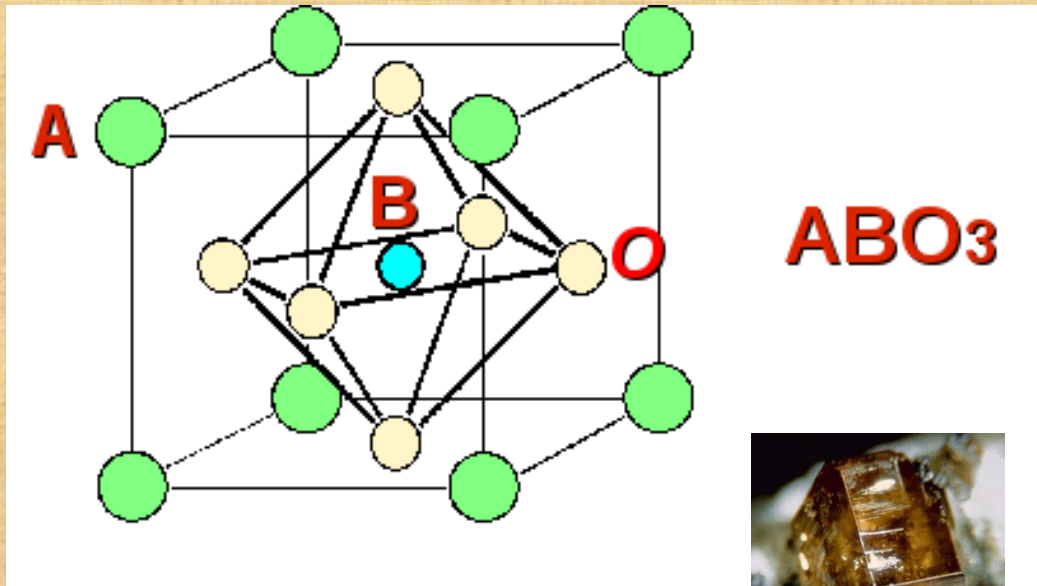
		T_c (K)	P_s ($\mu\text{C}/\text{cm}^2$)
KDP type	KH_2PO_4	123	4.75
	KD_2PO_4	213	4.83
	RbH_2PO_4	147	5.6
Perovskites	BaTiO_3	408	26
	KNbO_3	708	30
	PbTiO_3	765	>50
	LiTiO_3	938	50
	LiNbO_3	1480	71



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

Perovskite Structure

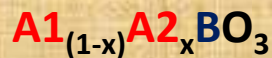
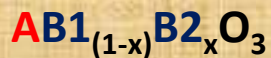
Perovskite is a mineral CaTiO_3 . The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist Lev Perovski.



Gustav Rose
1798-1873



Lev Perovski
1792-1856



typical complex oxides with
perovskite structure

New Perovskite Materials - Relaxors

B-site complex	Lead magnesium niobate (PMN)	$\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$
	Lead scandium tantalate (PST)	$\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$
	Lead zinc niobate (PZN)	$\text{PbZn}_{1/2}\text{Nb}_{1/2}\text{O}_3$
	Lead indium niobate (PIN)	$\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$
A-site complex	Lead lanthanum titanate (PLT)	$\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$
Both sites complex	Lead lanthanum zirconate titanate (PLZT)	$\text{Pb}_{1-x}\text{La}_x\text{Zr}_y\text{Ti}_{1-y}\text{O}_3$
	Potassium lead zinc niobate	$\text{K}_{1/3}\text{Pb}_{2/3}\text{Zn}_{2/9}\text{Nb}_{7/9}\text{O}_3$

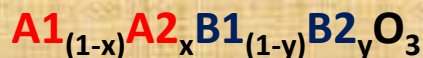
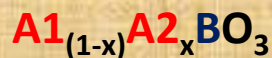
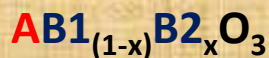


L. Eric Cross¹
(1923-2016)



Smolenskii G.A.²
(1910 – 1986)

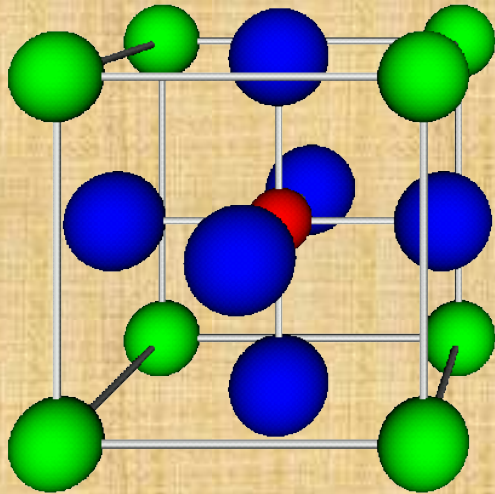
1. Pennsylvania State University, USA
2. A.F. Ioffe Institute, USSR



typical complex oxides with perovskite structure

Relaxors

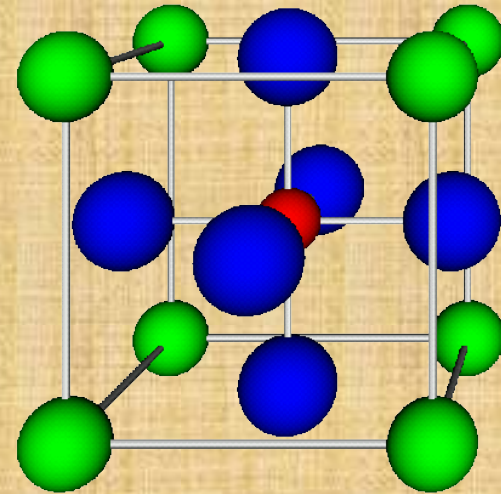
Regular ferroelectric BaTiO_3



$T > T_c$ (cubic)



Relaxor - PMN $\text{Pb}(\text{Mg}_{1/3} \text{Nb}_{2/3})\text{O}_3$

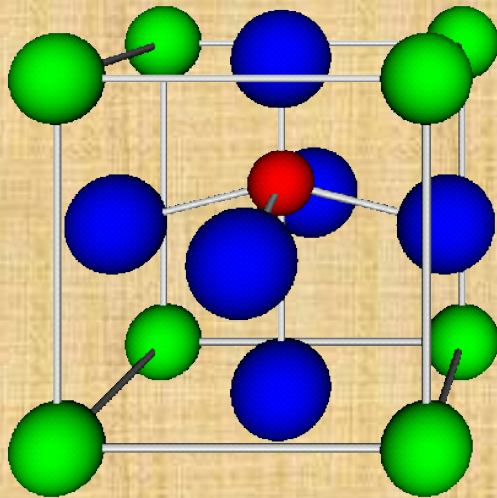


(cubic)



Relaxors

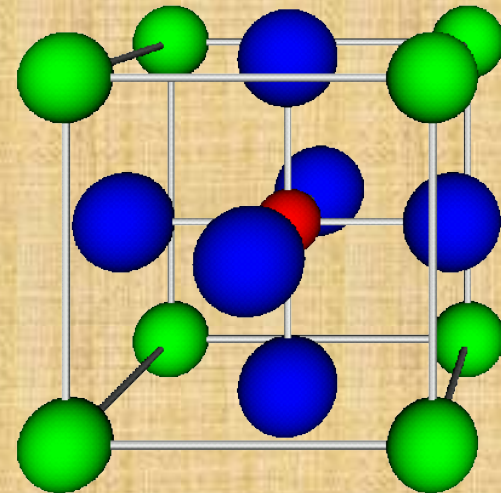
Regular ferroelectric BaTiO_3



$T < T_c$ (tetragonal)



