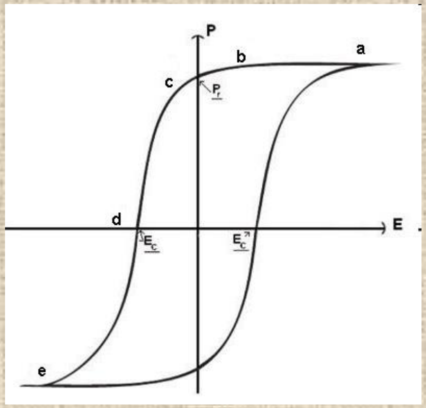
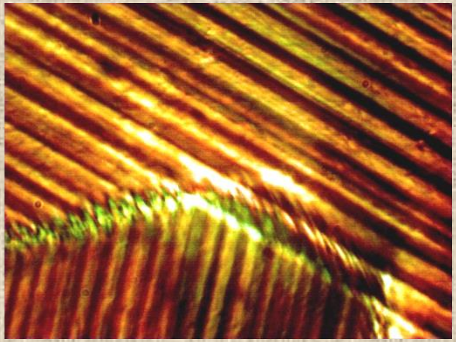
Ferroelectricity. Phase transition. Material properties





Ferroelectricity.
outline

- Ferroelectricity. Definition
- Discovery
- Main properties
- Phenomenological theory
- Some materials
- Relaxors
- Applications

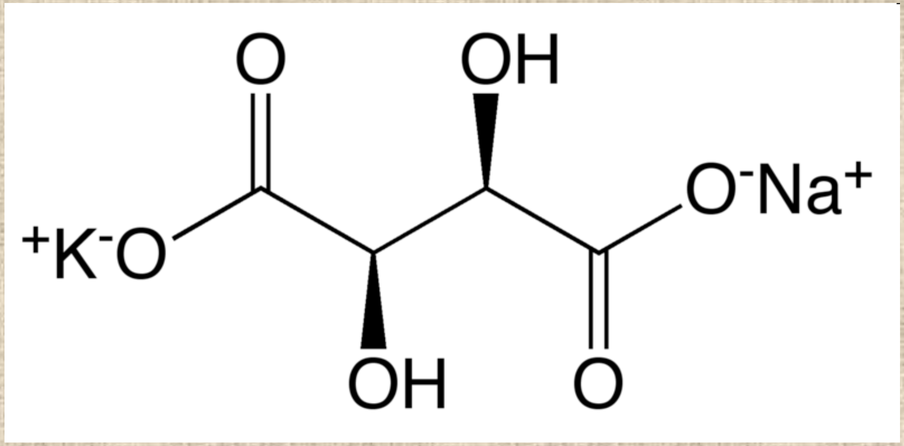
Ferroelectricity. Definitions.

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: Discovery

Rochelle Salt $KNaC_4H_4O_6*4H_2O$



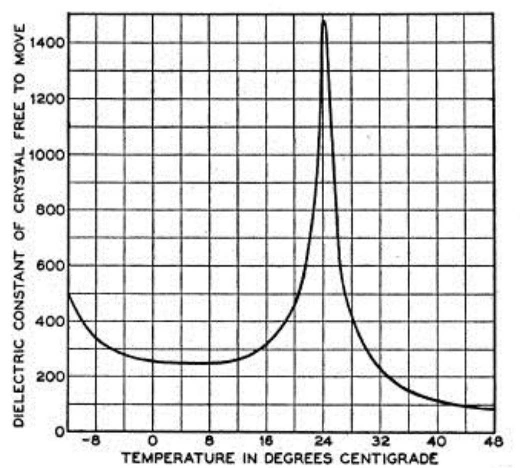
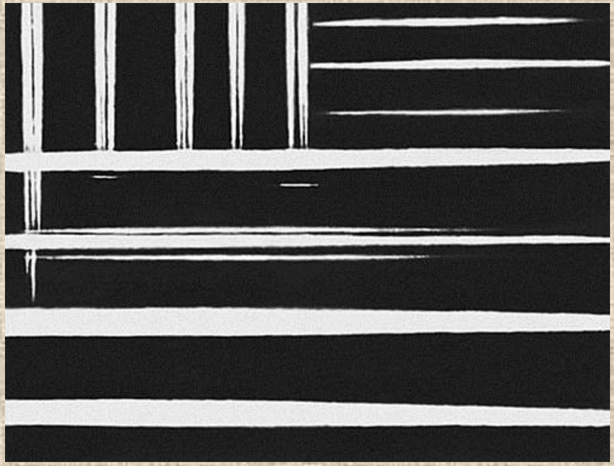


FIG. 3. Dielectric constant of an X cut Rochelle salt crystal free to move plotted as a function of the temperature.



