

# Ferroelectrics. Disordered Ferroelectrics

**Eugene V. Colla**  
**Physics 403 Summer 2021**



# Outline

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

# Ferroelectricity. Definition.

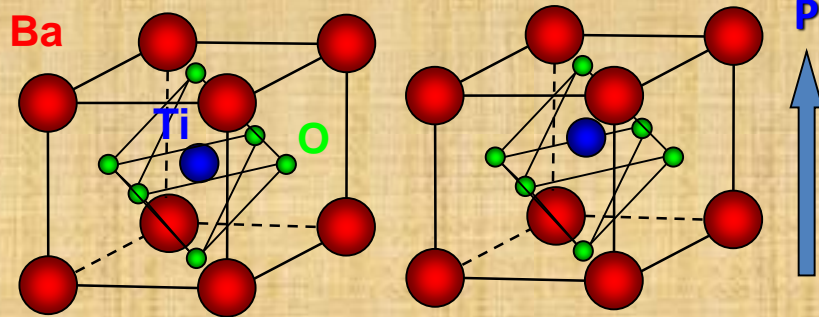
- **Ferroelectric Materials.** A ferroelectric material is a material that exhibits, over some range of temperature, a **spontaneous electric polarization** that can be reversed or reoriented by application of an electric field.

An American National Standard  
IEEE Standard Definitions of  
Primary Ferroelectric Terms

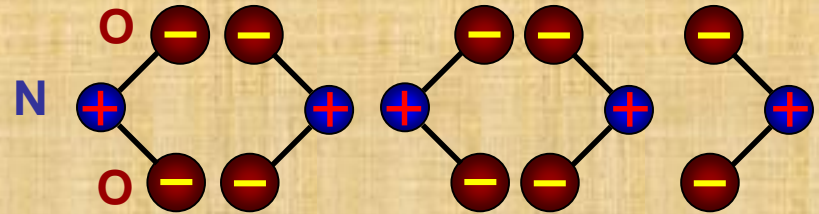
# Ferroelectricity: Two classes of ferroelectrics

## Order-Disorder

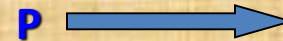
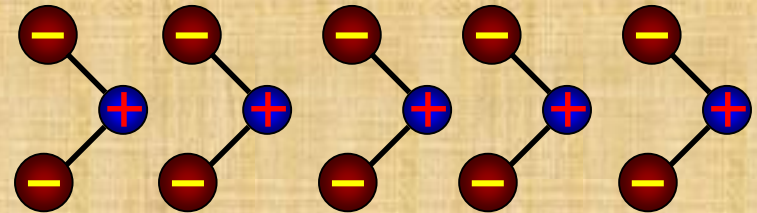
### Displacement type



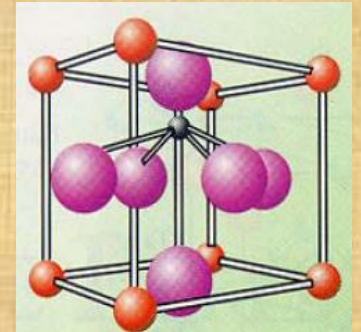
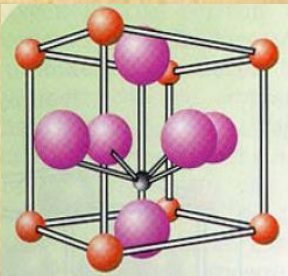
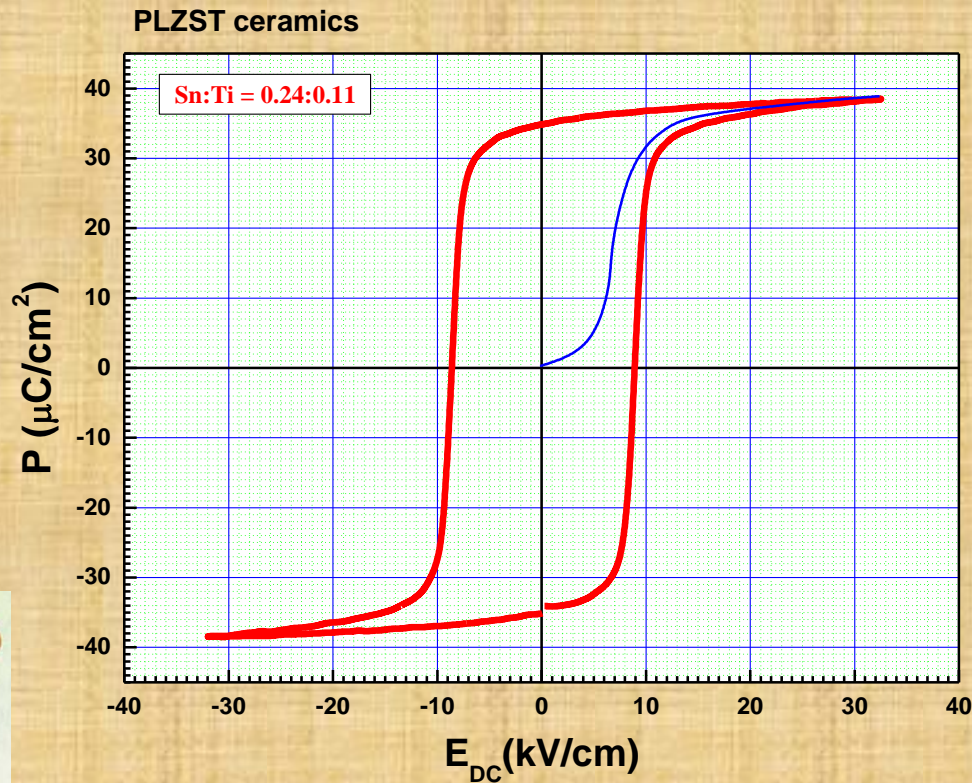
### disorder



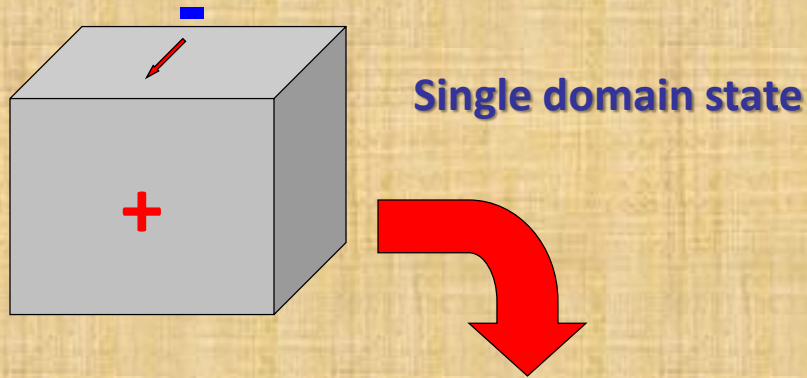
### order



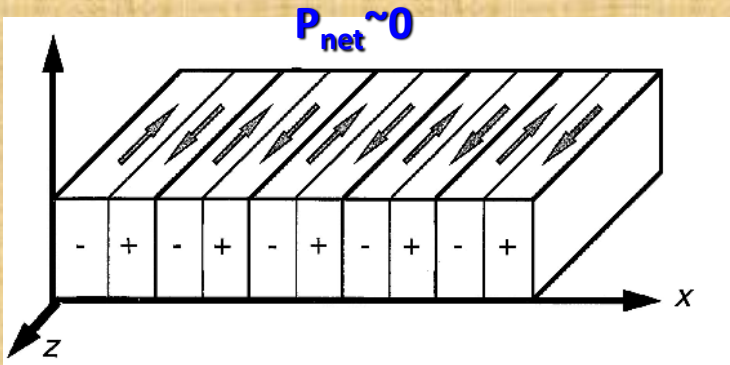
# Ferroelectricity: Polarization reversible. (P-E hysteresis)



# Ferroelectricity: Domains

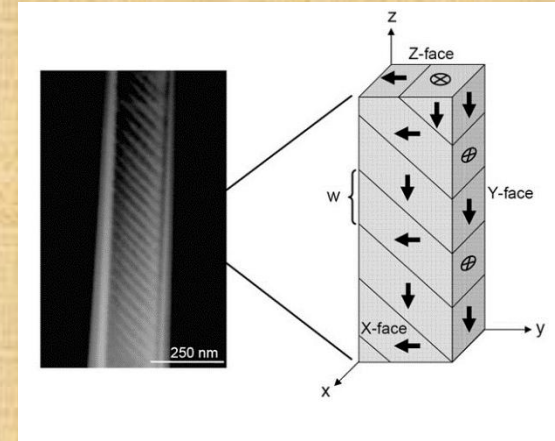


Multi domain state



180° domain pattern

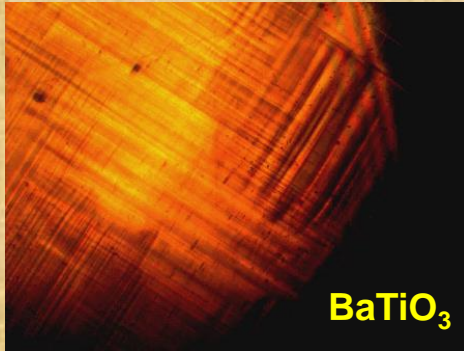
Y Lu et al. Science 1997;276:2004-2006



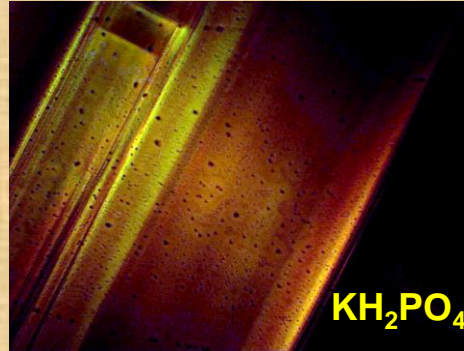
90° domains

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

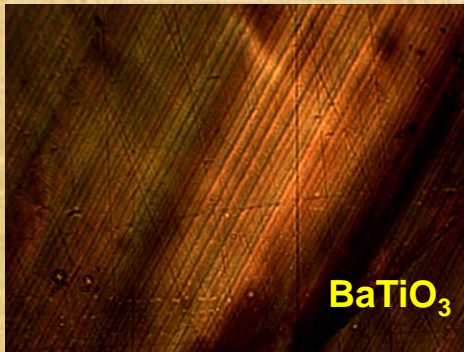
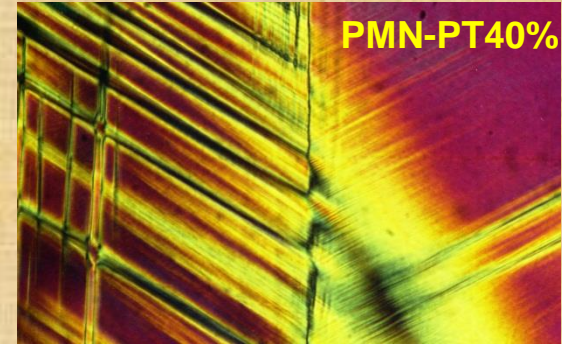
# Ferroelectricity: Domains



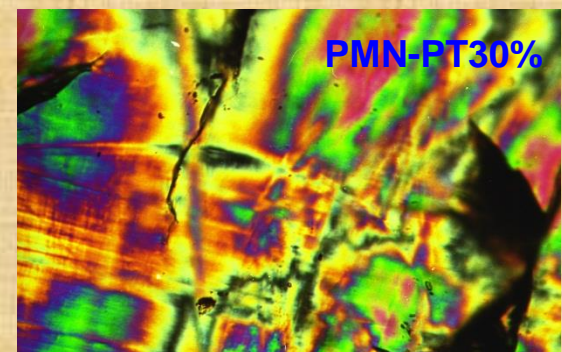
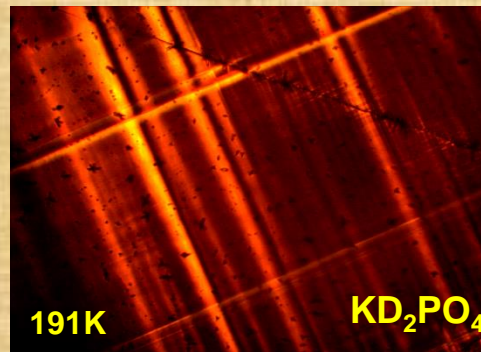
Courtesy of Benjamin Vega-Westhoff and Scott Scharfenberg, P403, Fall2009



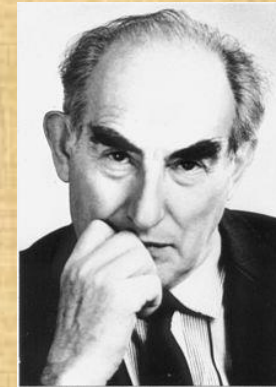
Courtesy of Allison Pohl, P403, Fall2009



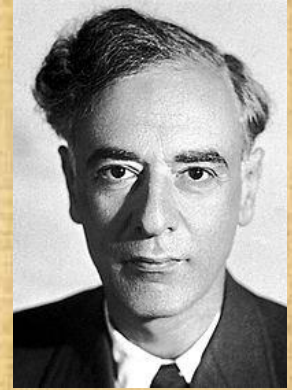
Crystal from Forschungsinstitut für mineralische und metallische Werkstoffe -Edelsteine/Edelmetalle



# Ferroelectricity: Landau-Ginzburg phenomenological theory



Vitaly Ginzburg  
1916-2009



Lev Landau  
1908-1968

Free energy

Order parameter (polarization)

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

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:

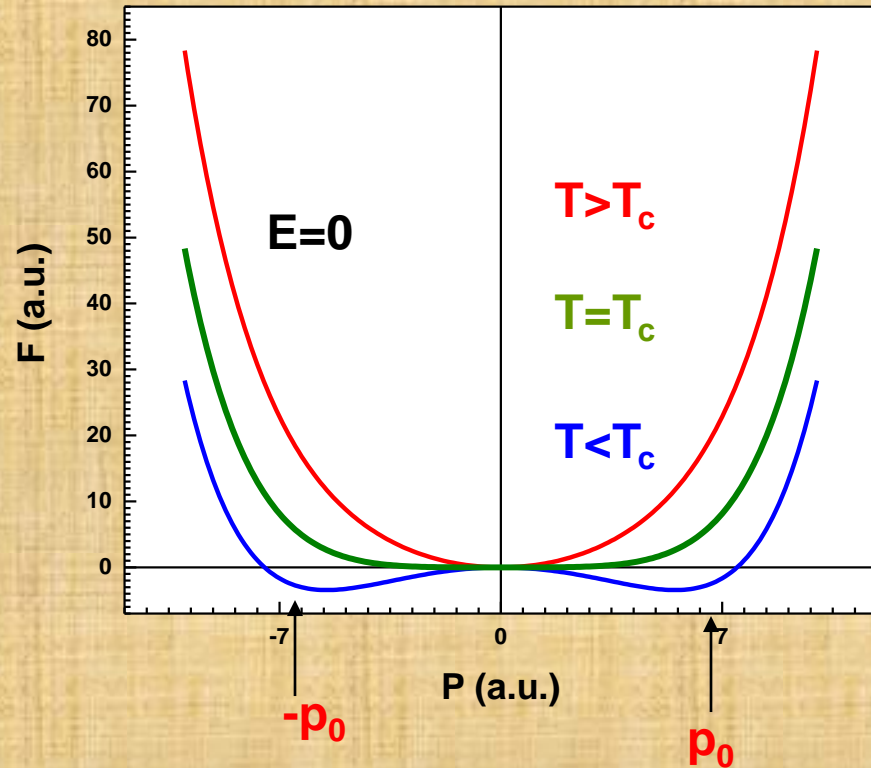
$$\alpha = \frac{1}{C}(T - T_c) \text{ and finally we will have Curie-Weiss law}$$