Relaxor - PMN $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

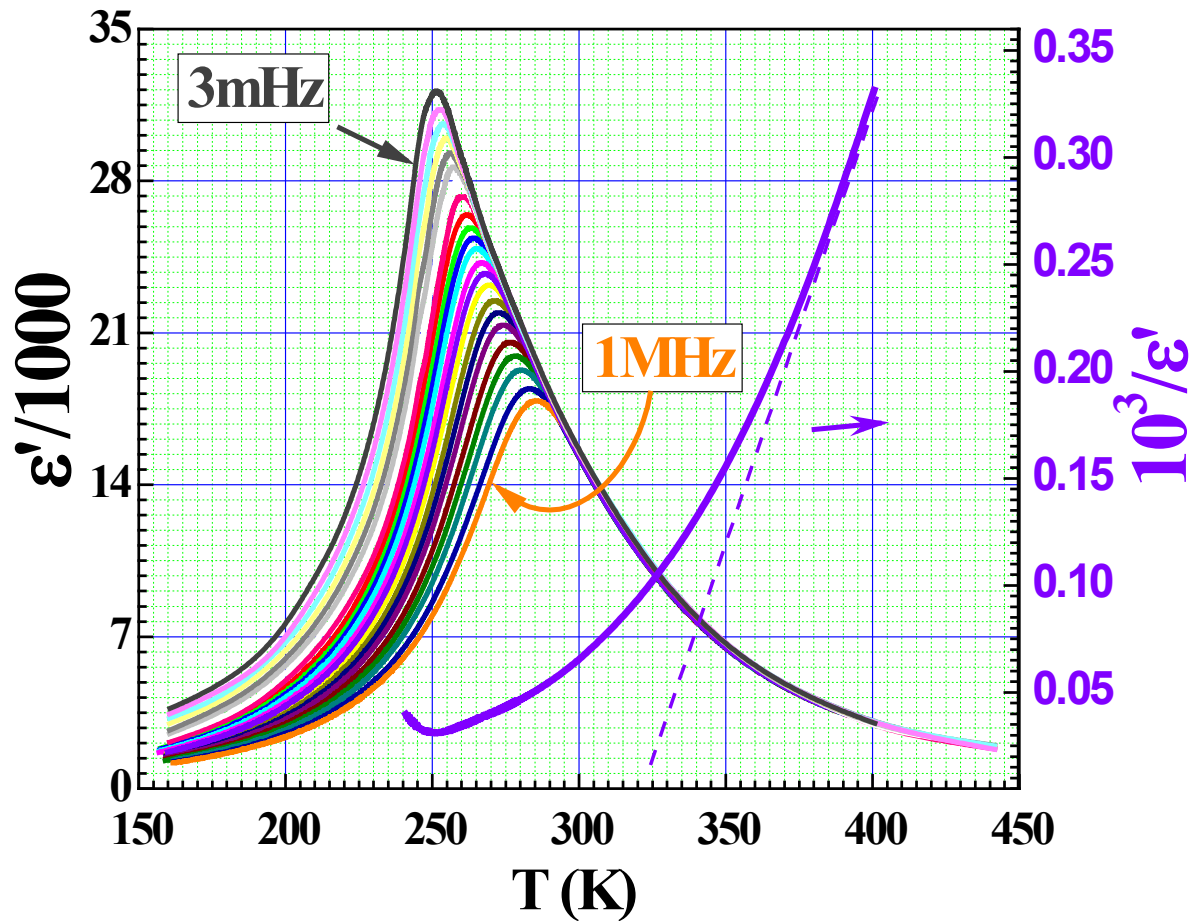


(cubic)



Relaxor. Frequency dispersion

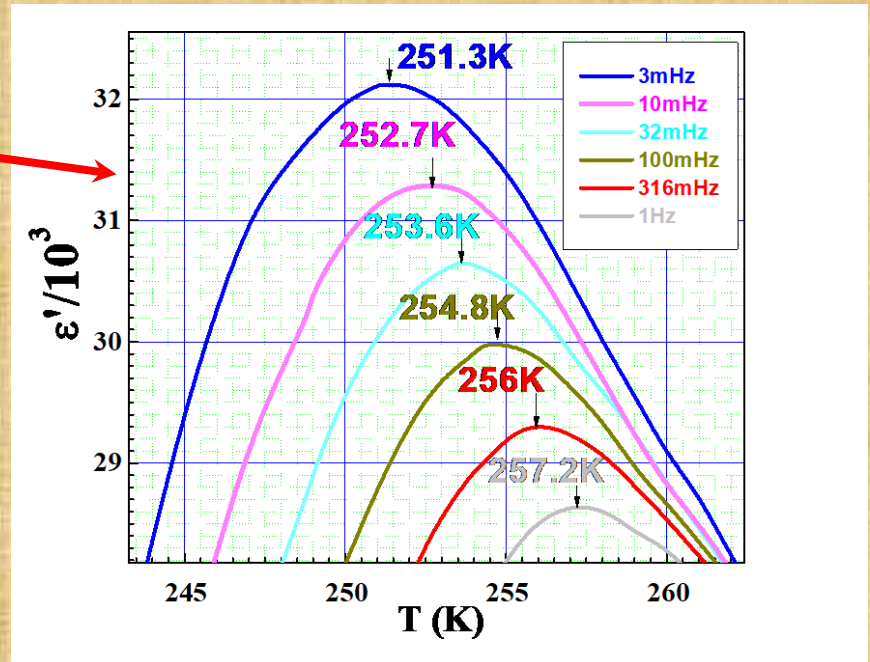
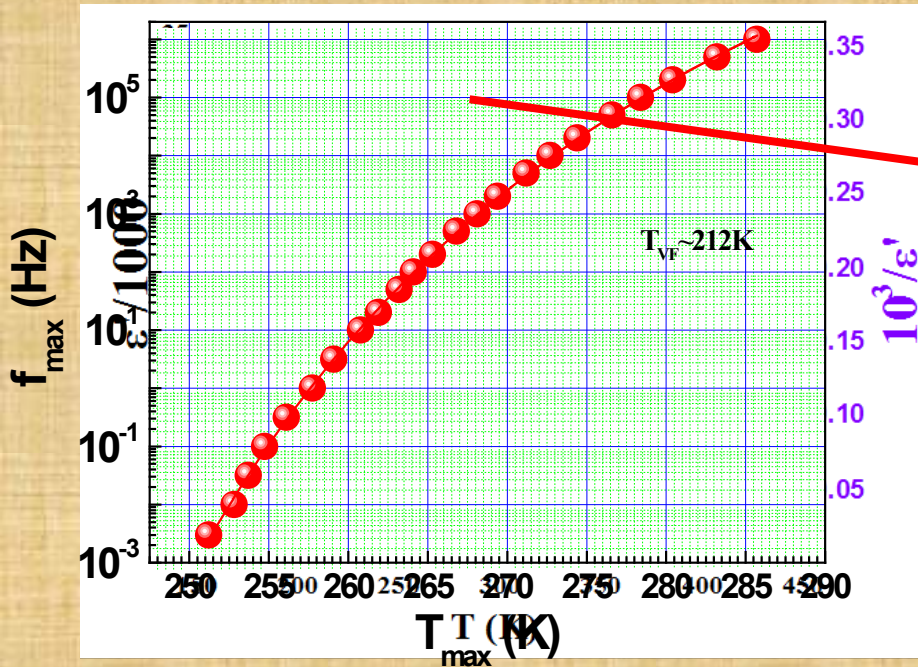
ϵ'_{\max} and T_{\max} depend on the measuring frequency



ϵ' does not follow Curie-Weiss law

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

PMN. Vogel – Fulcher dependence



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

Relaxors. Nanodomains.