Ferroelectricity: Discovery

Rochelle Salt $KNaC_4H_4O_6*4H_2O$

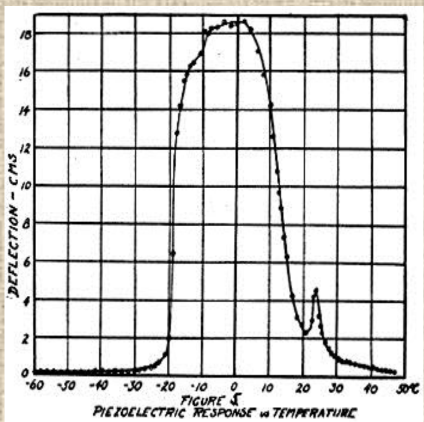


Fig3. Piezoelectric response as a function of temperature [2]

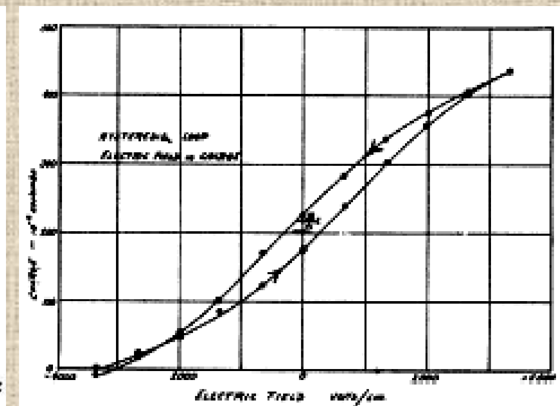


Fig.1. The first published hysteresis loop [1]

Joseph Valasek (1897-1993)
University of Minnesota

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

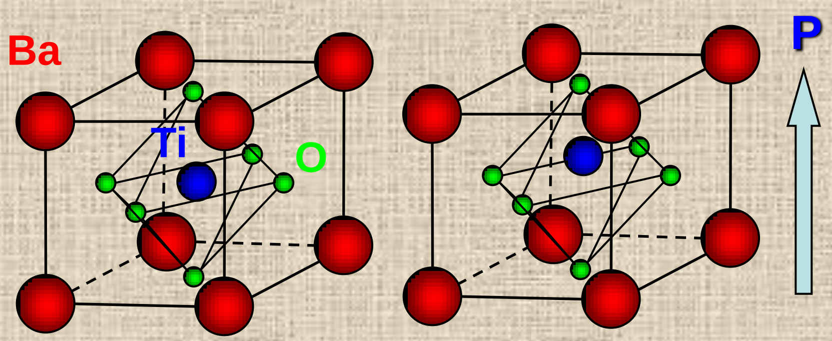
PIEZO-ELECTRIC AND ALLIED PHENOMENA IN ROCHELLE SALT.[1]

By J. Valasek.

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

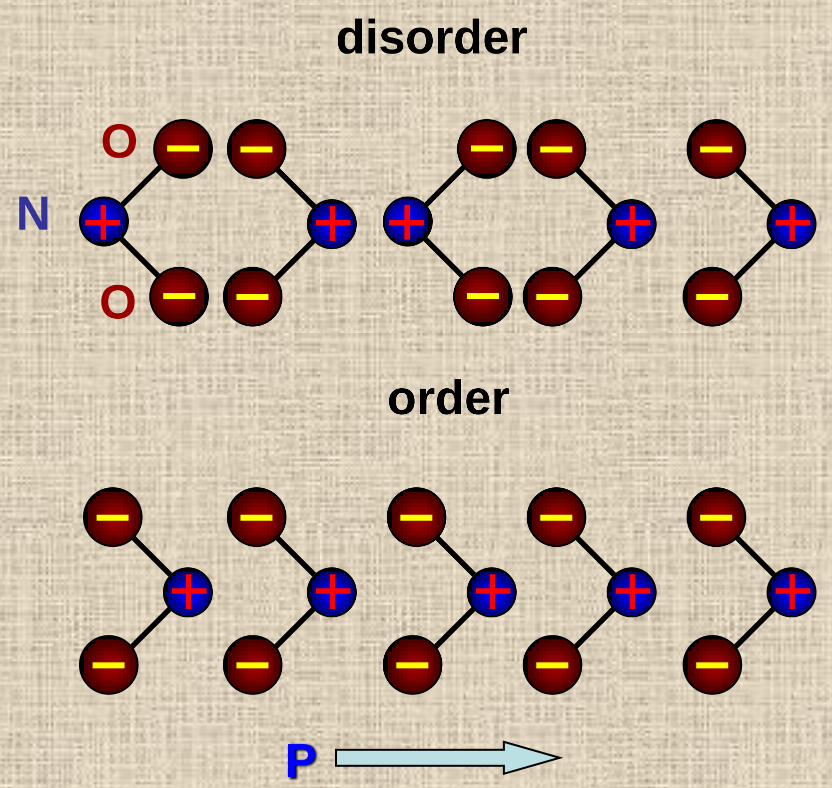
Ferroelectricity: Two classes of ferroelectrics