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

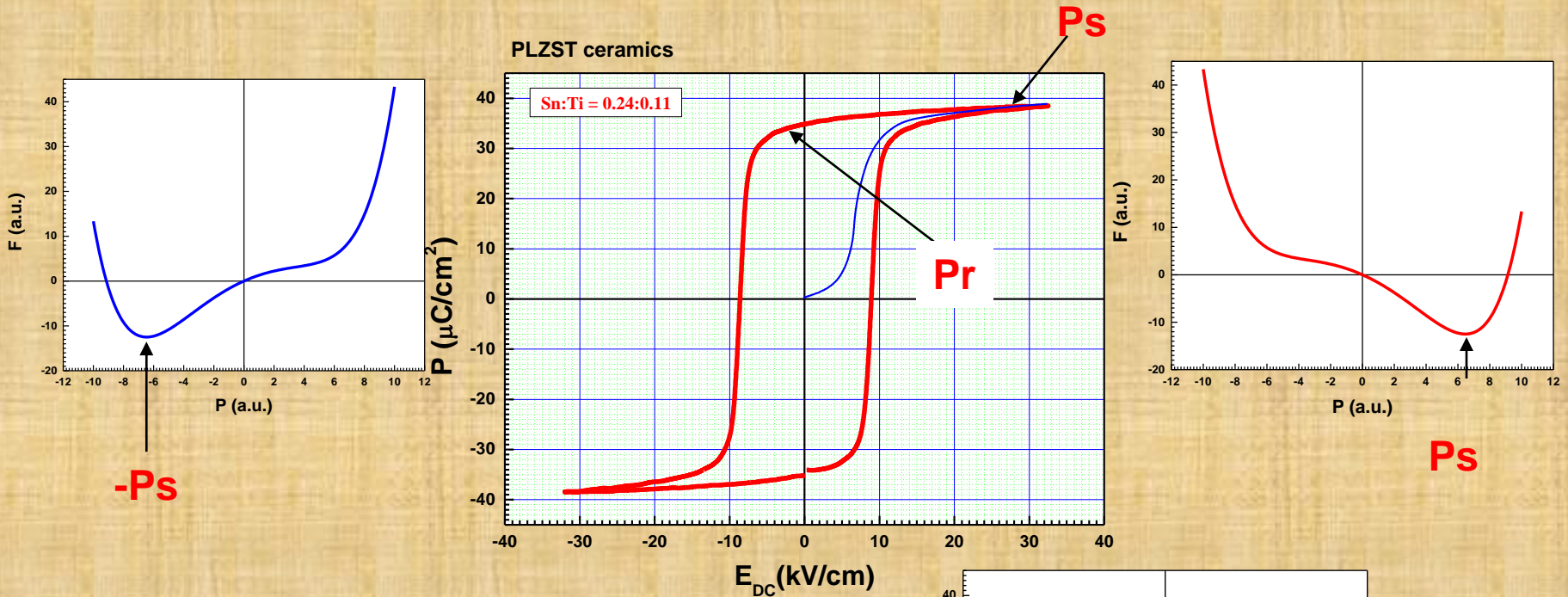


# Ferroelectricity: Landau-Ginzburg phenomenological theory

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

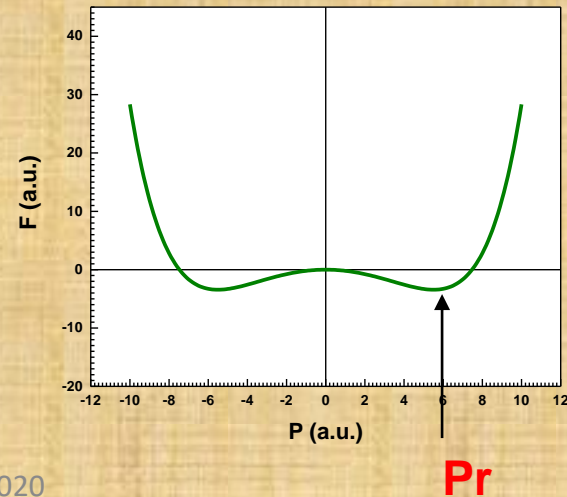


# Ferroelectricity: Landau-Ginzburg phenomenological theory



Including EP term can illustrate the P-E hysteretic behavior

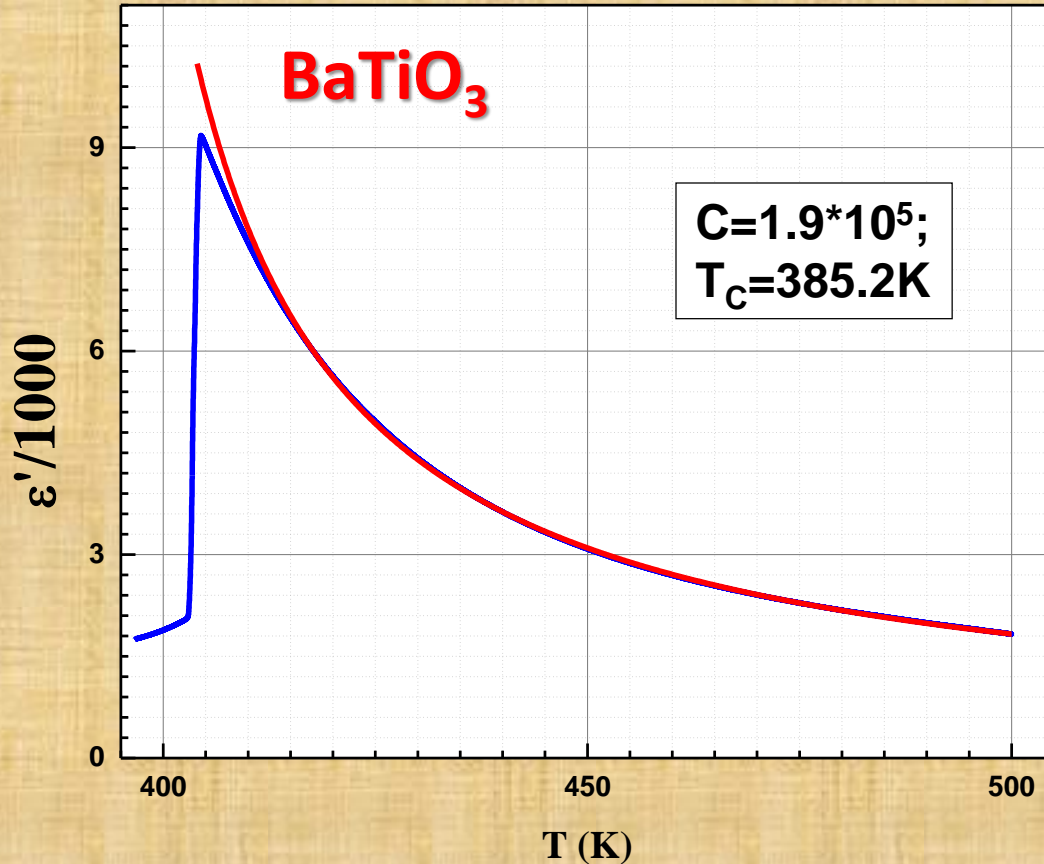
$$F_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots - EP$$



# 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

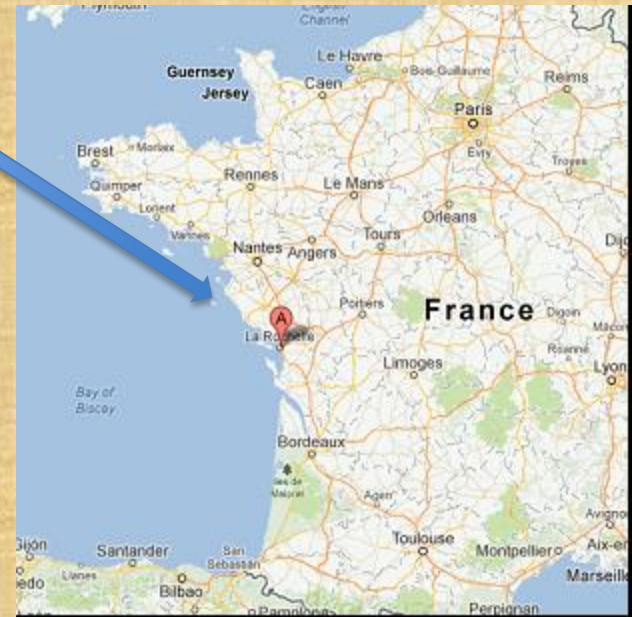
**Rochelle Salt**  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$



***Elie Seignette***

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

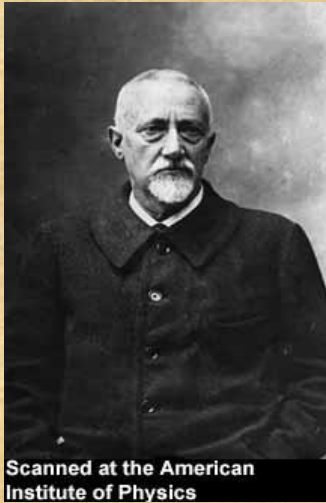
Rochelle Salt originates from French city of La Rochelle where it was produced by ***Pierre Seignette*** another name of this material is Seignette salt



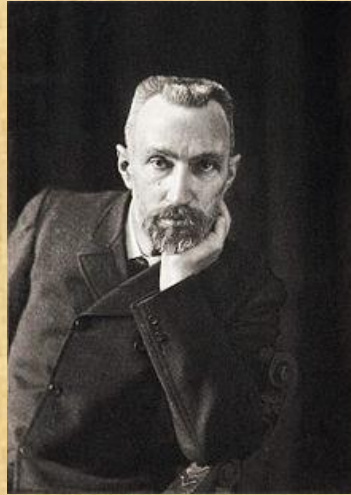
Rochelle Salt was used in medicine and food industry

# Ferroelectricity: Discovery

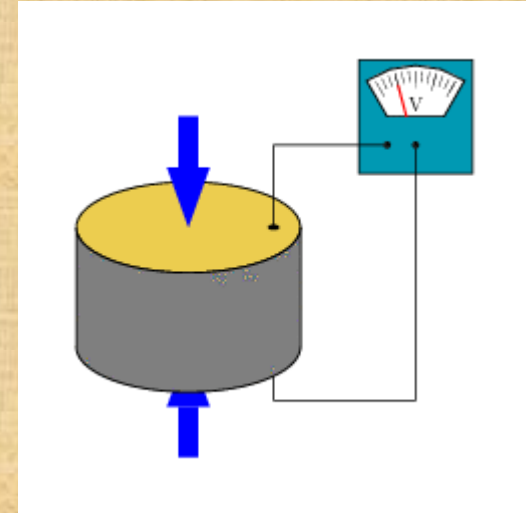
**Rochelle Salt**  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$



**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

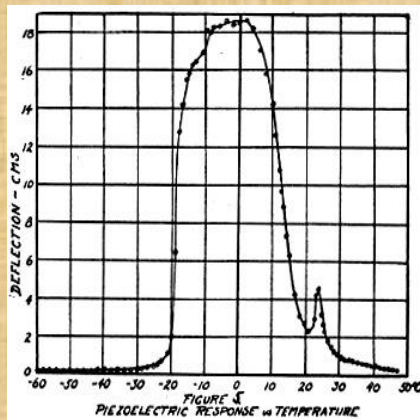
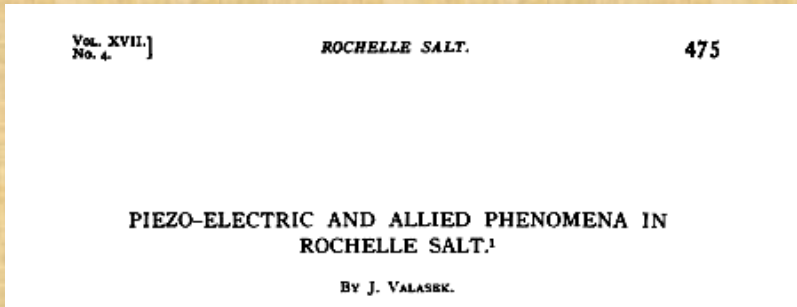


Fig3. Piezoelectric response as a function of temperature [2]

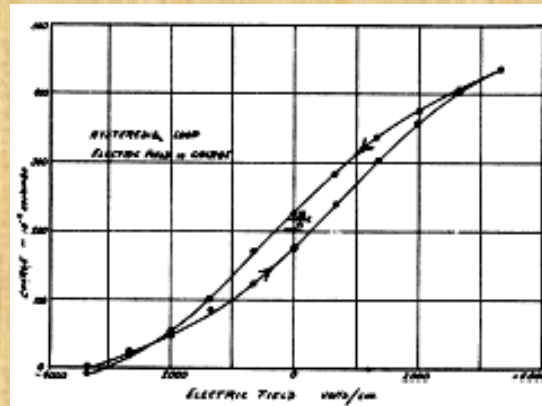


Fig.1. The first published hysteresis loop [1]

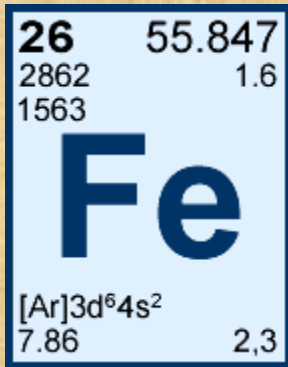


Joseph Valasek (1897-1993)  
University of Minnesota

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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Printed in the United States of America

## **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 Summer 2020

# Materials. KDP

KDP ( $\text{KH}_2\text{PO}_4$ ) - potassium dihydrophosphate

1935

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



Georg Busch  
1908-2000



Paul Scherrer  
1890-1969

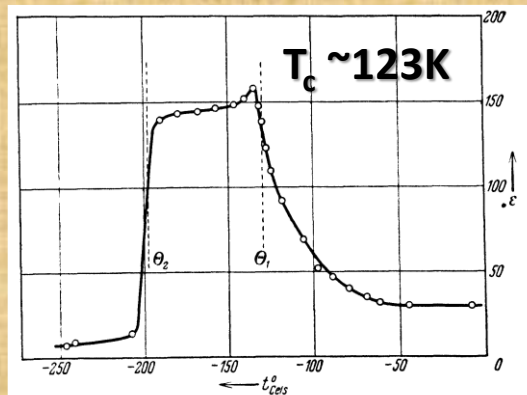


Fig. 1. Temperaturverlauf der Dielektrizitätskonstanten  $\epsilon_{33}$  an  $\text{KH}_2\text{PO}_4$ .