PNR – polar nanodomains
COR – chemically ordered regions

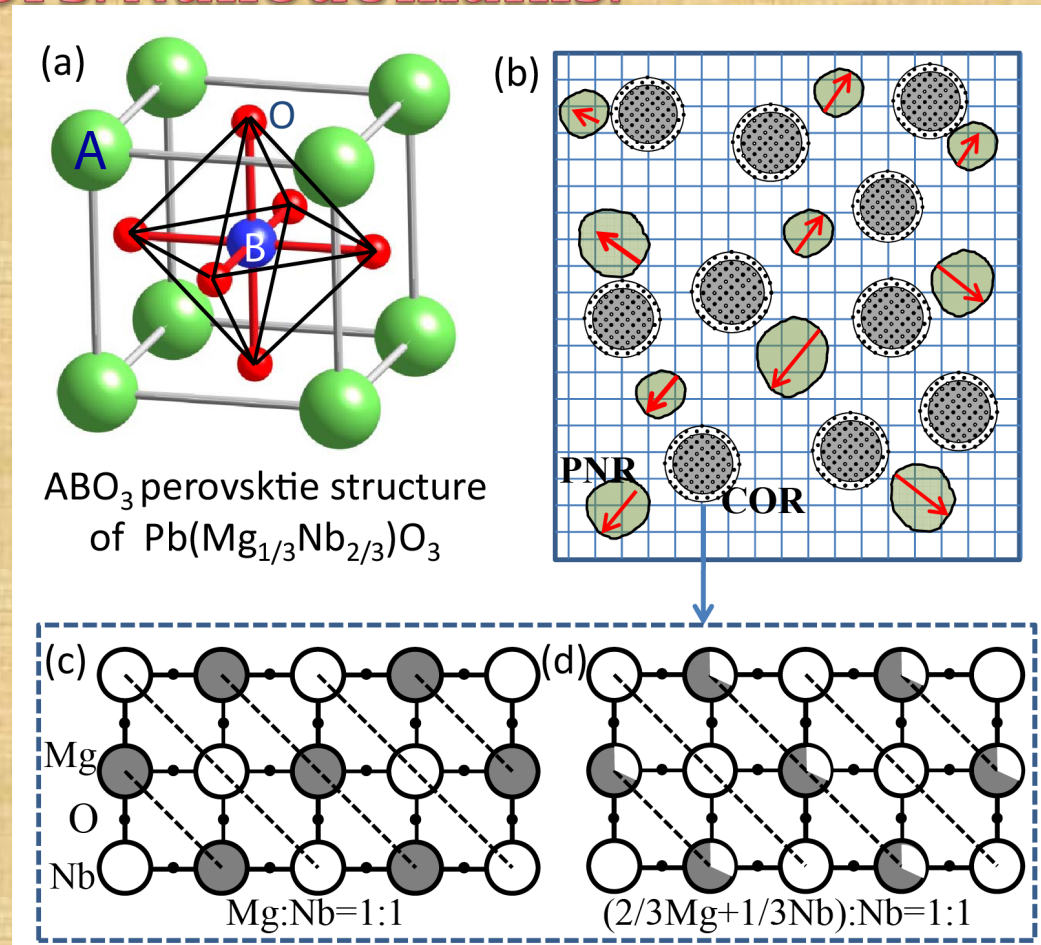
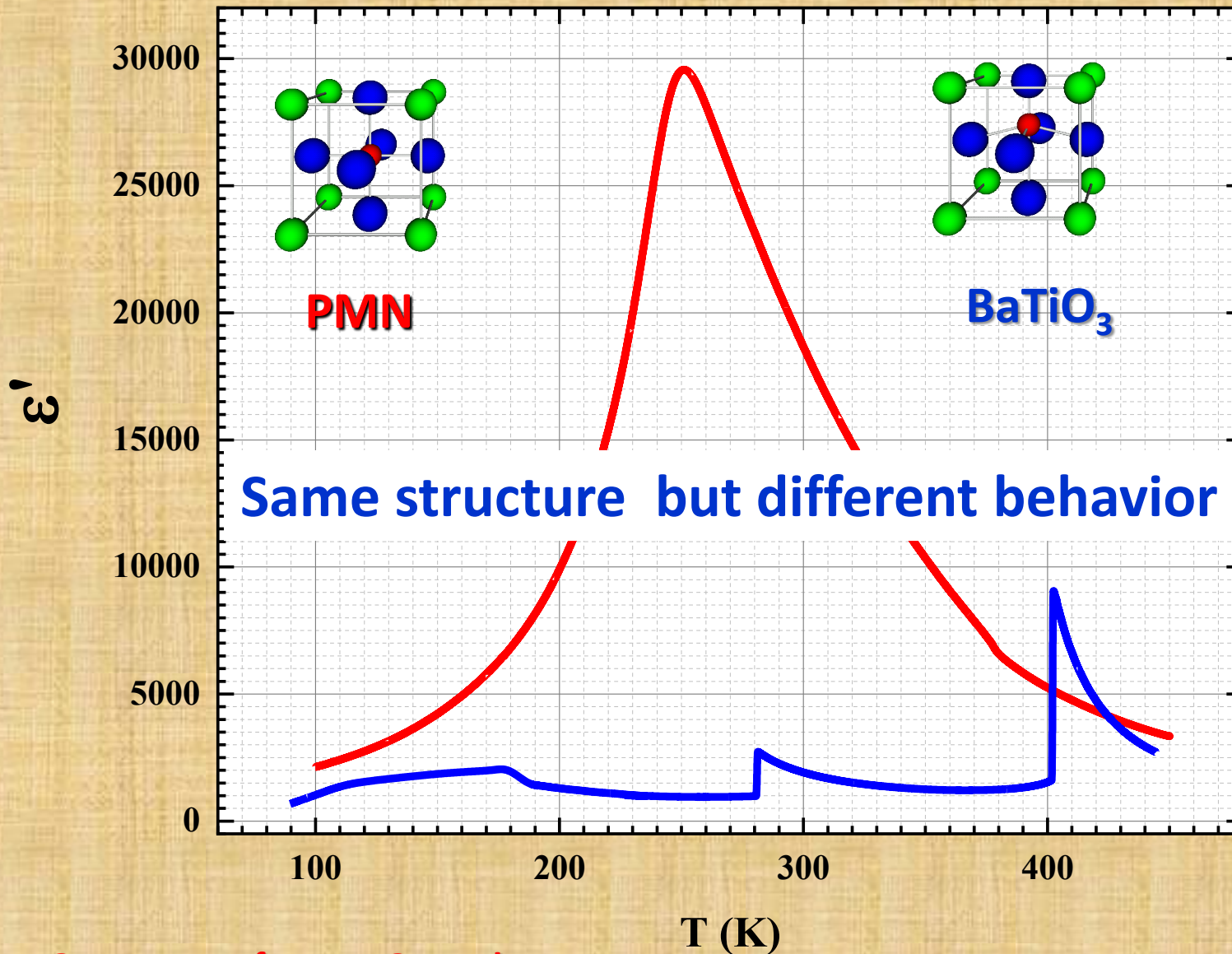


Figure 3.

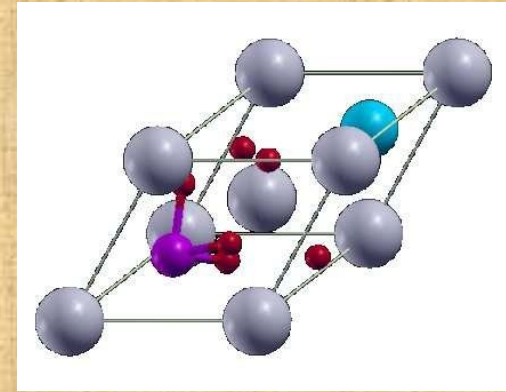
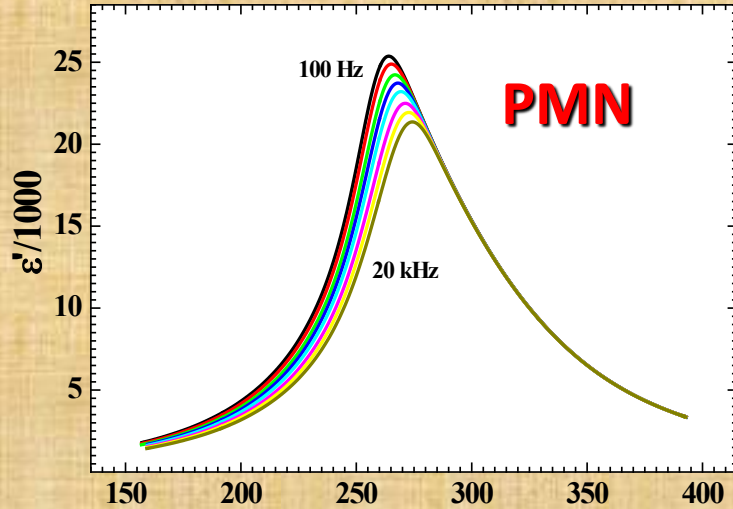
(a) ABO_3 perovskite structure. (b) Model for relaxor structure. PNR and COR represent the polar nano-region and chemically order region, respectively. (c) & (d) show two models of atom arrangement for COR. To maintain the electric neutrality, a Nb-rich layer is required for case (c).