Displacement type



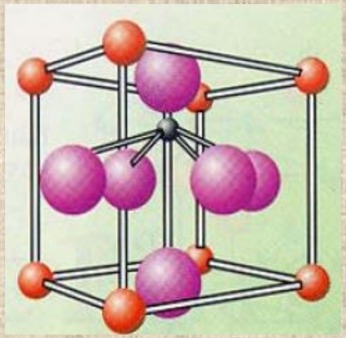
$BaTiO_3$

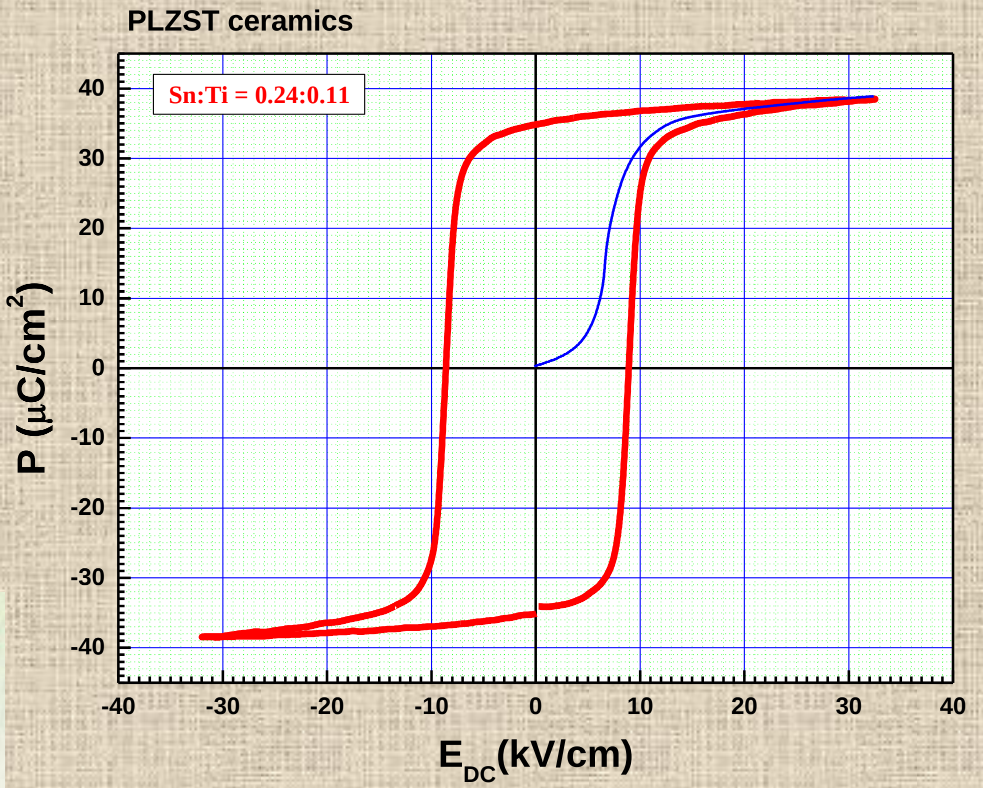
Order-Disorder

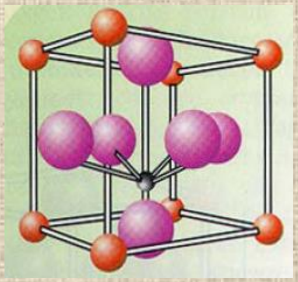


$NaNO_2$

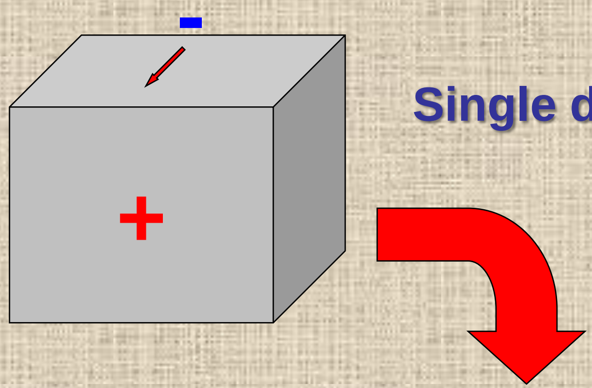
Ferroelectricity: Polarization reversible (P-E hysteresis)