## DIE NATURWISSENSCHAFTEN

23. Jahrgang

25. Oktober 1935

Heft 43

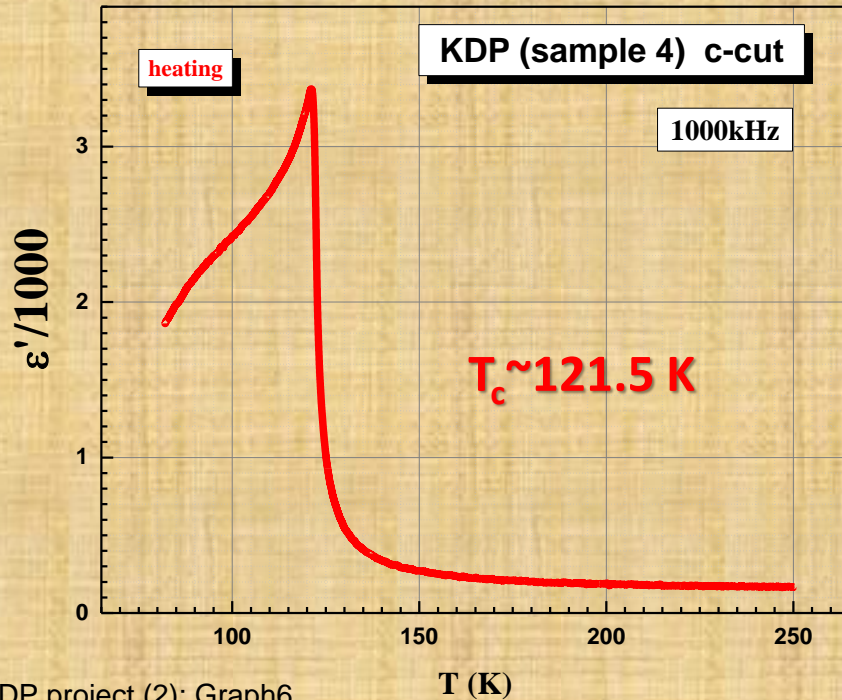
Eine neue seignette-elektrische Substanz.



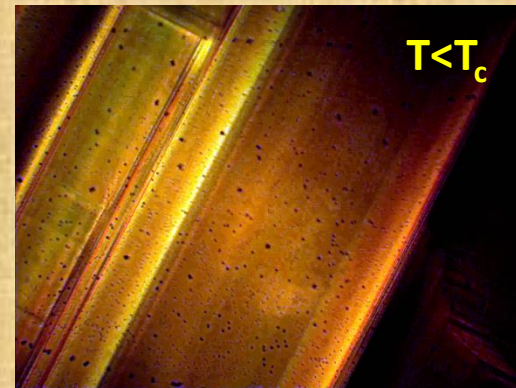
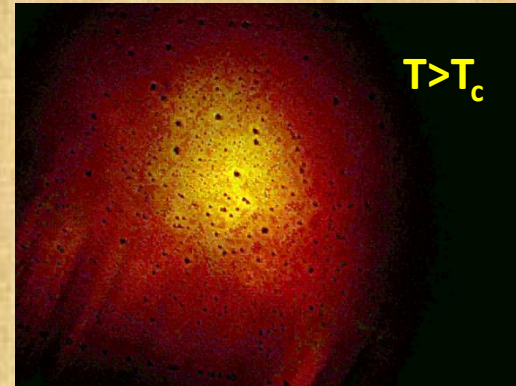
# Materials. KDP

KDP ( $\text{KH}_2\text{PO}_4$ ) - potassium dihydrophosphate

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



KDP project (2): Graph6

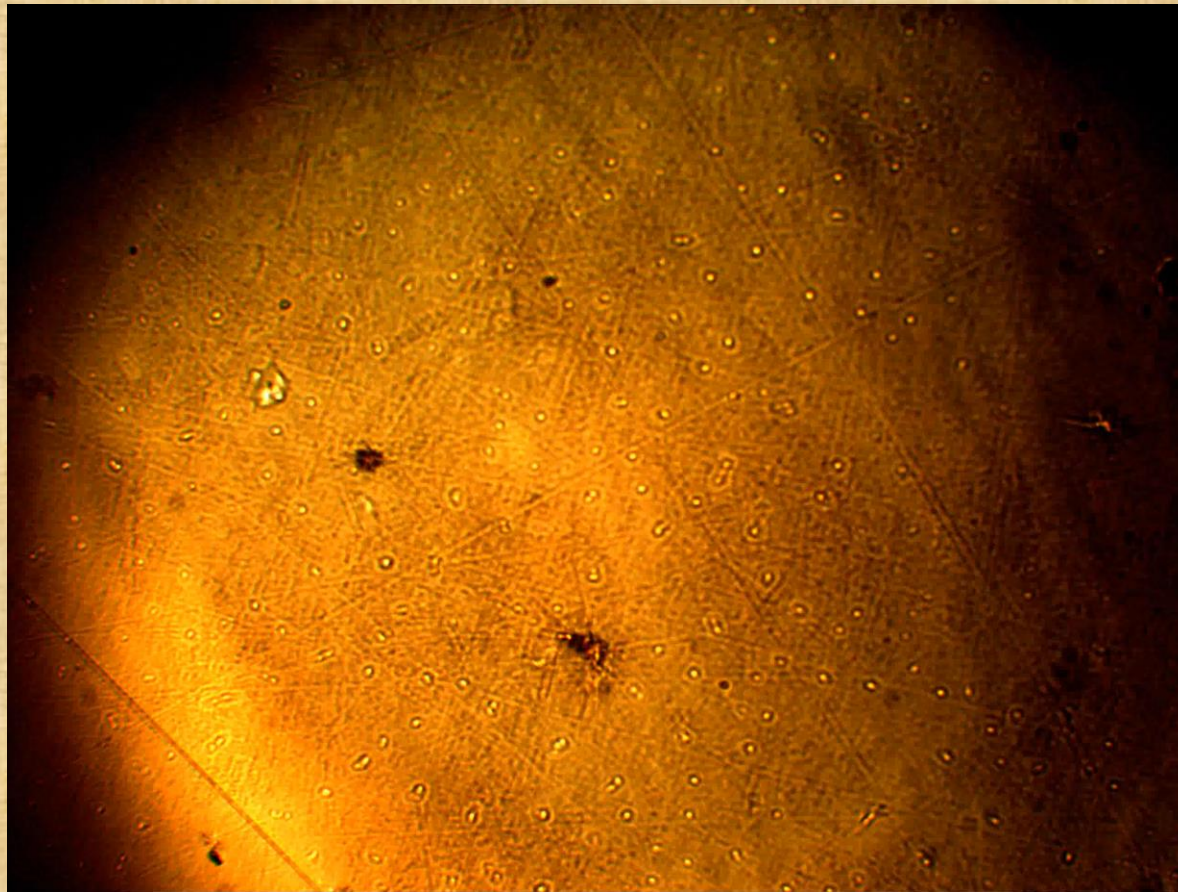


Courtesy of Tim S. Thorp, Zhangji Zhao, Physics 403, Spring 2013

Courtesy of Alison Pohl, Physics 403, Spring 2009

# Materials. DKDP

DKDP ( $\text{KD}_2\text{PO}_4$ ) – deuterated potassium dihydrophosphate  $T_m = 230\text{K}$



$T_c$

$T_c$

# 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  $\text{BaTiO}_3$  A. von Hippel (USA); Wul, Goldman (USSR))

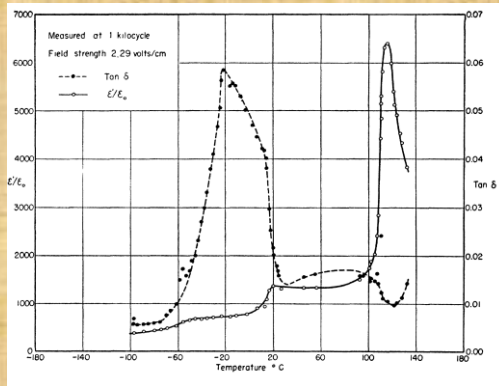
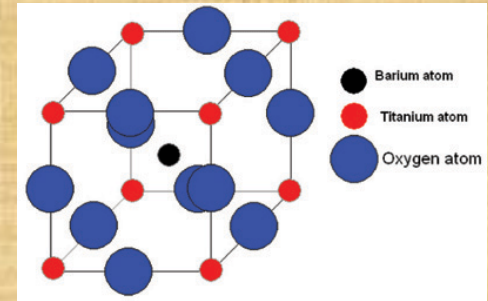


FIG. 6. Dielectric constant and loss of barium titanate ceramic.

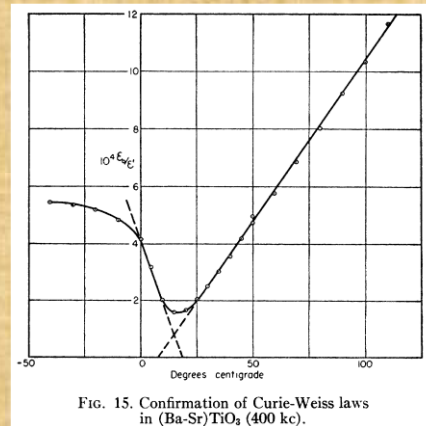
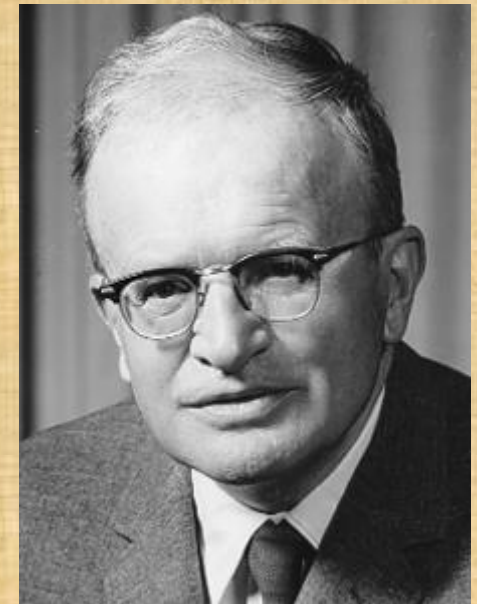
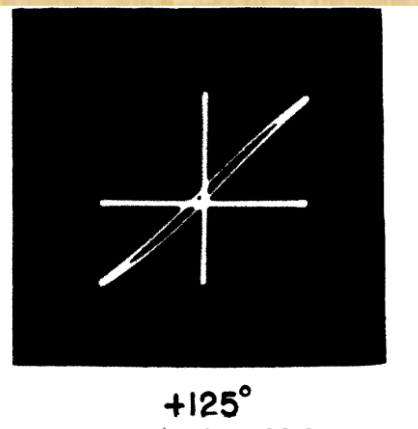
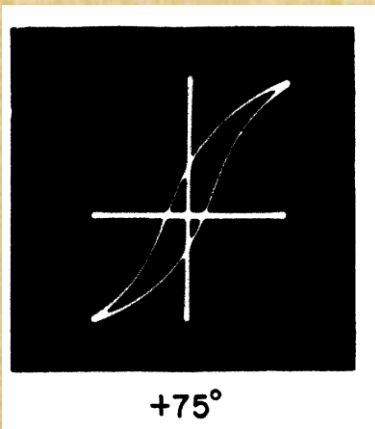


FIG. 15. Confirmation of Curie-Weiss laws in  $(\text{Ba-Sr})\text{TiO}_3$  (400 kc).

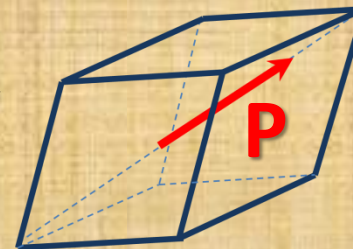
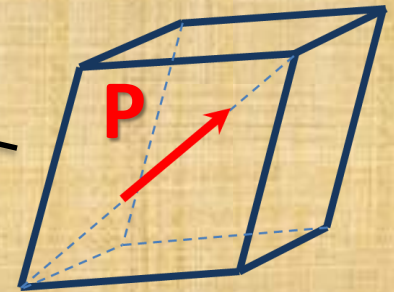
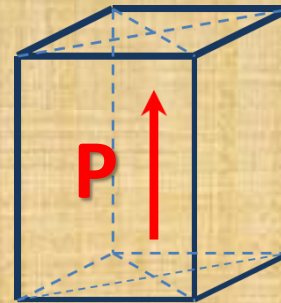
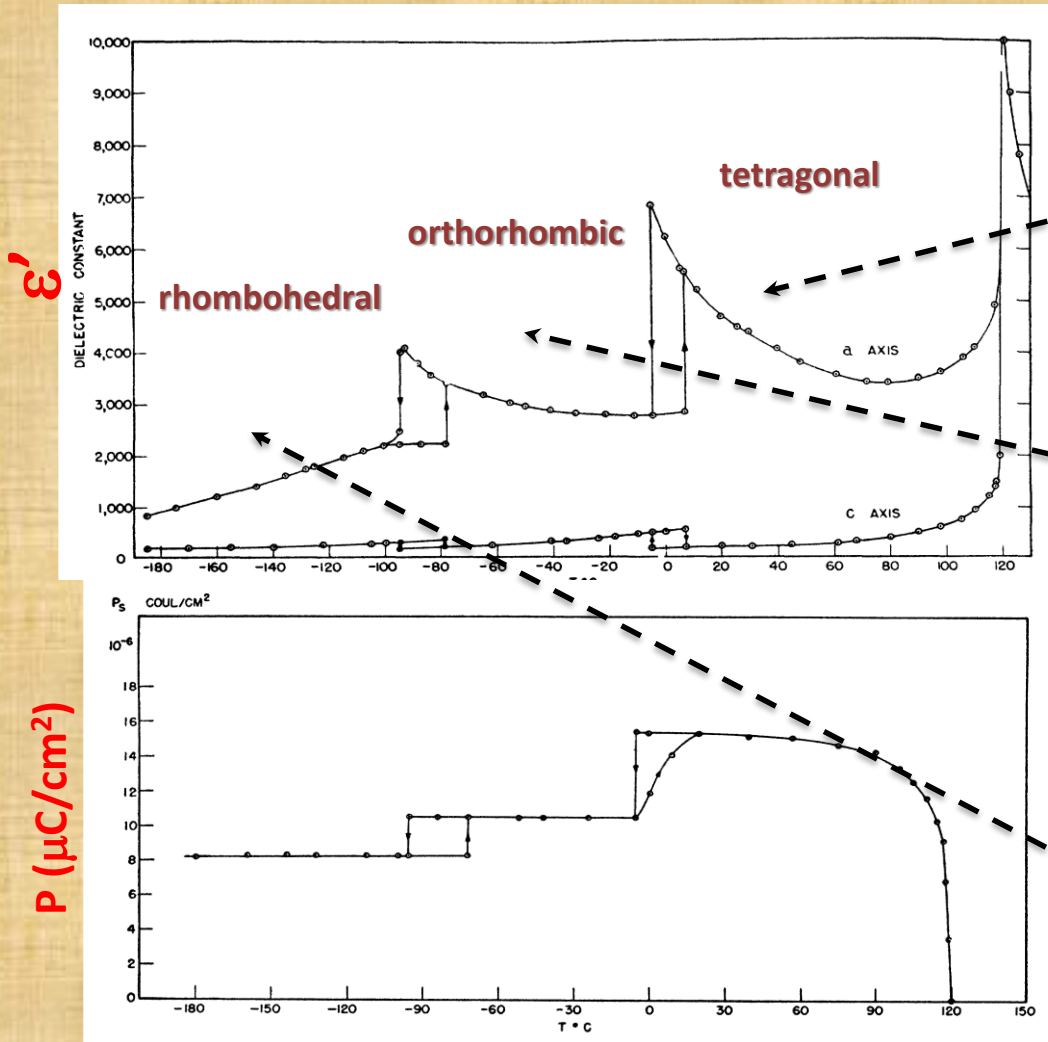
$T_c \sim 400\text{K}$