Regular Ferroelectrics - Relaxors

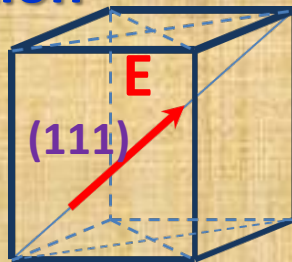


BTO courtesy of James Graessle

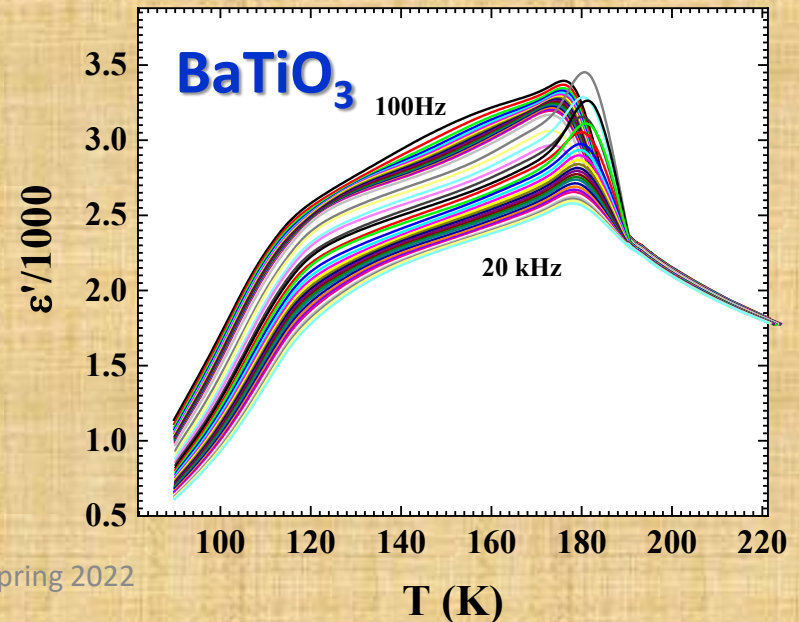
Disorder in Regular Ferroelectrics



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



BaTiO₃ Rhombohedral phase



BTO courtesy of James Graessle

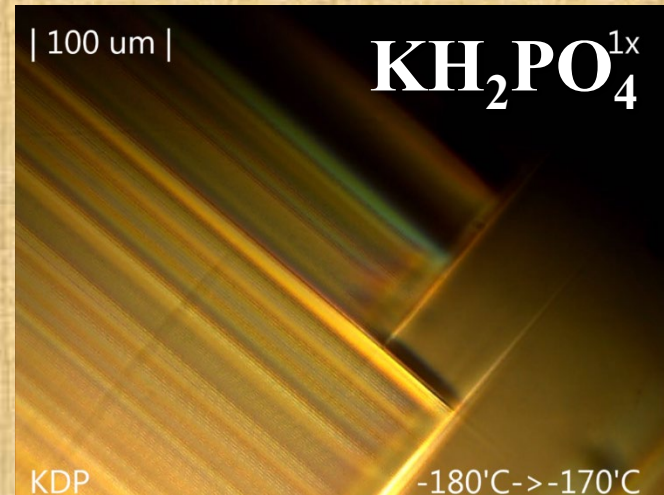
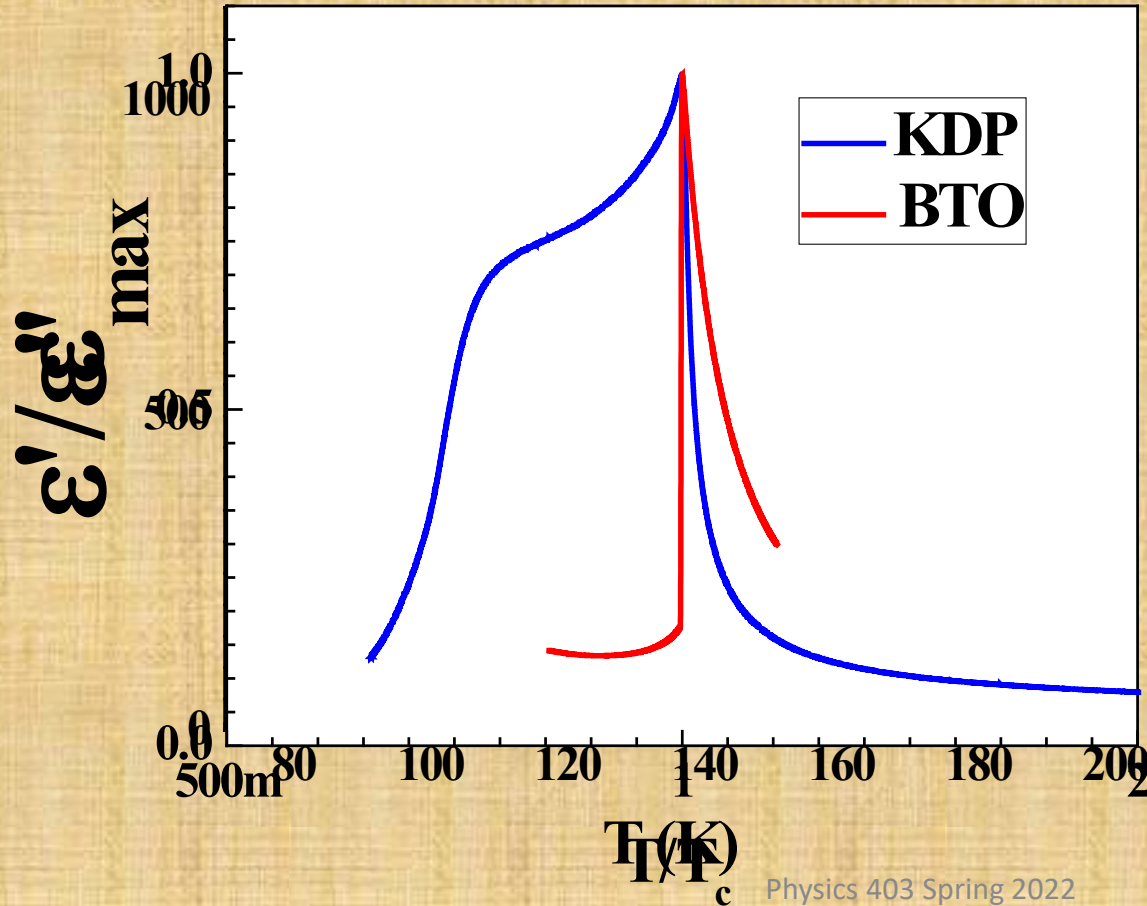
Disorder in Regular Ferroelectrics. KDP family



KDP - $T_c \sim 120$ K

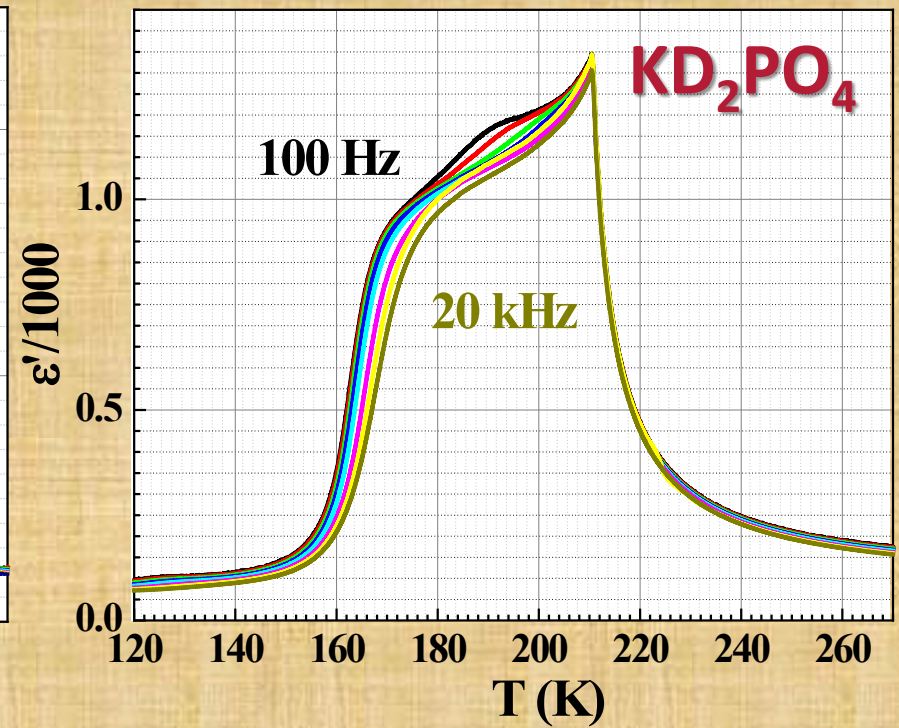
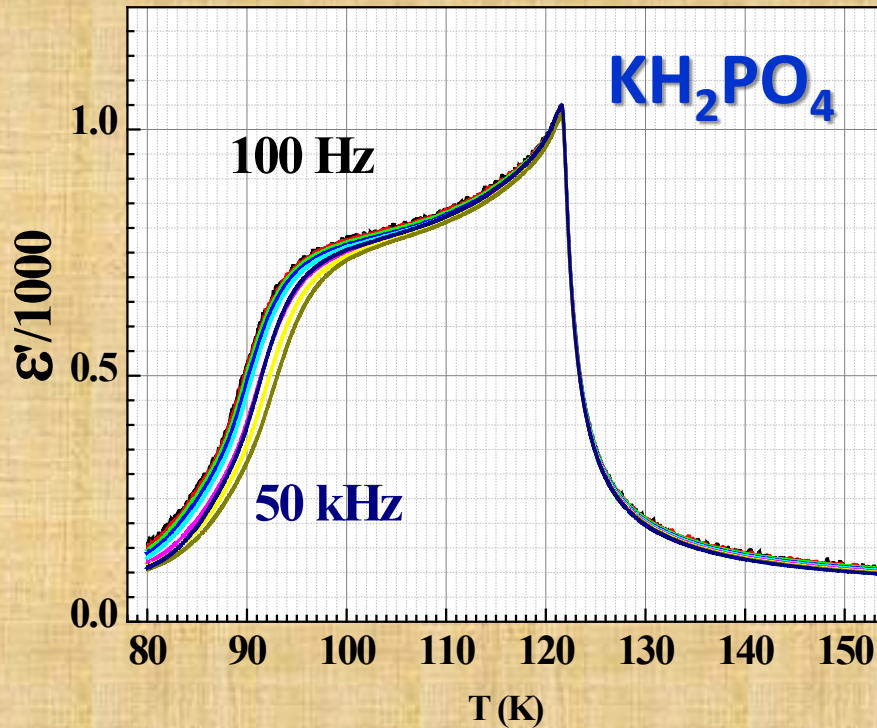