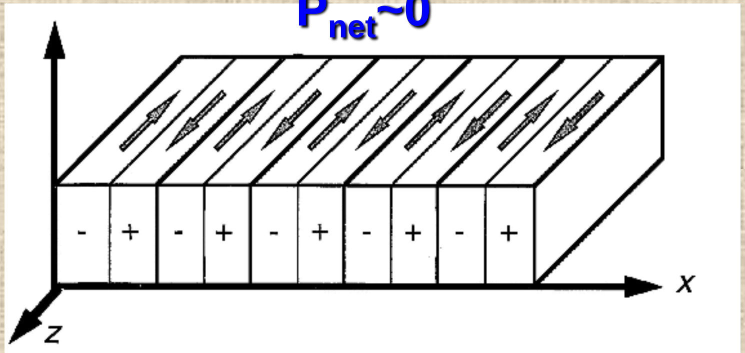
Ferroelectricity: Domains



Single domain state

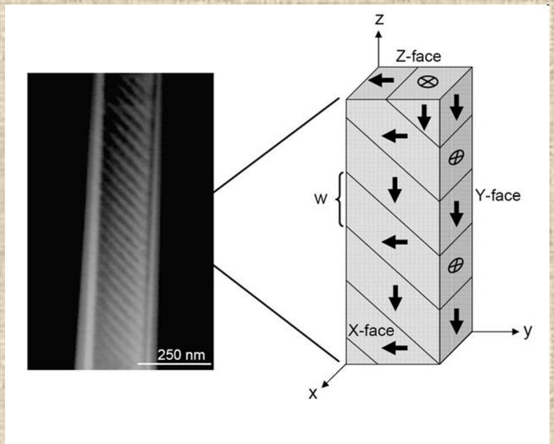
Multi domain state

P_{net}~0



180º domain pattern

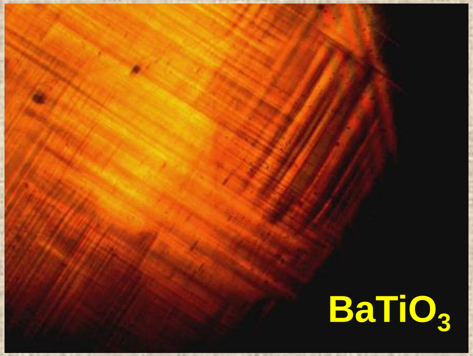
Y Lu et al. Science 1997;276:2004-2006



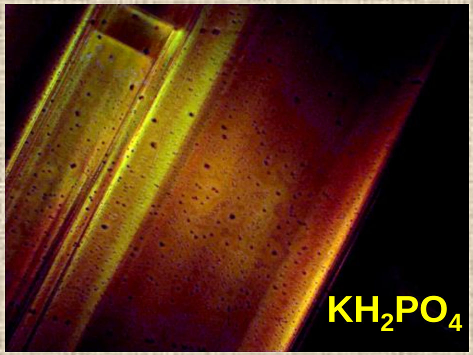
90º domains

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

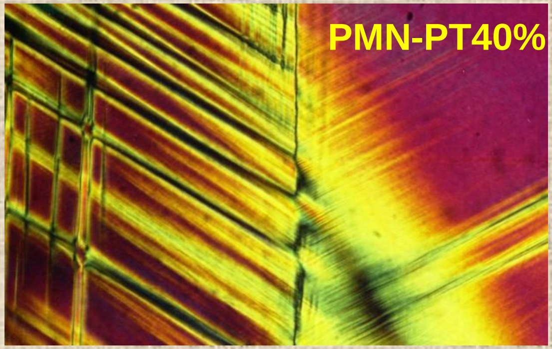
Ferroelectricity: Domains

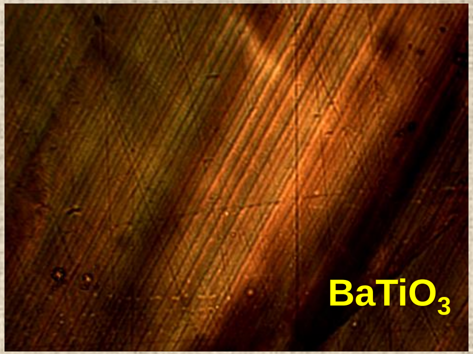


Courtesy of Benjamin Vega-Westhoff and Scott Scharfenberg, P403, Fall2009



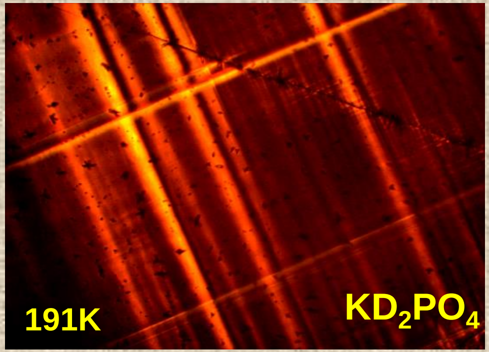
Courtesy of Allison Pohl, P403, Fall2009

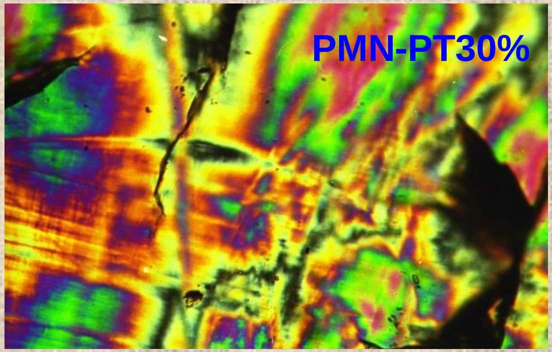