Arthur R. von Hippel  
1898-2003



# Materials. Barium Titanate.



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

# Materials. BaTiO<sub>3</sub>. Domains.

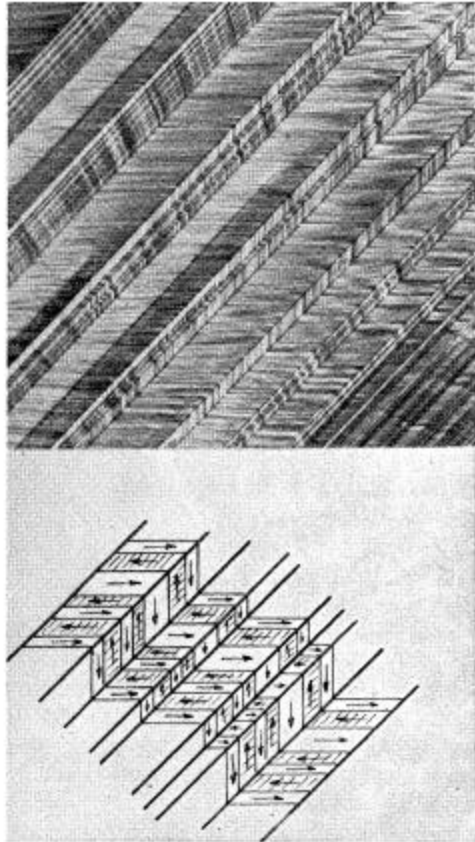
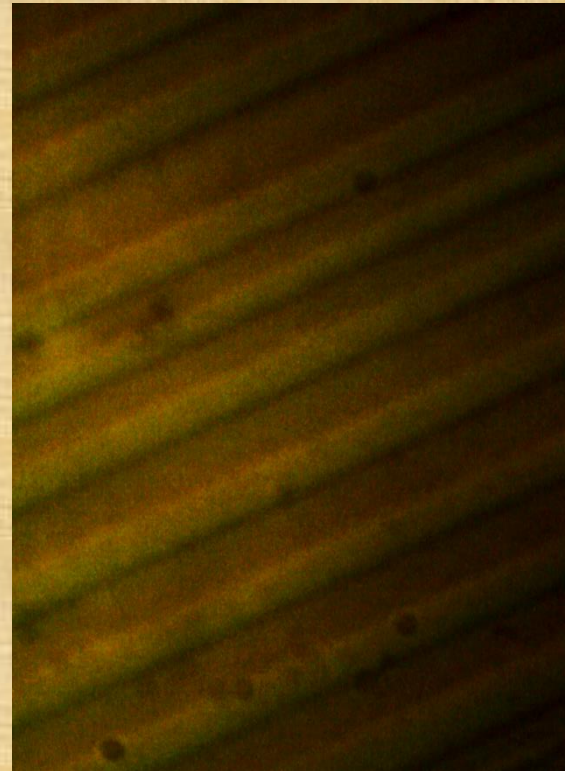


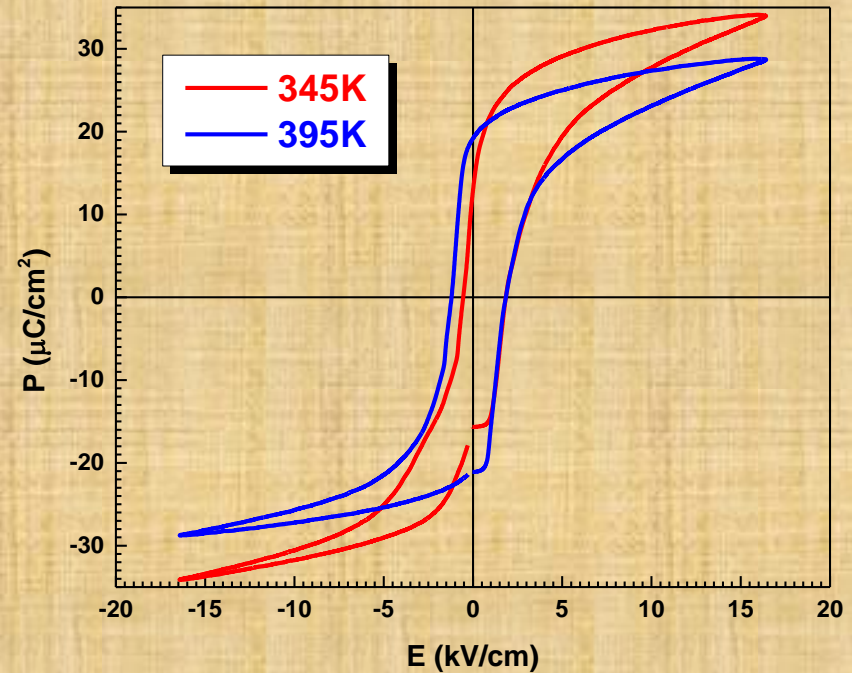
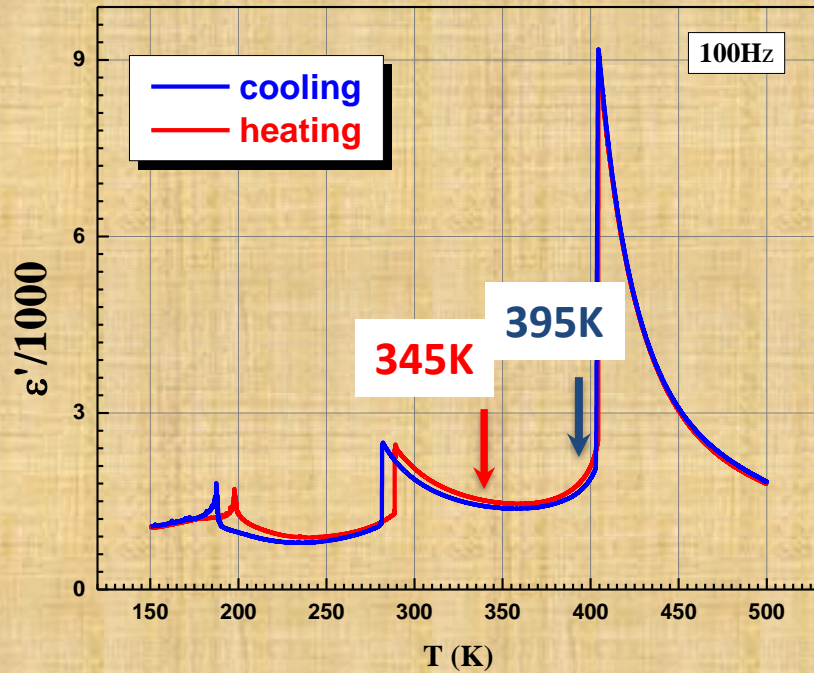
FIG. 4. Surface of an  $a$ -domain crystal showing  $90^\circ$  walls and antiparallel domains.



Physics 403 Lab, August 2011

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

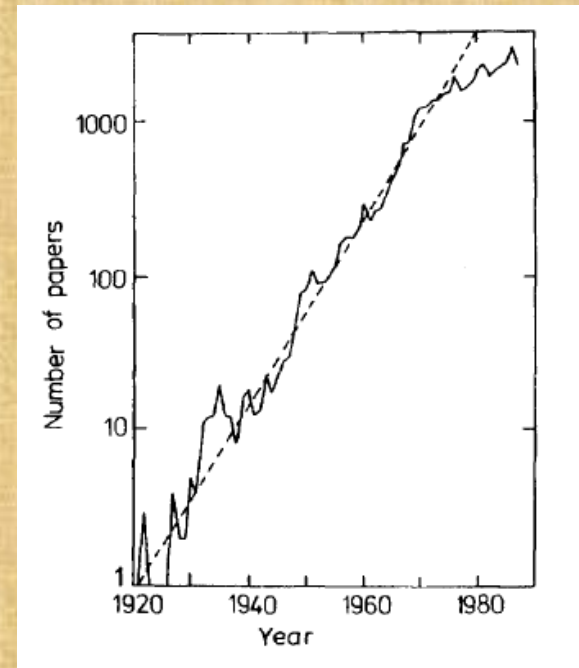
# Materials. BaTiO<sub>3</sub>. P-E hysteresis.



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

# Ferroelectricity: Typical ferroelectric materials

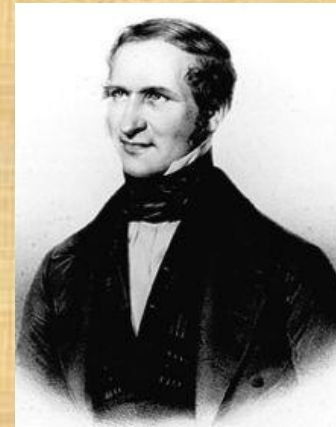
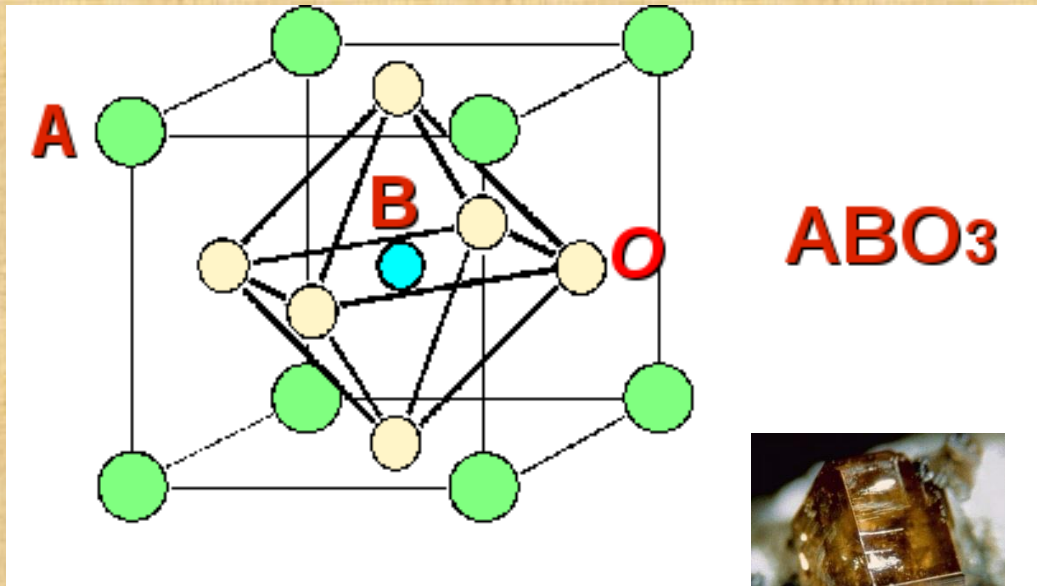
		$T_c$ (K)	$P_s$ ( $\mu\text{C}/\text{cm}^2$ )
KDP type	$\text{KH}_2\text{PO}_4$	123	4.75
	$\text{KD}_2\text{PO}_4$	213	4.83
	$\text{RbH}_2\text{PO}_4$	147	5.6
Perovskites	$\text{BaTiO}_3$	408	26
	$\text{KNbO}_3$	708	30
	$\text{PbTiO}_3$	765	>50
	$\text{LiTiO}_3$	938	50
	$\text{LiNbO}_3$	1480	71



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

# Perovskite Structure

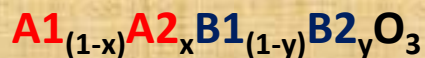
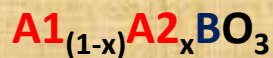
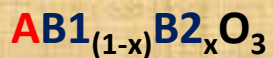
*Perovskite* is a mineral  $\text{CaTiO}_3$ . The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist Lev Perovski.



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	$\text{K}_{1/3}\text{Pb}_{2/3}\text{Zn}_{2/9}\text{Nb}_{7/9}\text{O}_3$

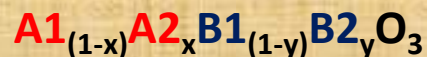
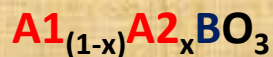
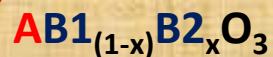


L. Eric Cross<sup>1</sup>  
(1923-2016)



Smolenskii G.A.<sup>2</sup>  
(1910 – 1986)

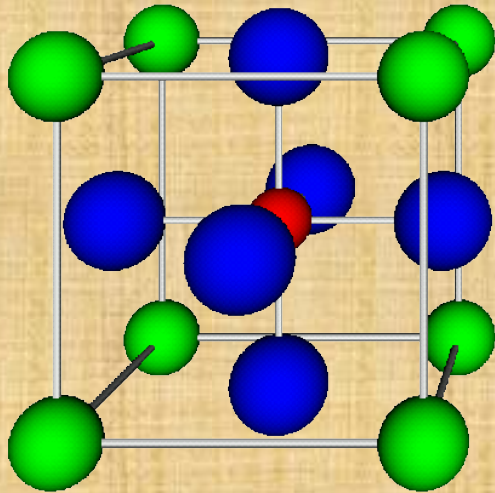
1. Pennsylvania State University, USA
2. A.F. Ioffe Institute, USSR



typical complex oxides with perovskite structure

# Relaxors

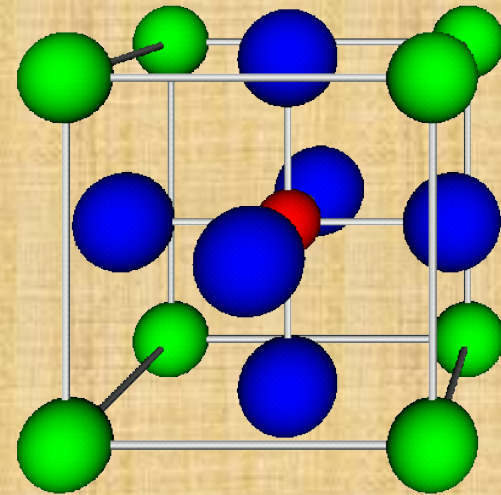
Regular ferroelectric  $\text{BaTiO}_3$



$T > T_c$  (cubic)



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

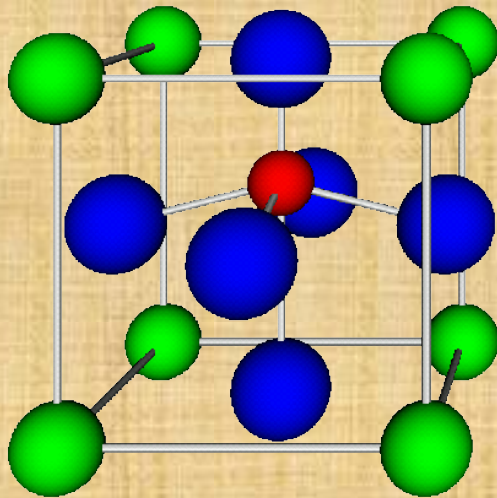


(cubic)