Deuterated analog DKDP $T_c \sim 230$ K



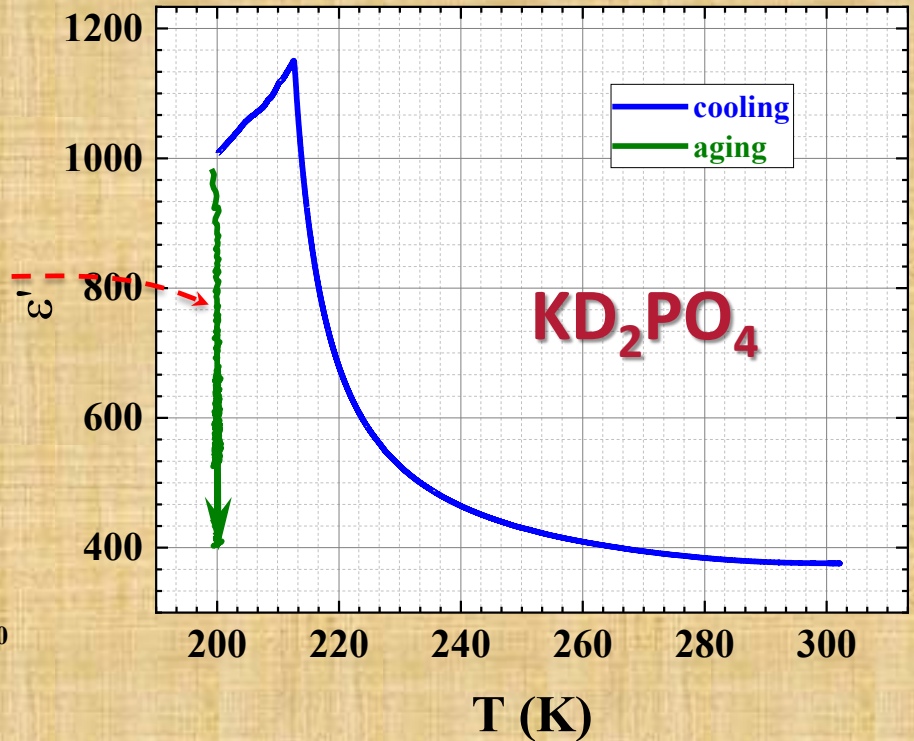
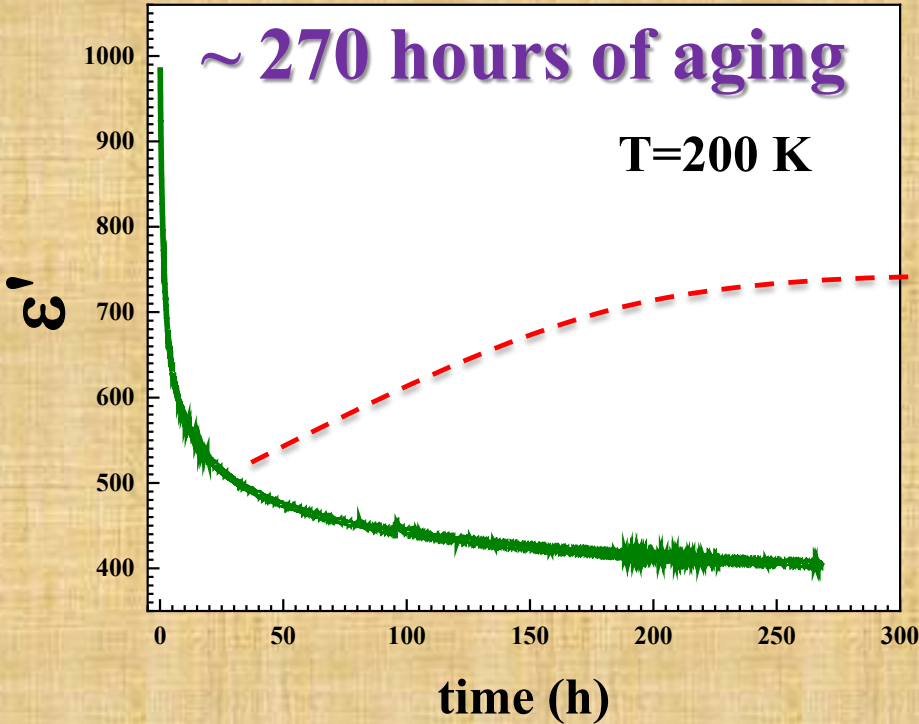
Disorder in Regular Ferroelectrics. KDP family

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



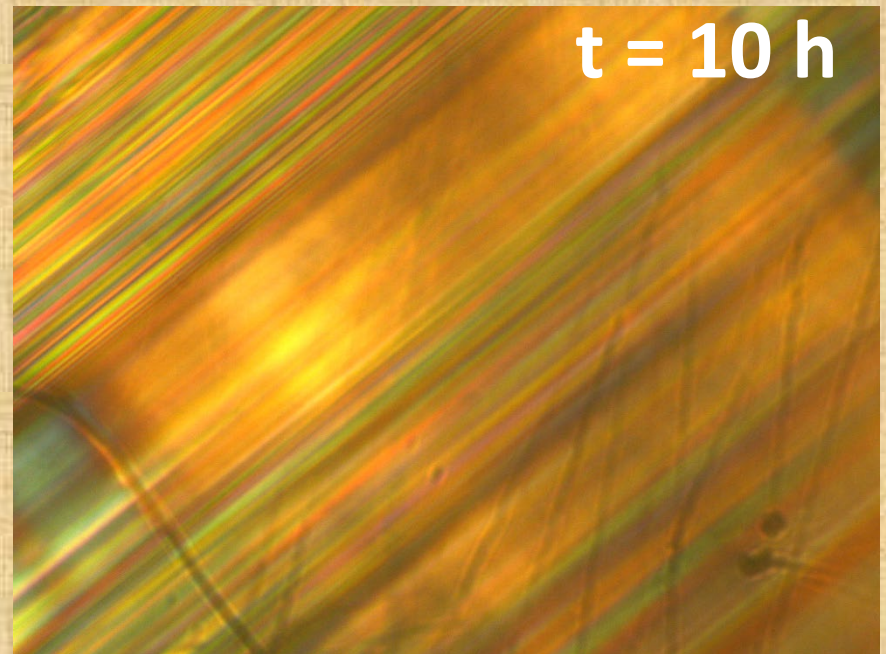
Disorder in Regular Ferroelectrics. KDP family

Aging depends on the concentration of deuterium in $(\text{KH}_2\text{PO}_4)_{(1-x)}(\text{KD}_2\text{PO}_4)_x$ composition



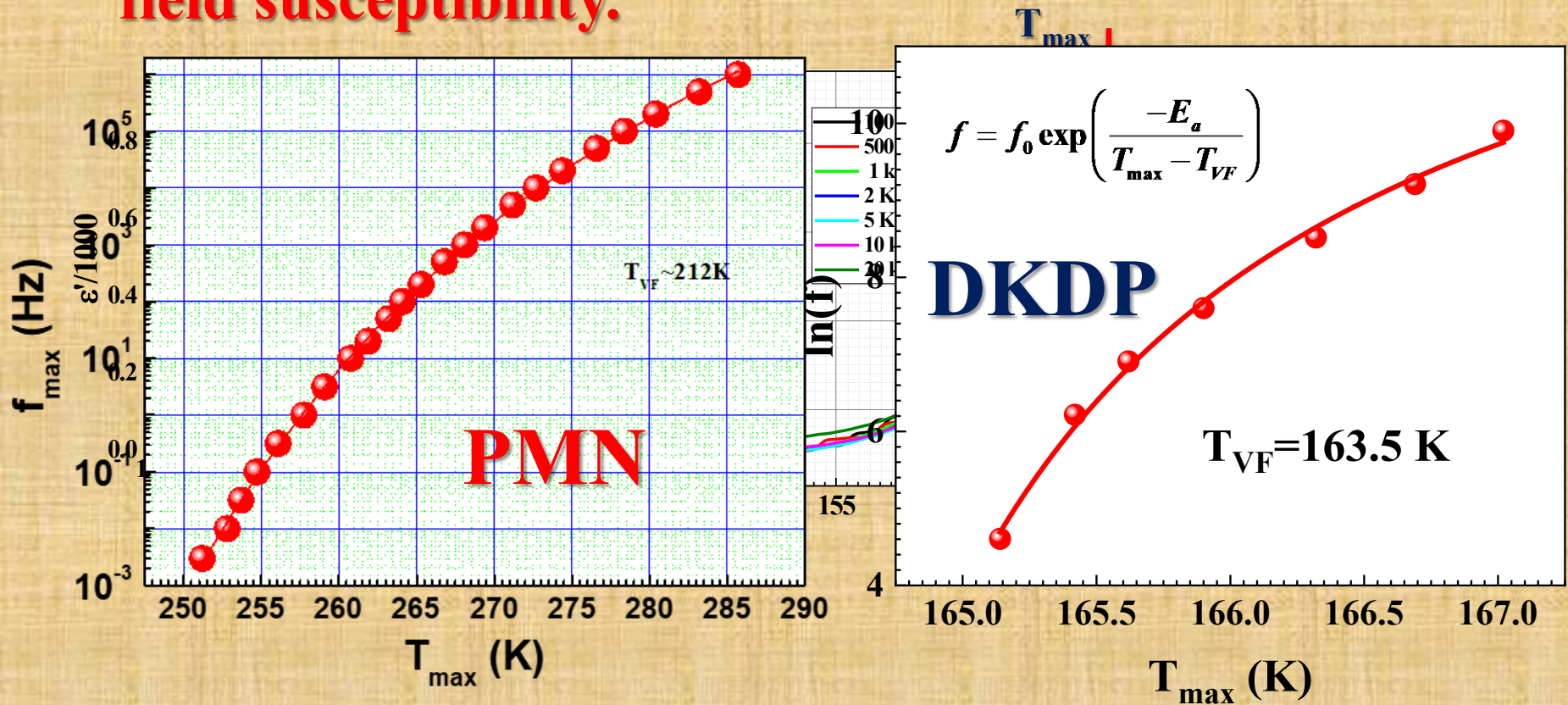
Disorder in Regular Ferroelectrics. KDP family

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.



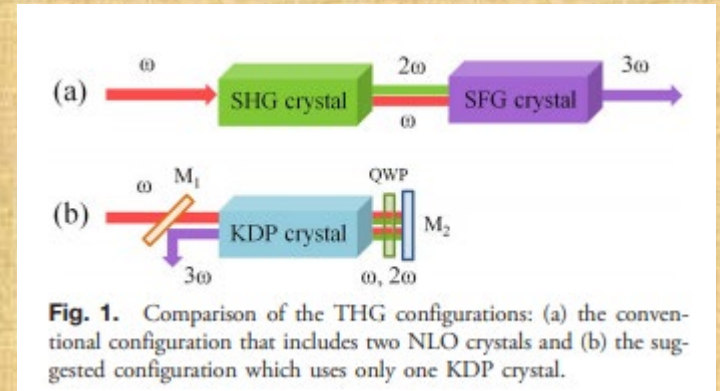
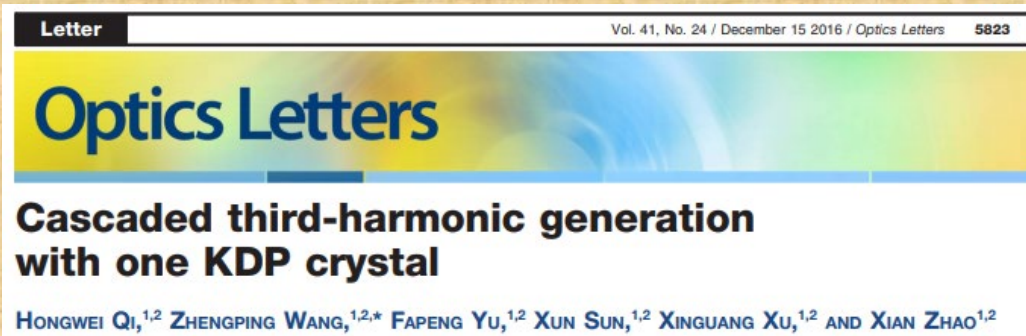
Disorder in Regular Ferroelectrics. KDP family

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



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

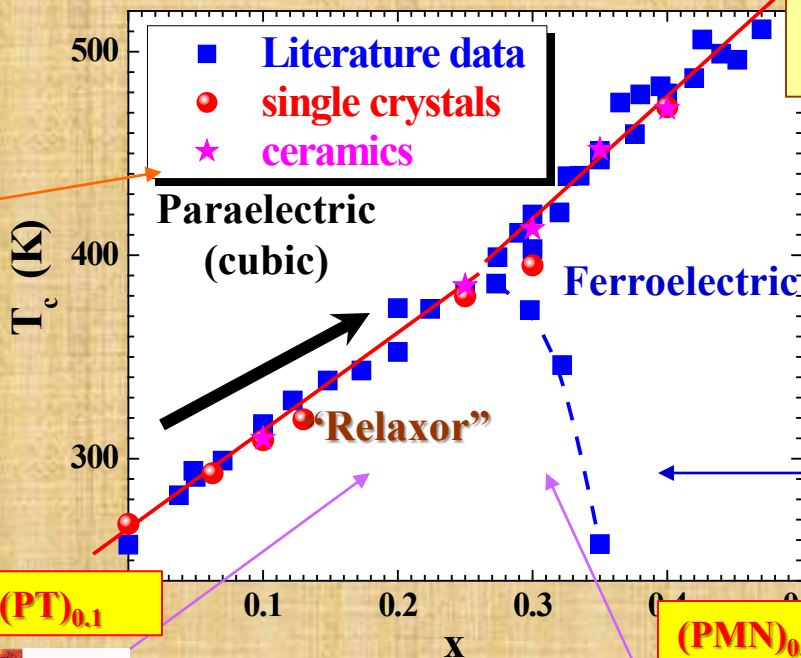
* [Structure or Molec](#)
[Read full description](#)
[See details](#)

Solid solution relaxor-regular ferroelectric.

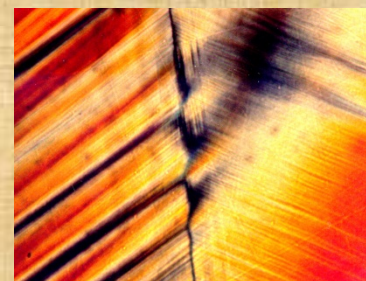
$(\text{PMN})_{0.97}(\text{PT})_{0.03}$

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

PT: PbTiO_3 , ferroelectric with Curie temperature 763K

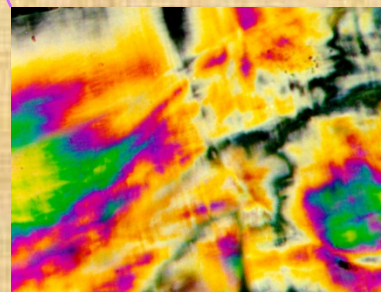
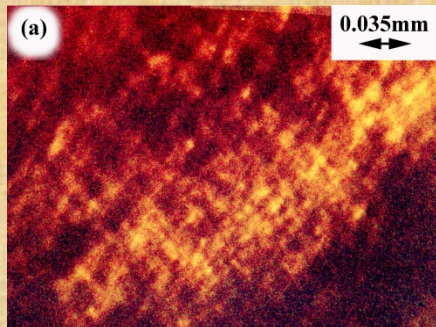