# Relaxors

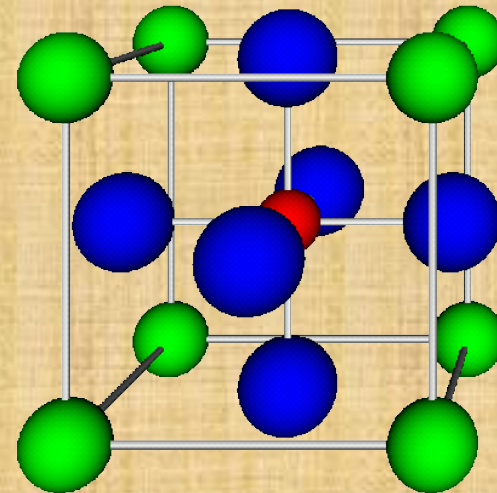
Regular ferroelectric  $\text{BaTiO}_3$



$T < T_c$  (tetragonal)



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

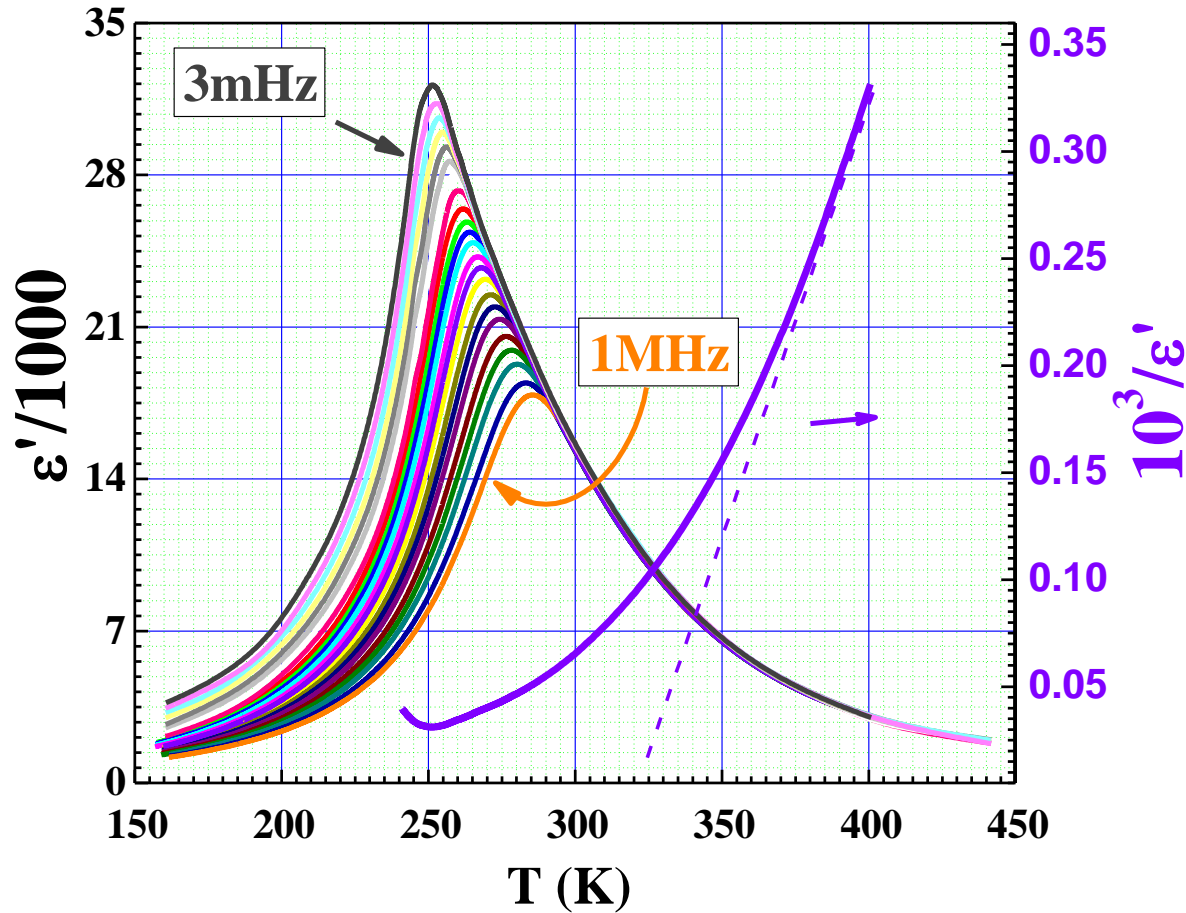


(cubic)



# Relaxor. Frequency dispersion

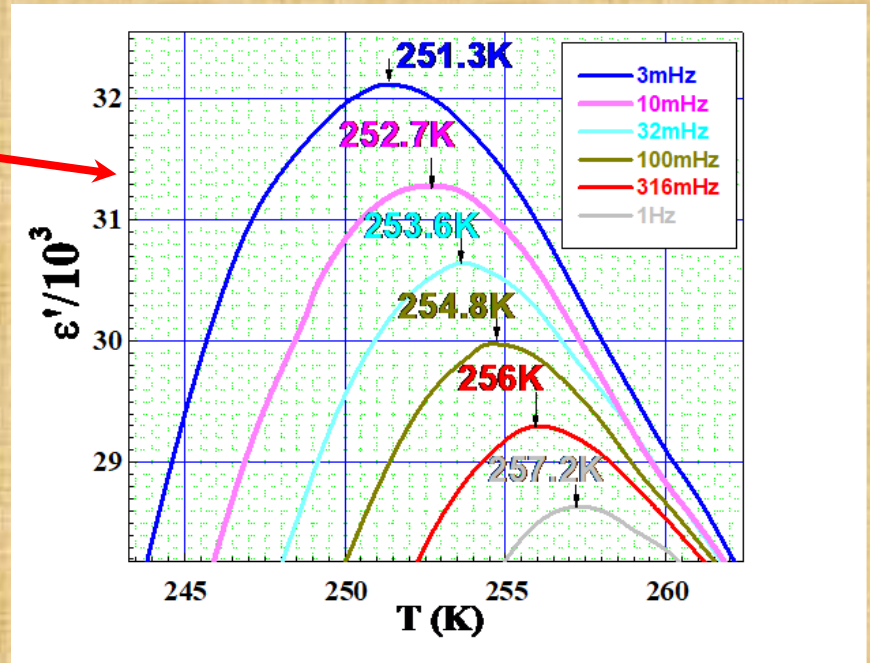
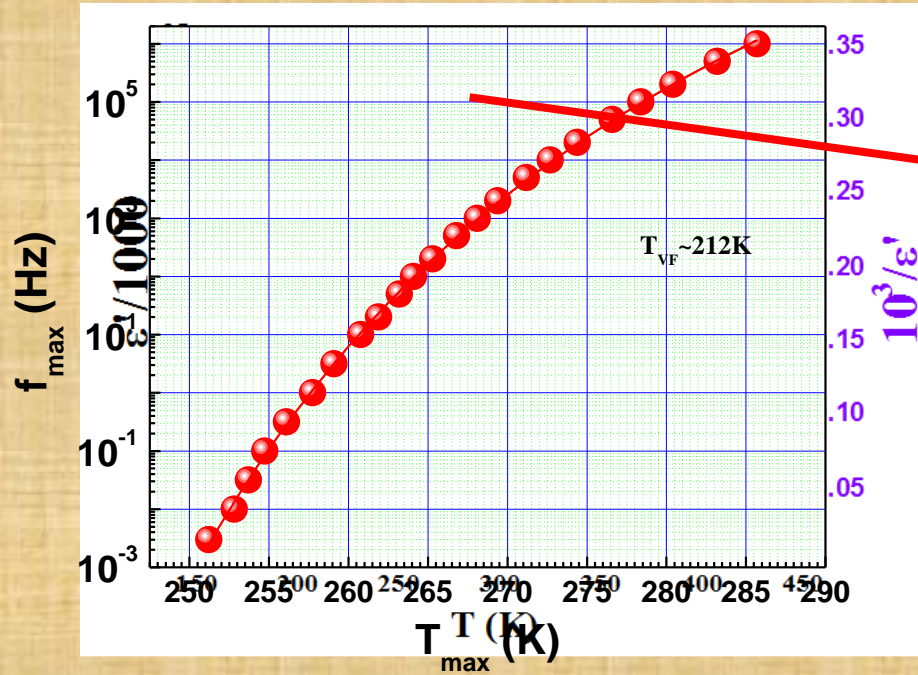
$\epsilon'_{\max}$  and  $T_{\max}$  depend on the measuring frequency



$\epsilon'$  does not follow Curie-Weiss law

Temperature dependencies of  $\epsilon'$  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

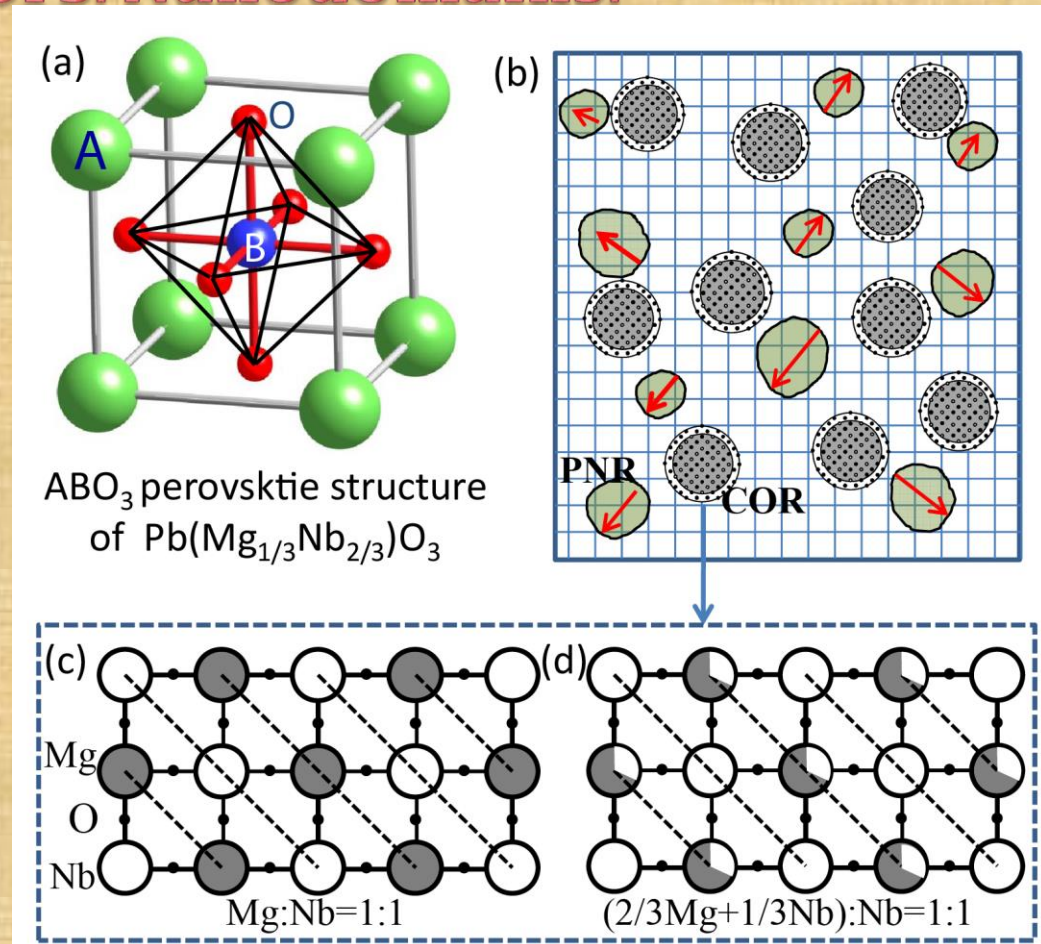
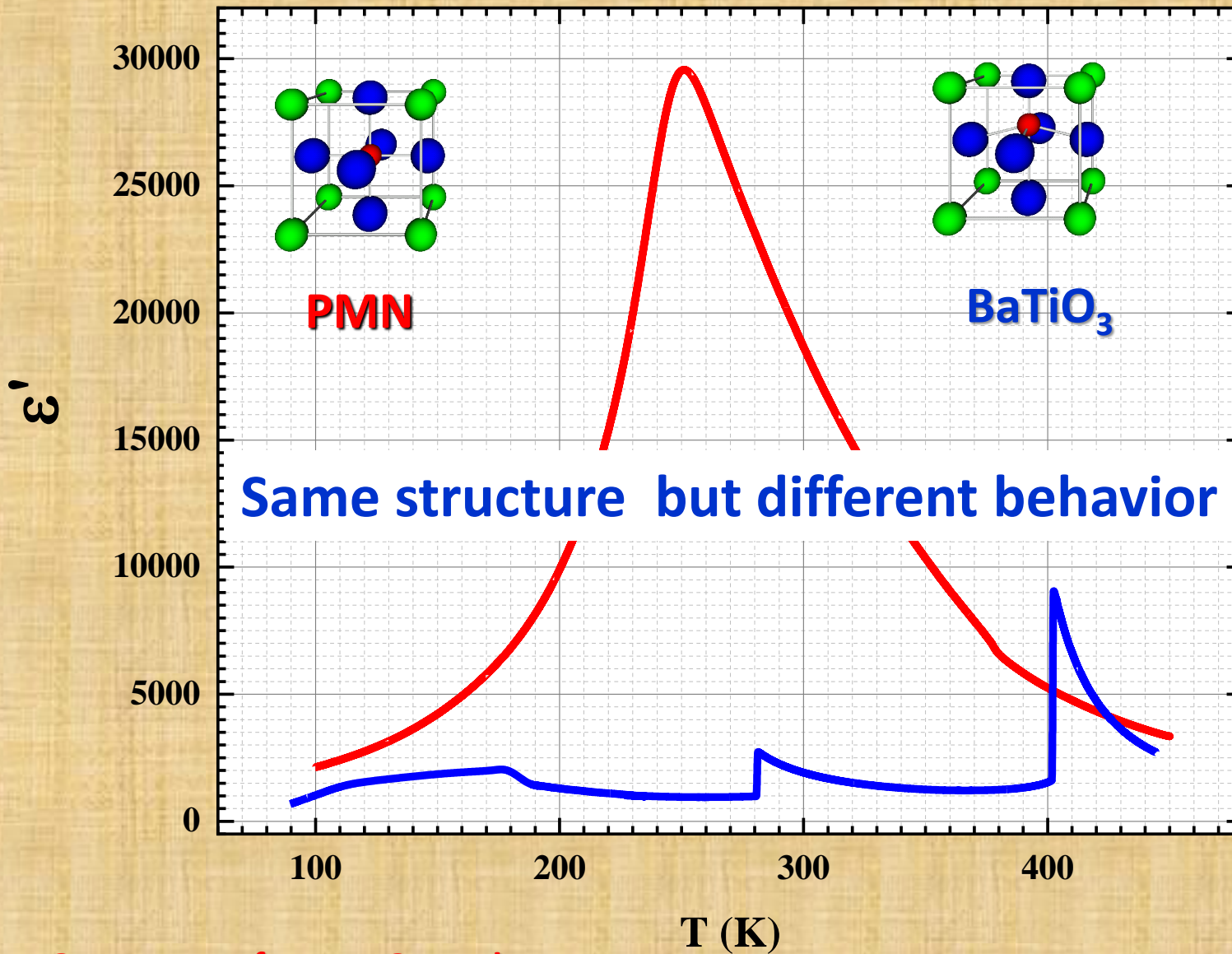


Figure 3.