$(\text{PMN})_{0.6}(\text{PT})_{0.4}$

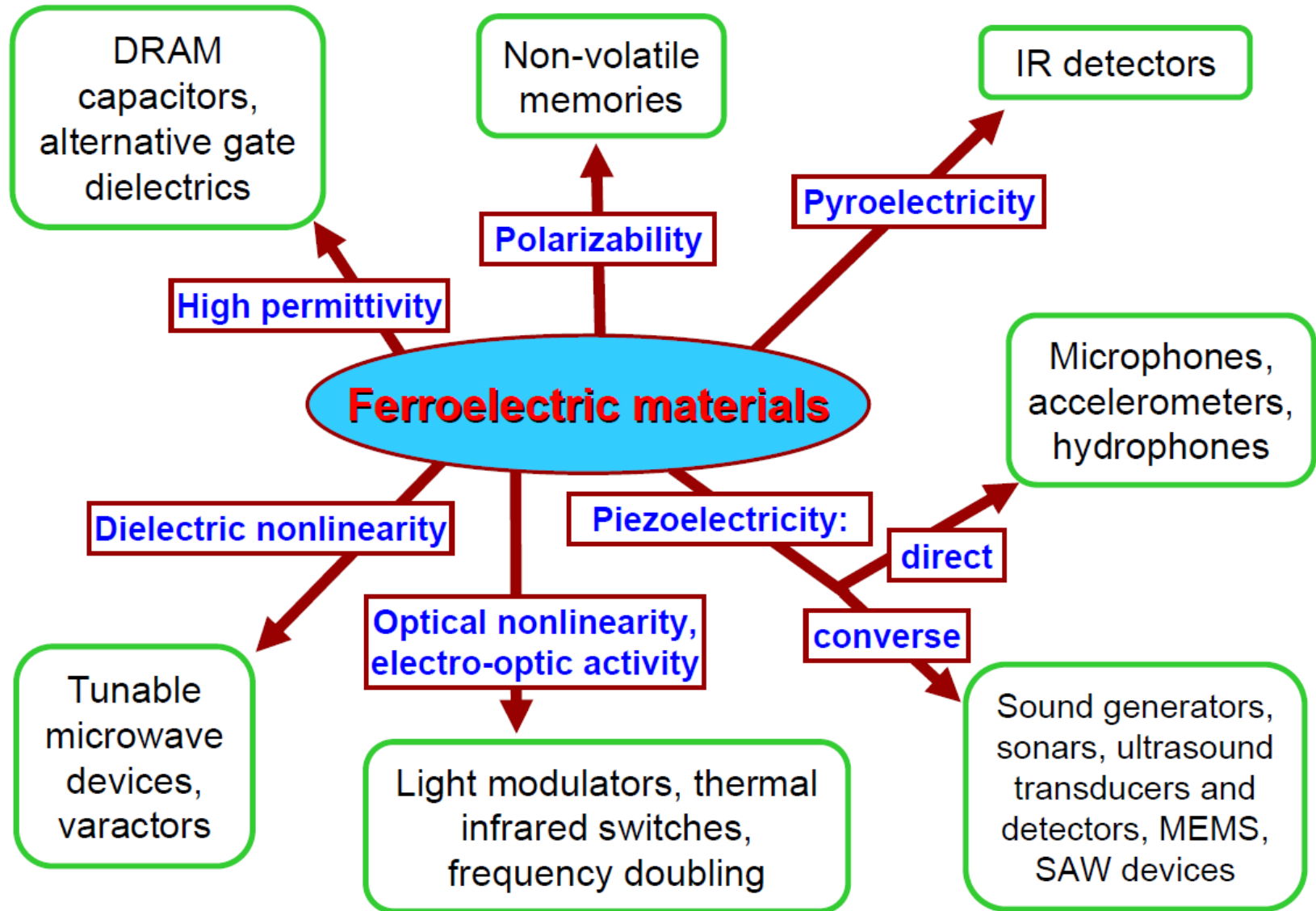


$(\text{PMN})_{0.9}(\text{PT})_{0.1}$

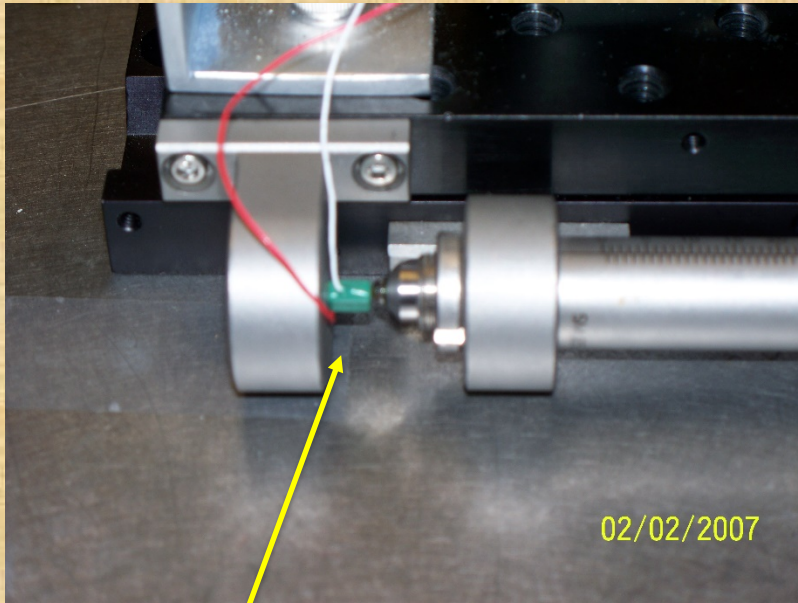
$(\text{PMN})_{0.7}(\text{PT})_{0.3}$



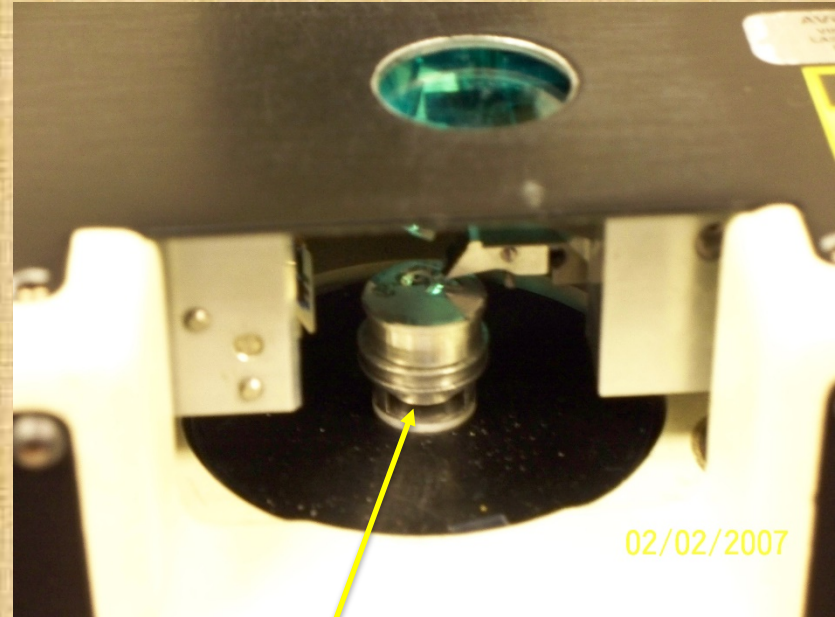
Applications of ferroelectrics



Applications of Ferroelectrics. Physics 403 Lab



Quantum Optics

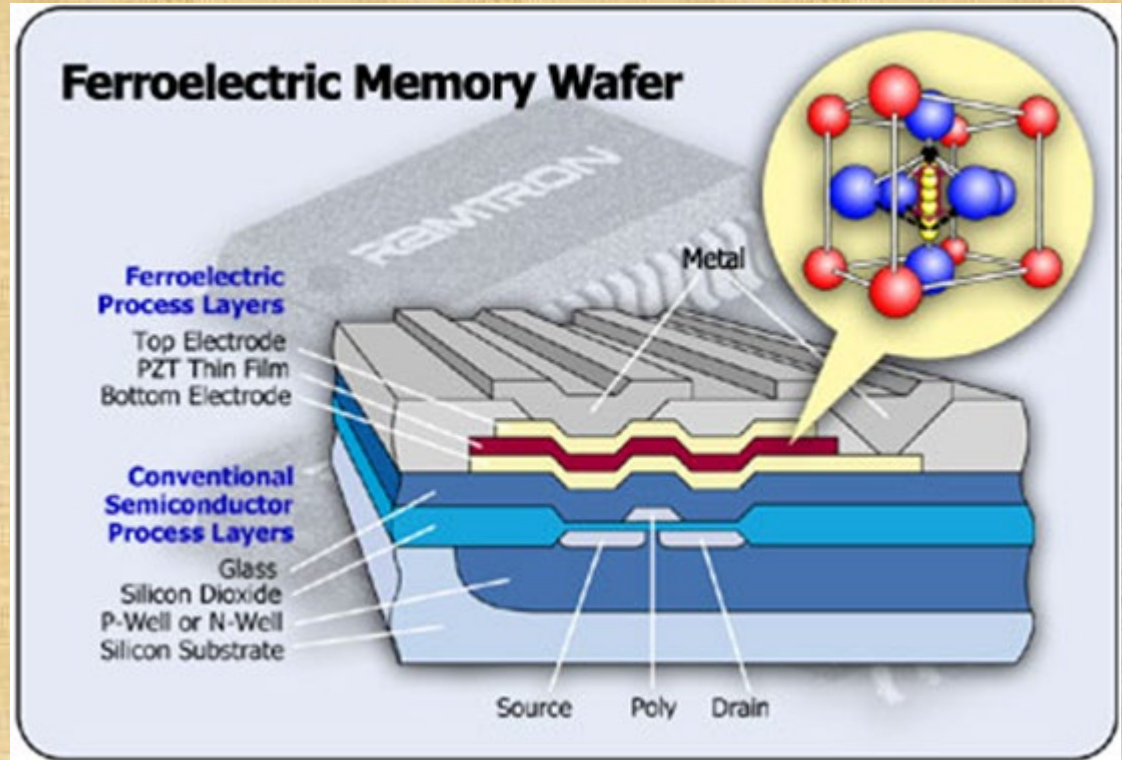


AFM experiment

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

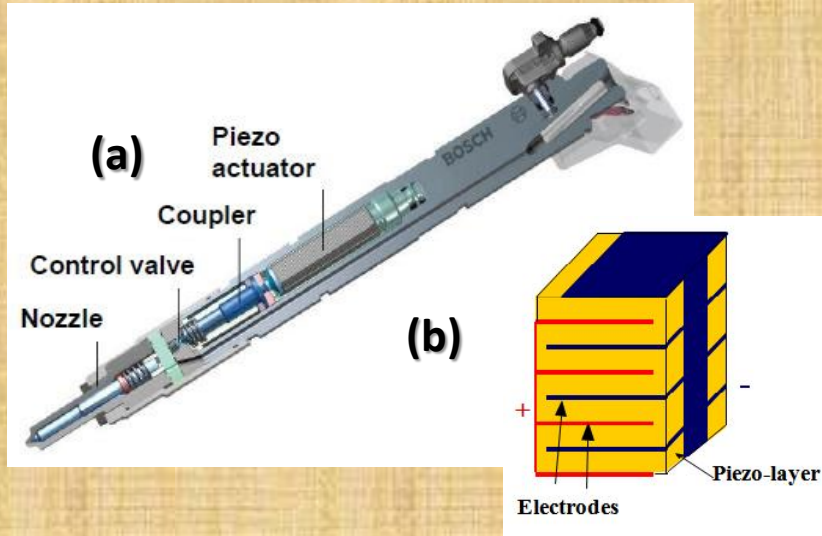
Dafei Jin,¹ Anshuman Kumar,¹ Kin Hung Fung,^{1,2} Jun Xu,¹ and Nicholas X. Fang¹