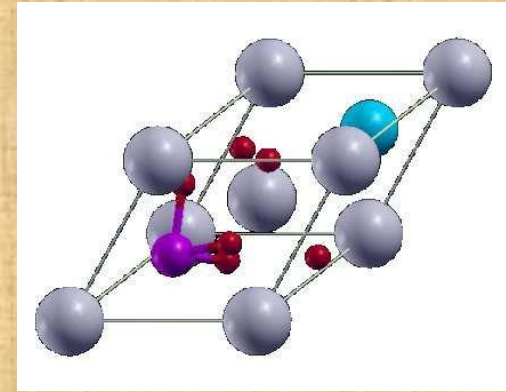
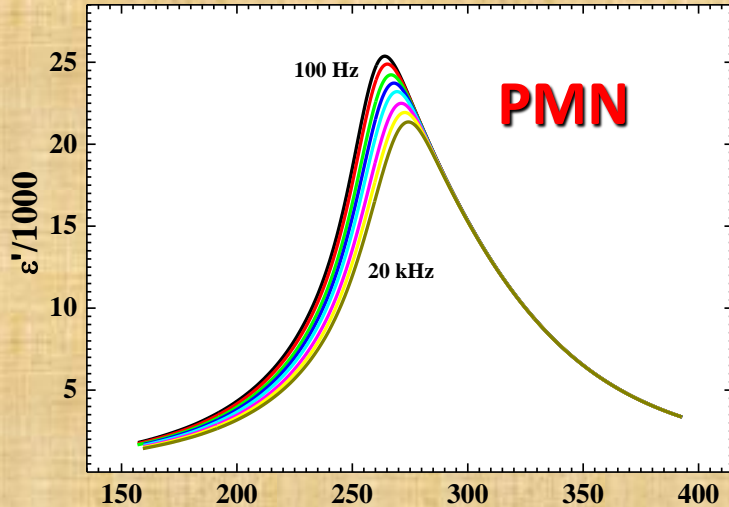
(a)  $ABO_3$  perovskite structure. (b) Model for relaxor structure. PNR and COR represent the polar nano-region and chemically order region, respectively. (c) & (d) show two models of atom arrangement for COR. To maintain the electric neutrality, a Nb-rich layer is required for case (c).

# Regular Ferroelectrics - Relaxors

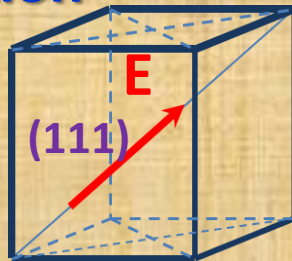


BTO courtesy of James Graessle

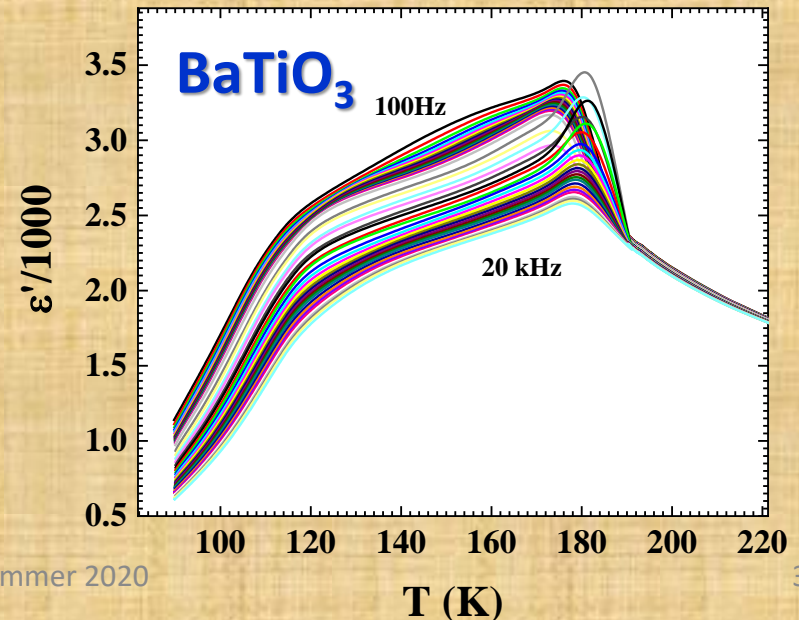
# Disorder in Regular Ferroelectrics



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



**BaTiO<sub>3</sub>** Rhombohedral phase



**BTO** courtesy of James Graessle



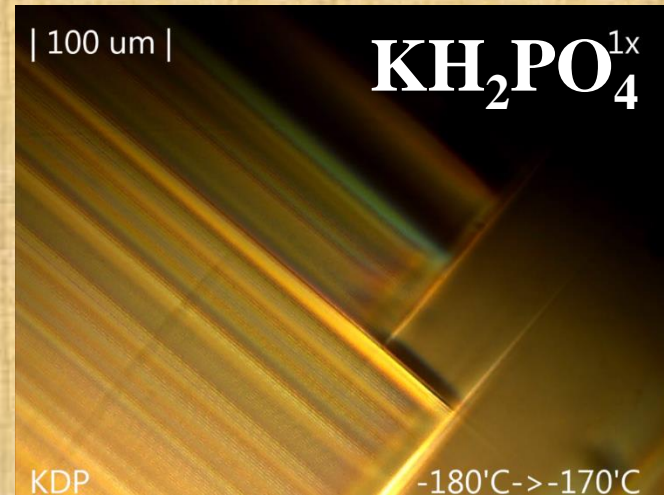
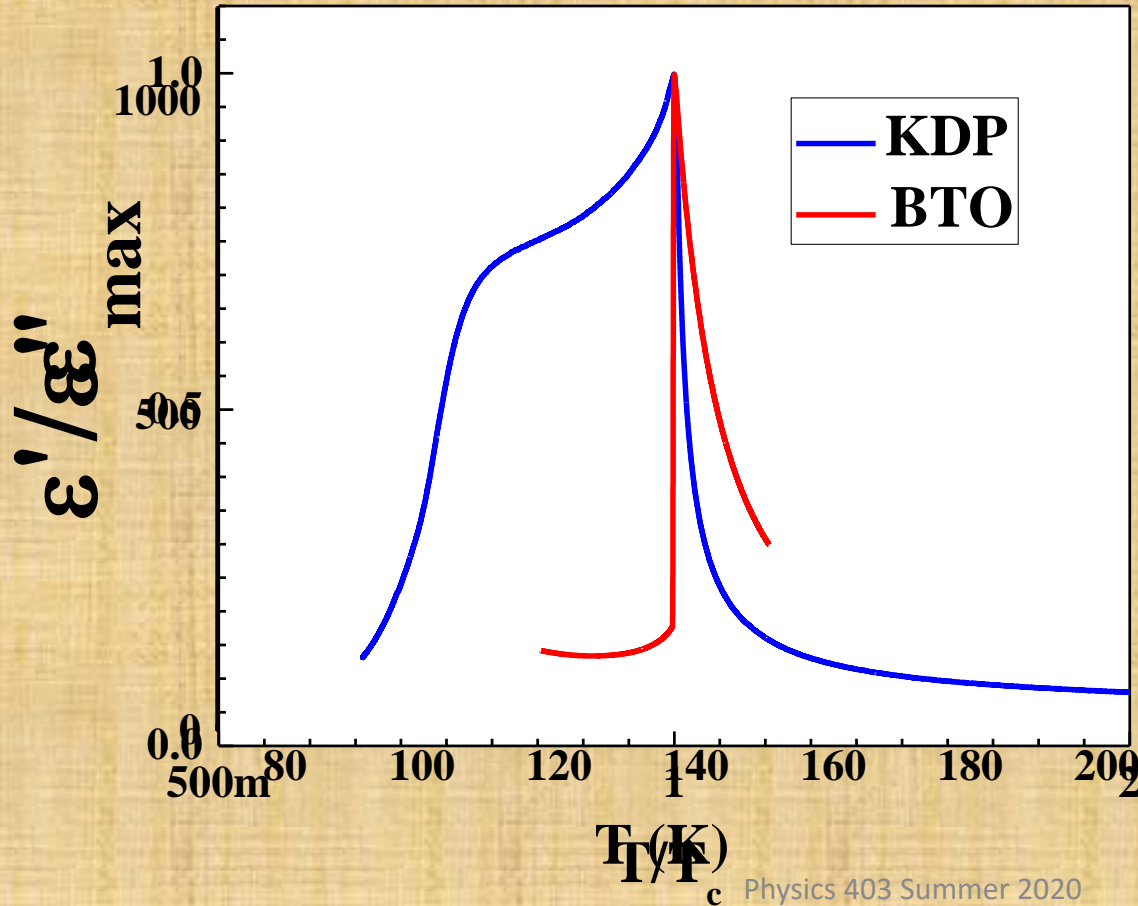
# Disorder in Regular Ferroelectrics. KDP family



KDP -  $T_c \sim 120$  K

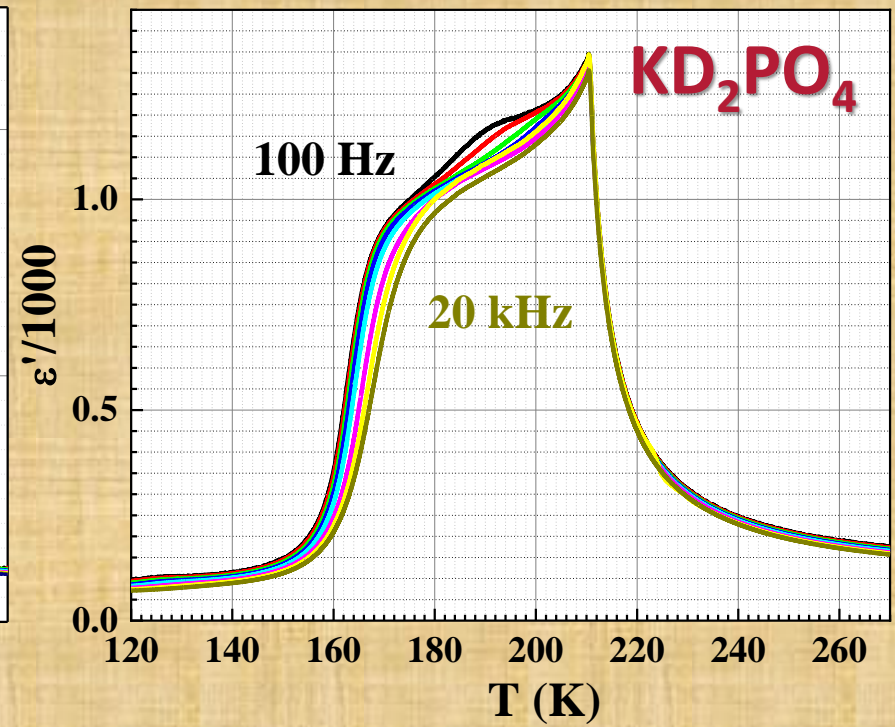
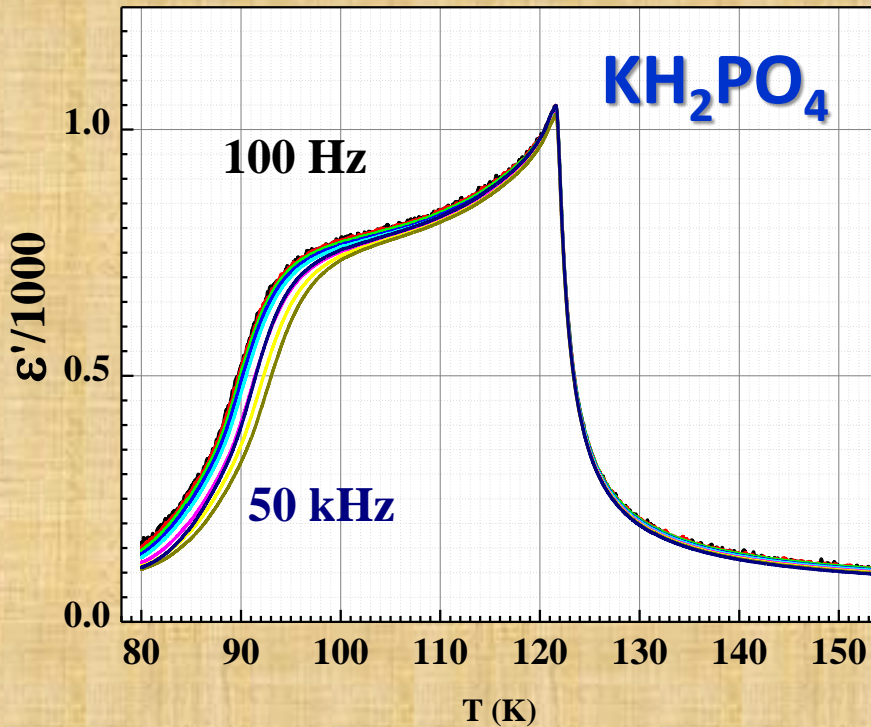


Deuterated analog DKDP  $T_c \sim 230$  K



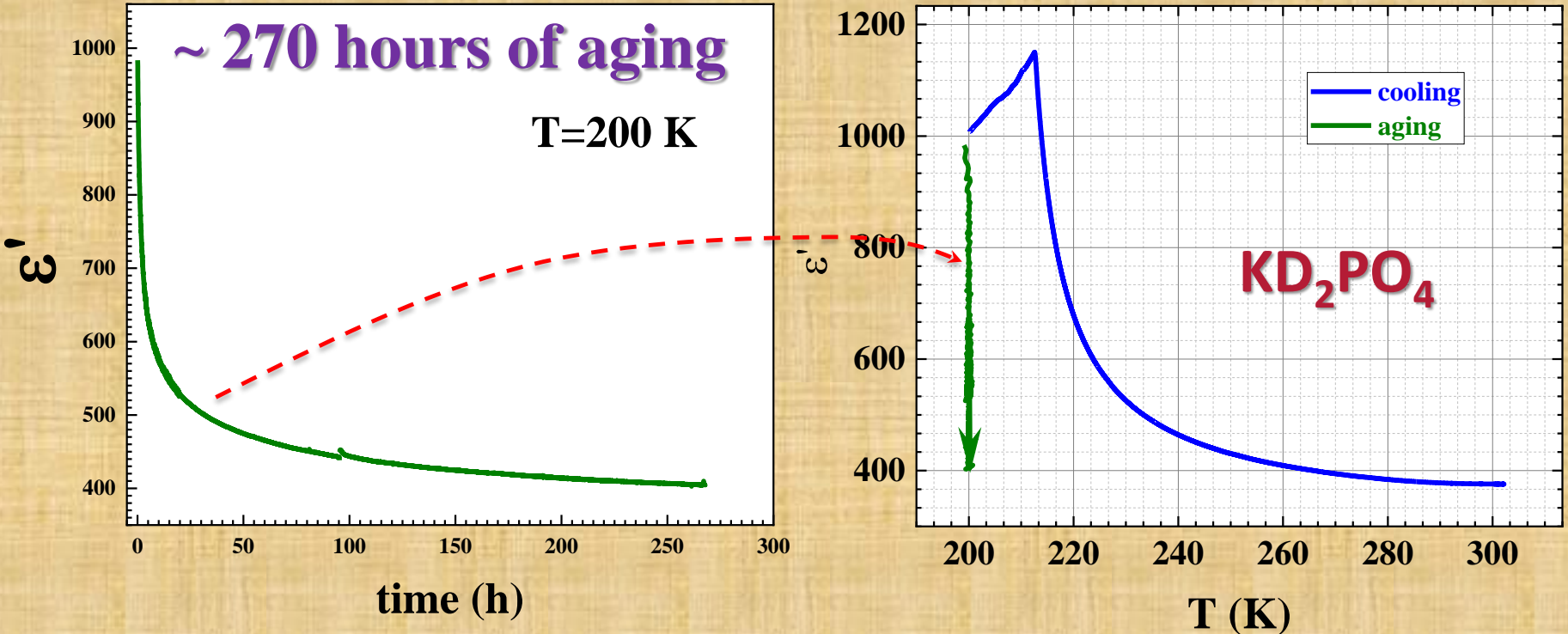
# Disorder in Regular Ferroelectrics. KDP family