¹Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

²Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China



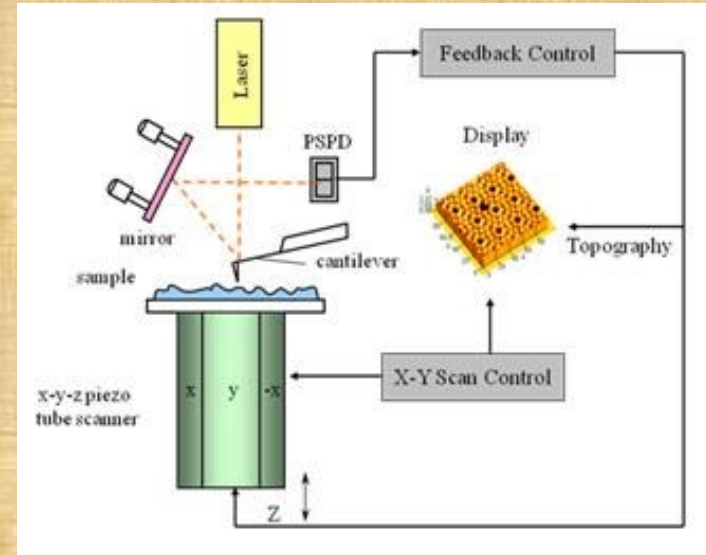
Applications. Actuators



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

Courtesy Technische Universität Darmstadt

Atomic Force Microscope



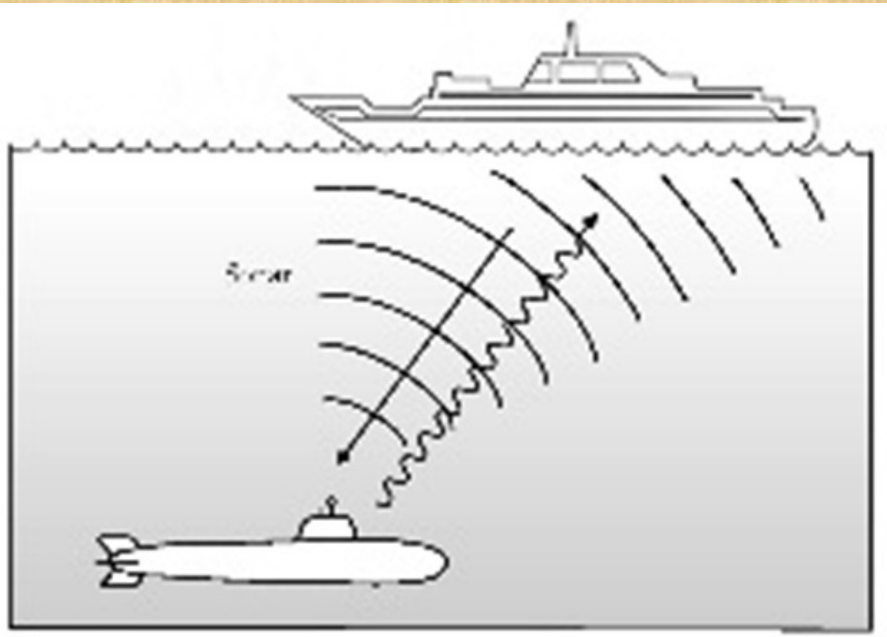
Lead Zirconium Titanate piezo scanner

PI (www.pi.ws)



Applications. Sonars

Military Applications



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

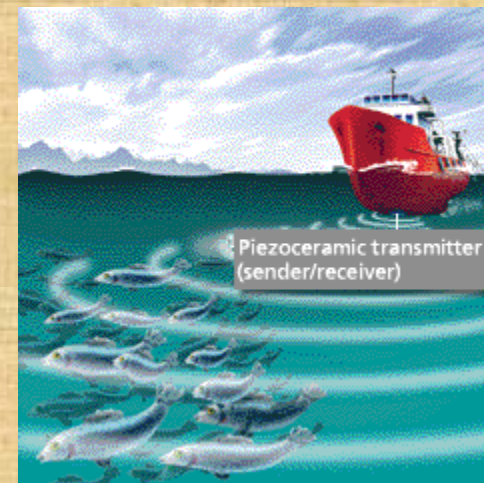


APPLICATIONS:

MINE HUNTING
WEAPONS SONAR
COUNTERMEASURES
ACOUSTIC COMMUNICATIONS
PROJECTOR ARRAYS
HYDROPHONE ARRAYS
VIBRATION CONTROL

Applications. Sonars

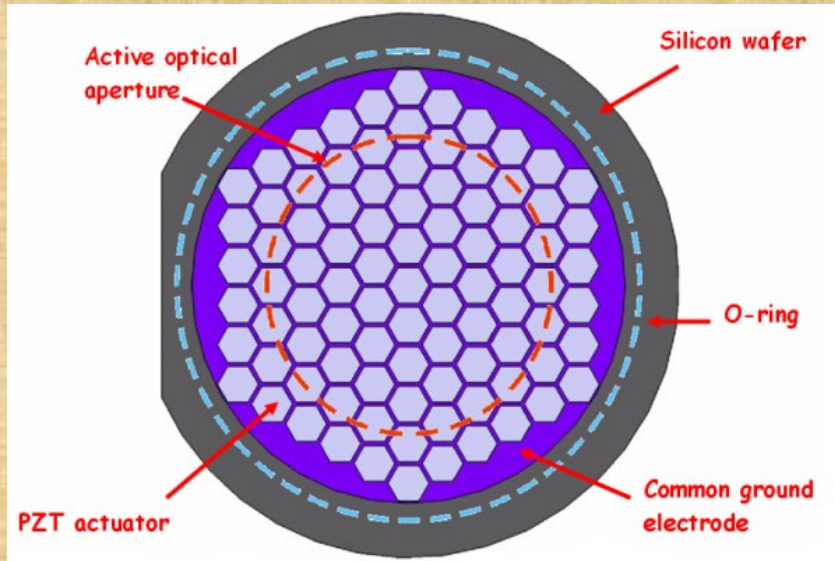
Civil Applications



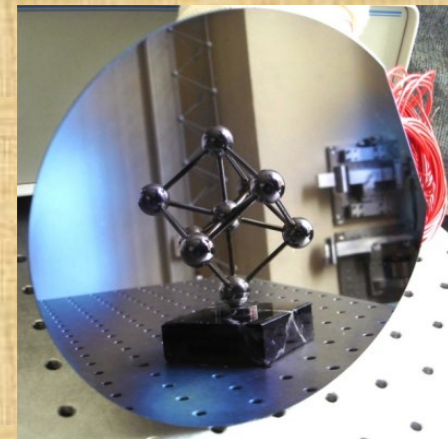
Fish Finder

Courtesy **FURUNO**

Applications. Adaptive Optics

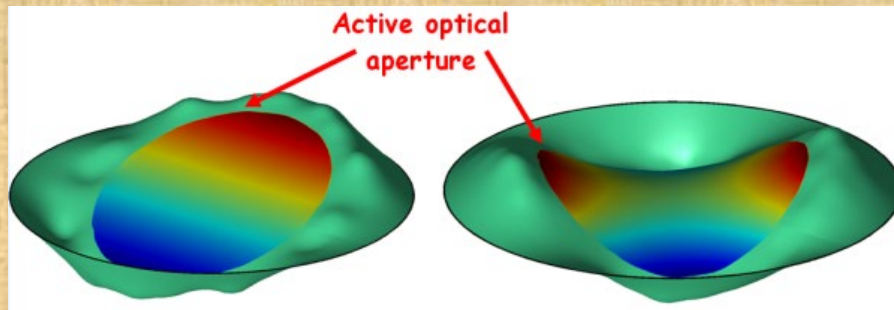


Soldered control and mass wires



Reflecting surface

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



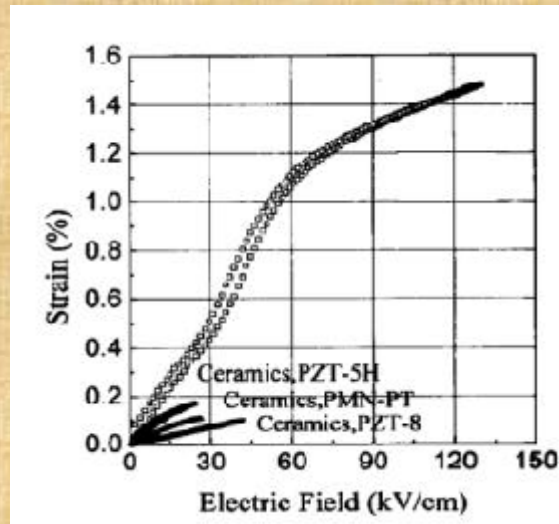
Courtesy of

Active Structures Laboratory

Physics 403 Spring 2022

<http://scmero.ulb.ac.be>

Ferroelectricity: Relaxors - applications



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	0.60
PMN-PT (sc)	4200	2200	0.92-0.94
PZN-PT (sc)	2500	2400	0.91-0.93

Piezoelectric properties of different materials