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)



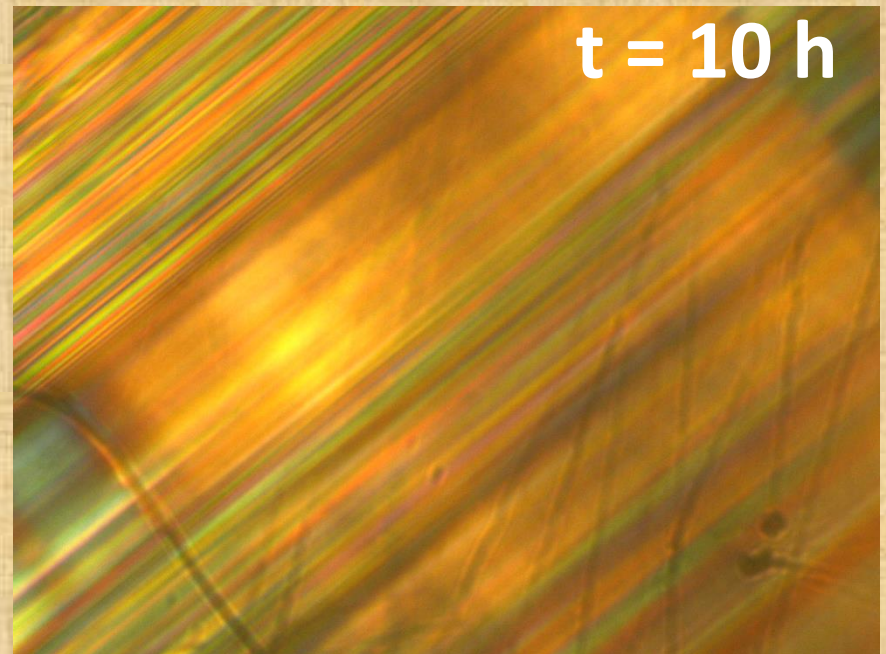
# Disorder in Regular Ferroelectrics. KDP family

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



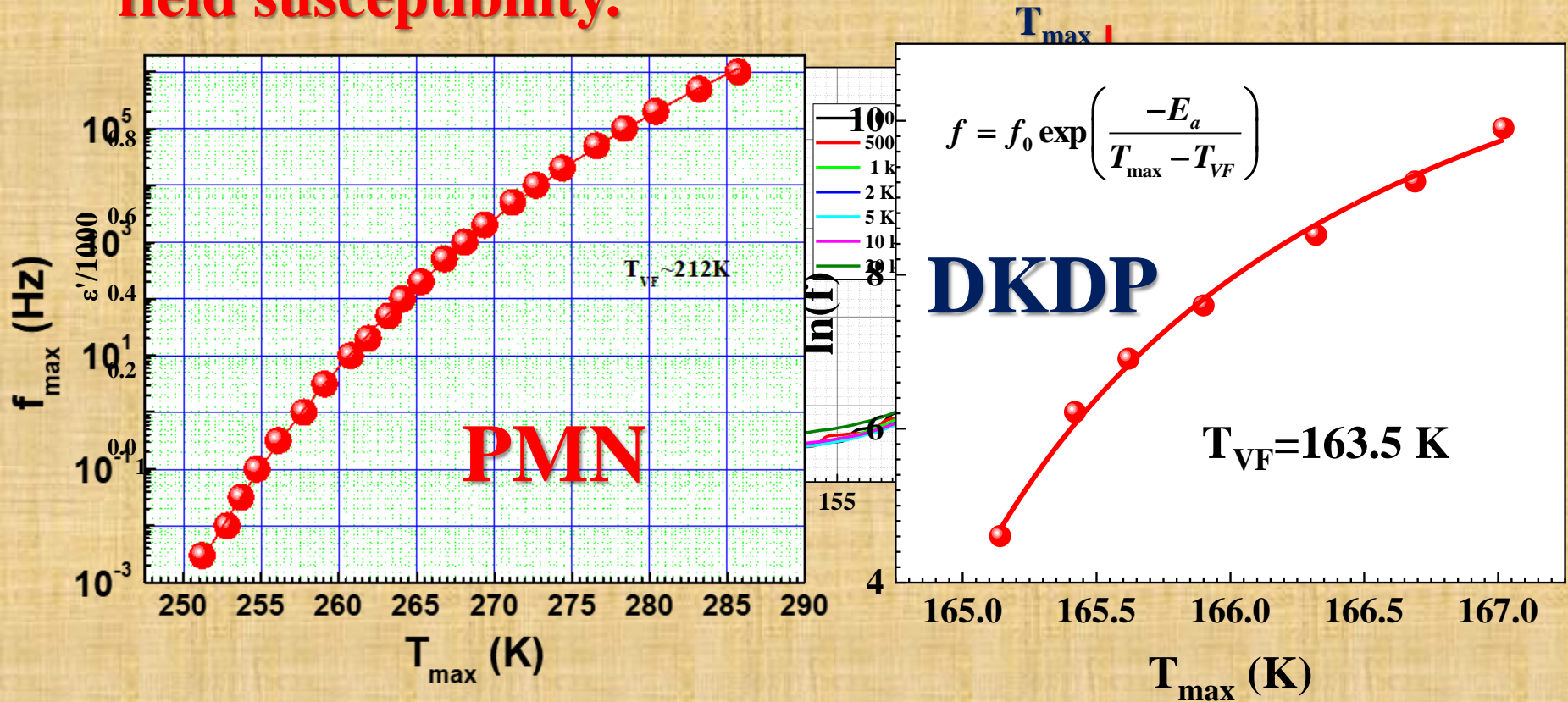
# Disorder in Regular Ferroelectrics. KDP family

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.



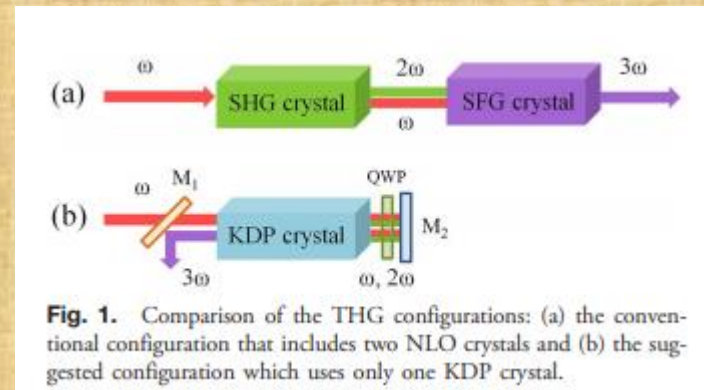
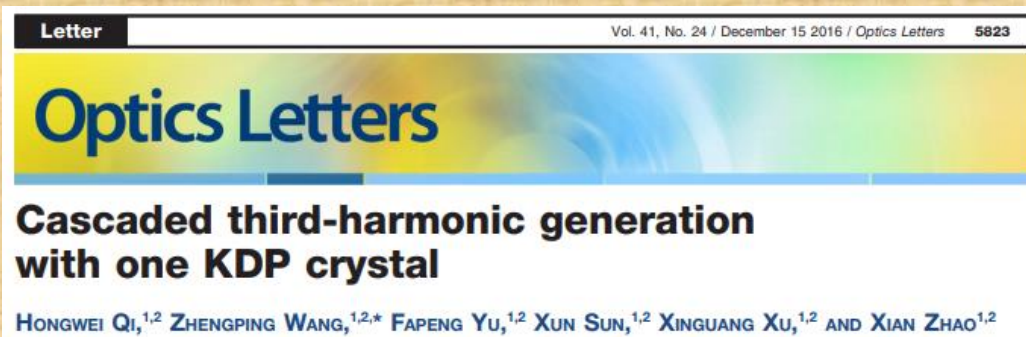
# Disorder in Regular Ferroelectrics. KDP family

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](#)

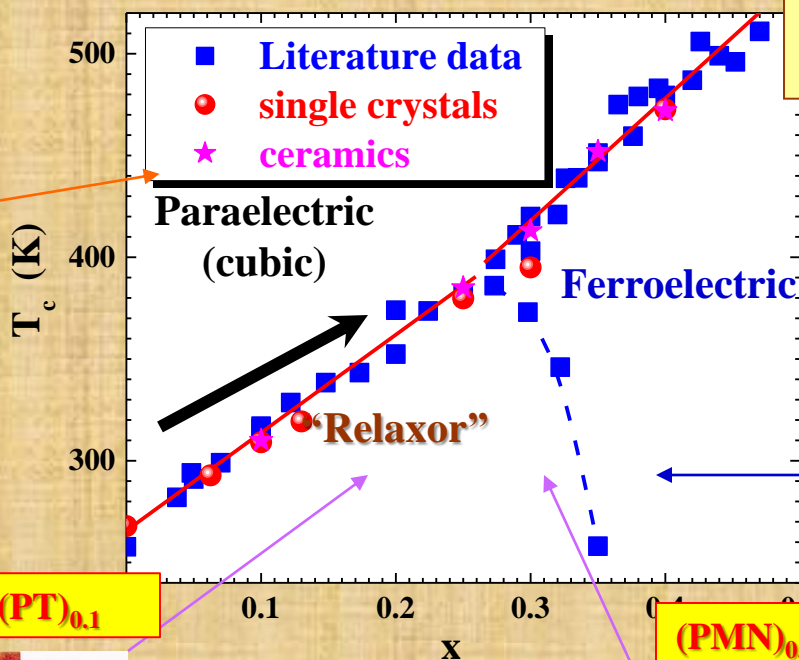
# Solid solution relaxor-regular ferroelectric.

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

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



610K

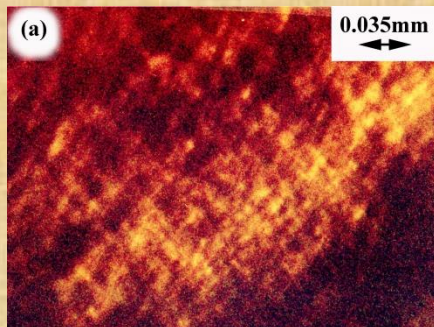


PT:  $\text{PbTiO}_3$ , ferroelectric with Curie temperature 763K

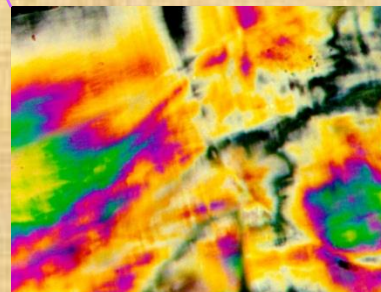
$(\text{PMN})_{0.6}(\text{PT})_{0.4}$



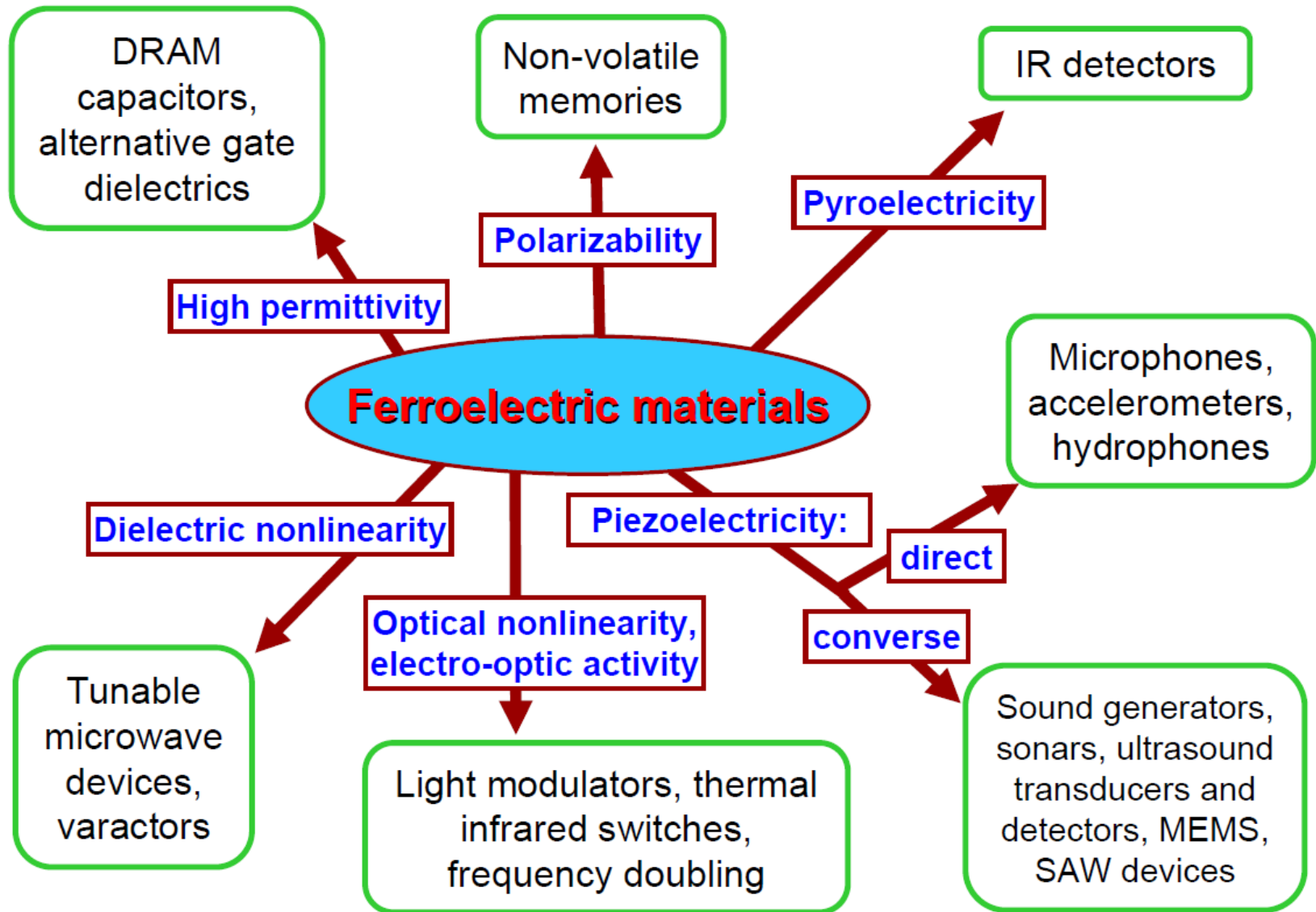
$(\text{PMN})_{0.9}(\text{PT})_{0.1}$



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

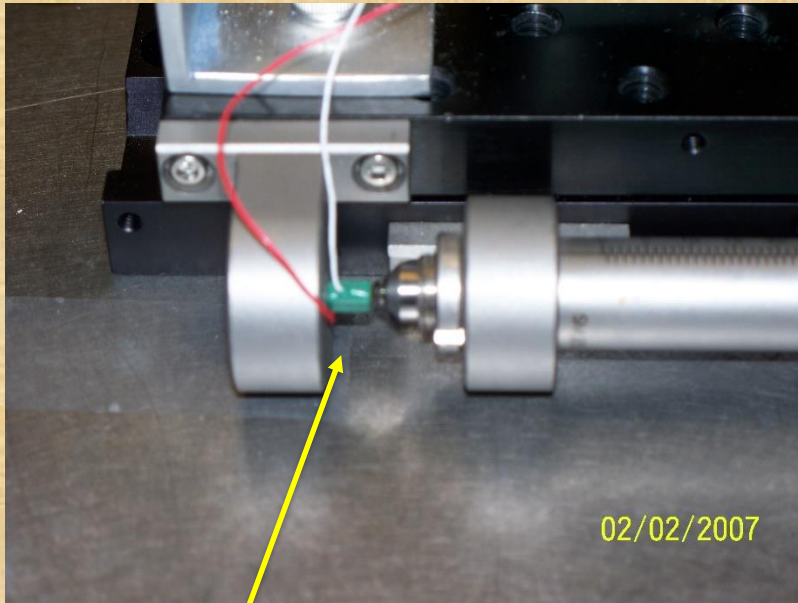


# Applications of ferroelectrics

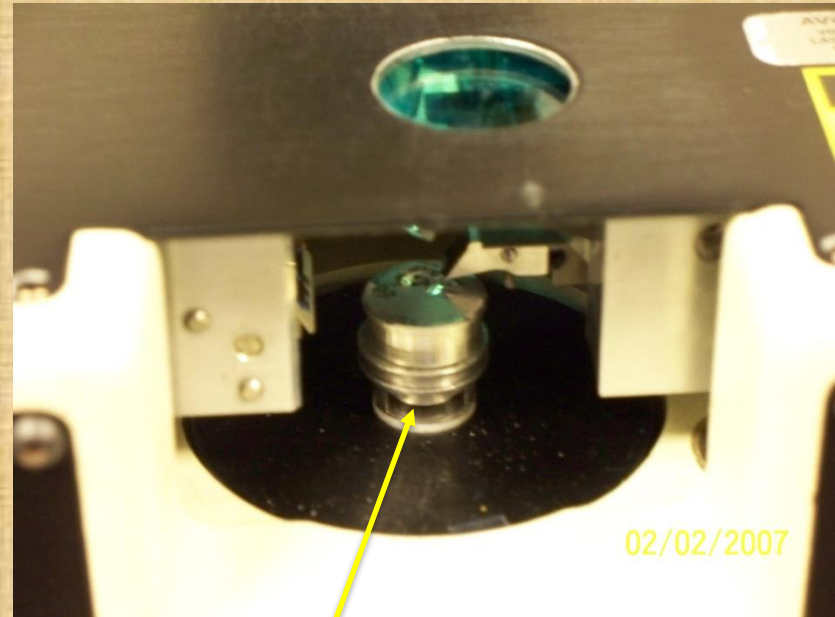




# Applications of Ferroelectrics. Physics 403 Lab



**Quantum Optics**

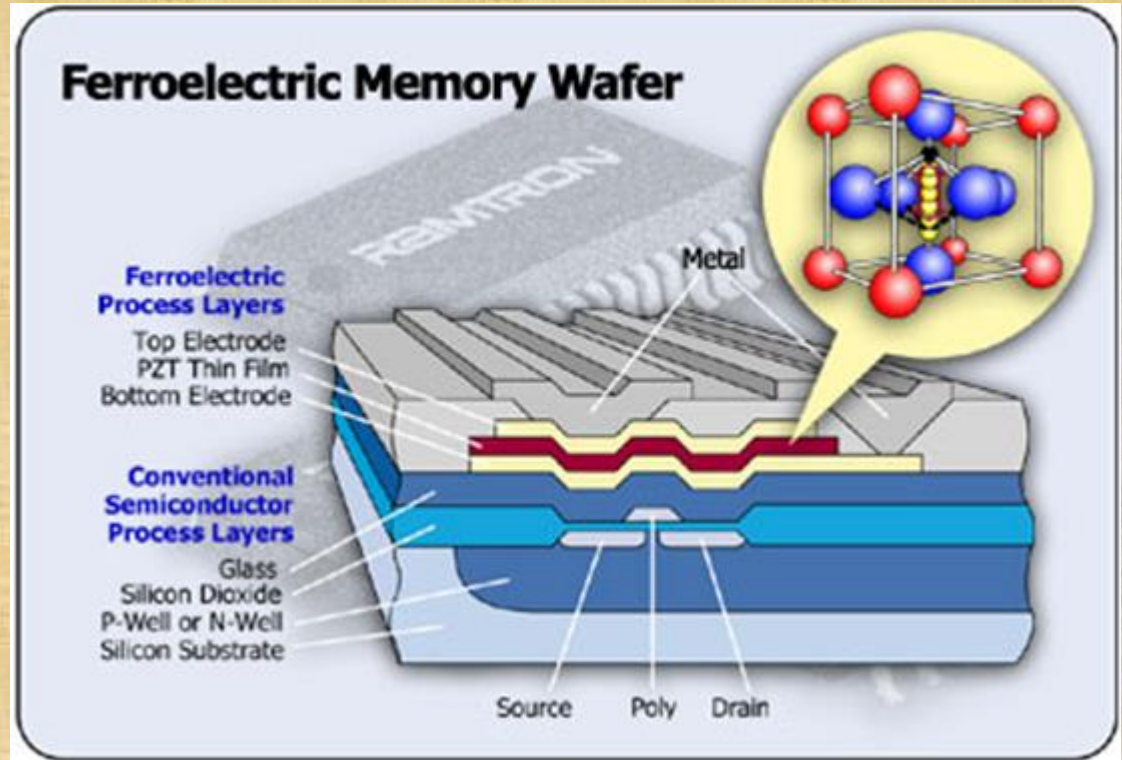


**AFM experiment**

# 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

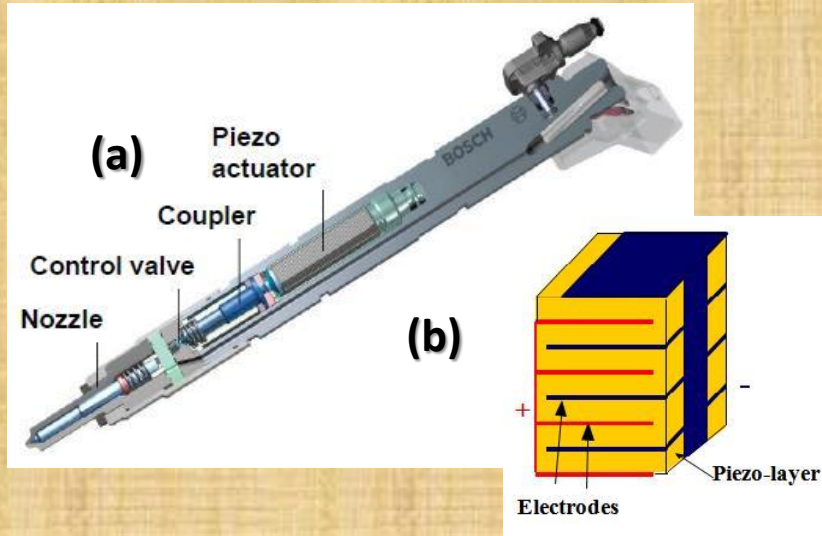
Dafei Jin,<sup>1</sup> Anshuman Kumar,<sup>1</sup> Kin Hung Fung,<sup>1,2</sup> Jun Xu,<sup>1</sup> and Nicholas X. Fang<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

<sup>2</sup>Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China



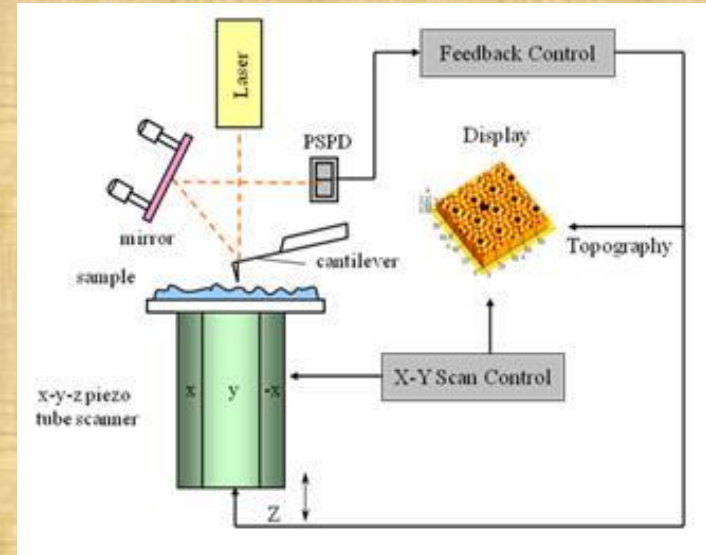
# Applications. Actuators



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

Courtesy Technische Universität Darmstadt

## Atomic Force Microscope



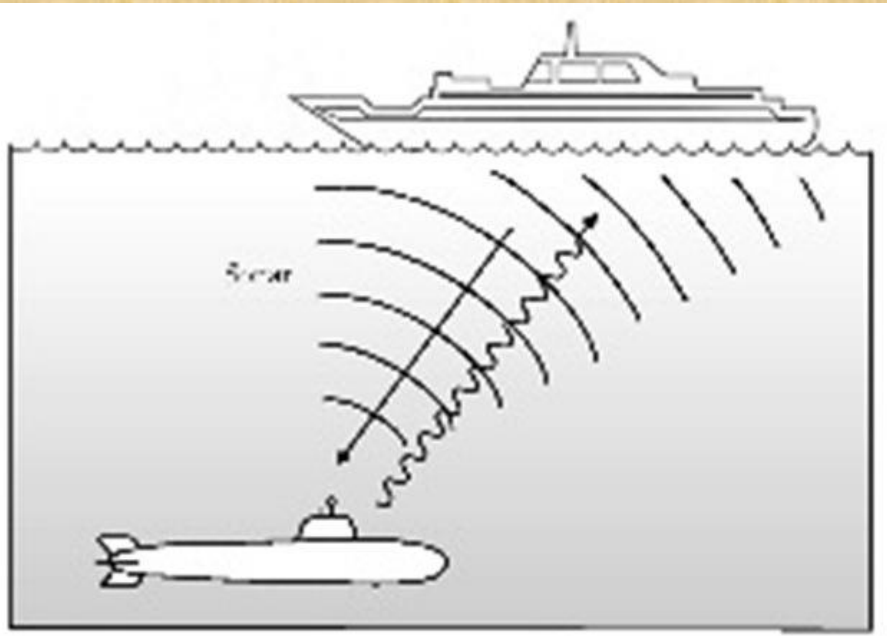
Lead Zirconium Titanate piezo scanner

**PI** ([www.pi.ws](http://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

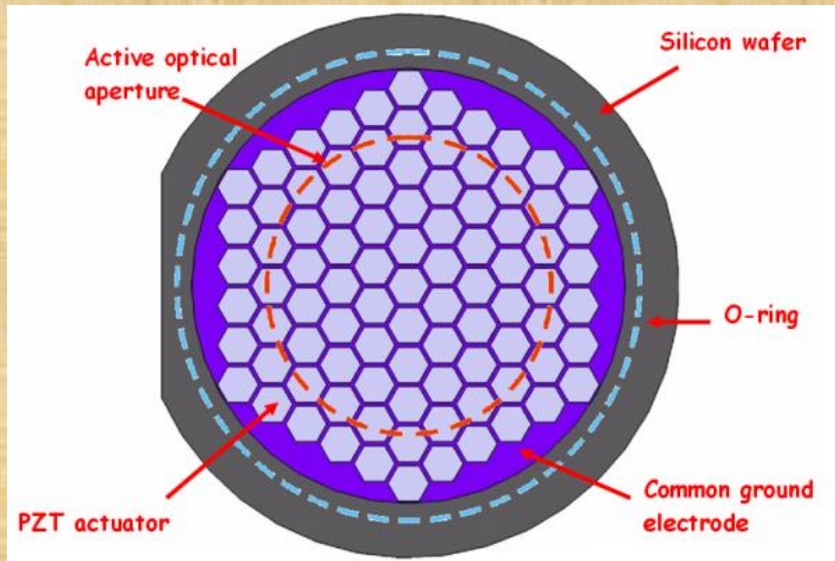
## Civil Applications



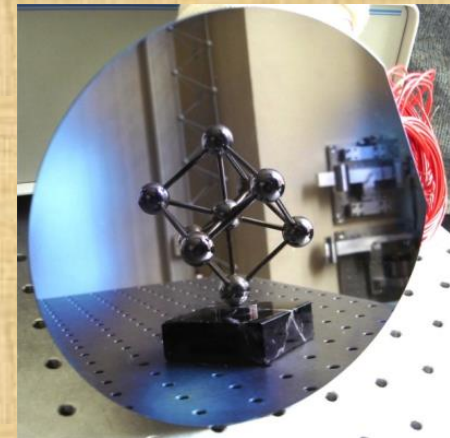
Fish Finder

Courtesy **FURUNO**

# Applications. Adaptive Optics

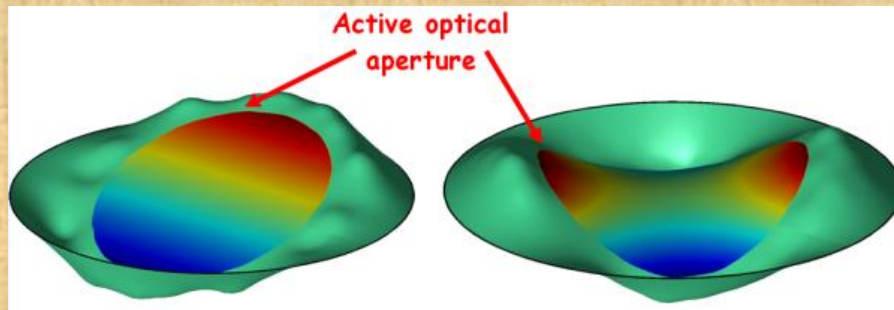


Soldered control and mass wires



Reflecting surface

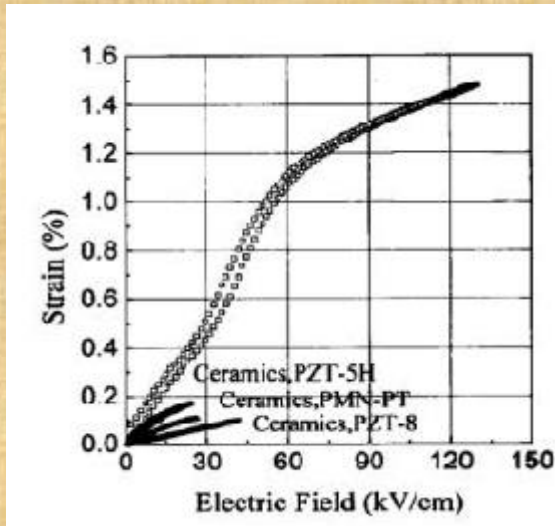
PZT – Lead Zirconium Titanate  $\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$



Courtesy of

Active Structures Laboratory

# 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