Crystal from Forschungsinstitut für mineralische und metallische

Werkstoffe -Edelsteine/Edelmetalle





Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy — Order parameter (polarization) — Electric field

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

To find the equilibrium solution we need to find the minima of FP by solving the equation:

$$\frac{\partial F}{\partial P} = 0$$

Ignoring higher terms we can get the linear solution:

$$\frac{\partial F}{\partial P} = aP - E = 0$$

$$\chi = \frac{\partial P}{\partial E} = \frac{1}{a}$$

Assuming linear dependence of a on temperature we will have:

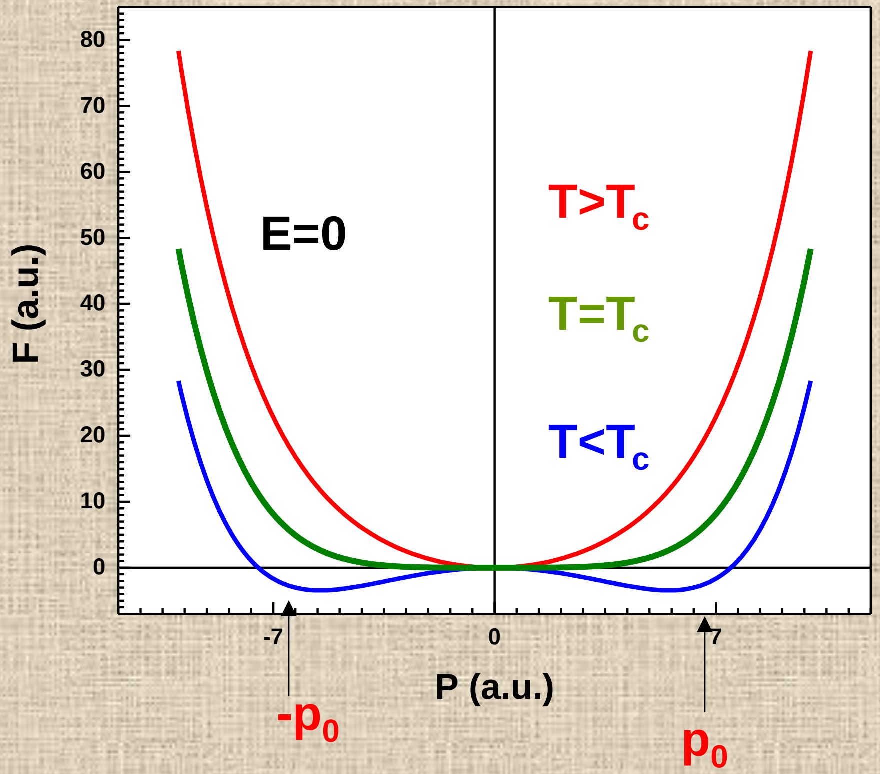
$$\alpha = \frac{1}{C}(T - T_c)$$

and finally we will have Curie-Weiss law

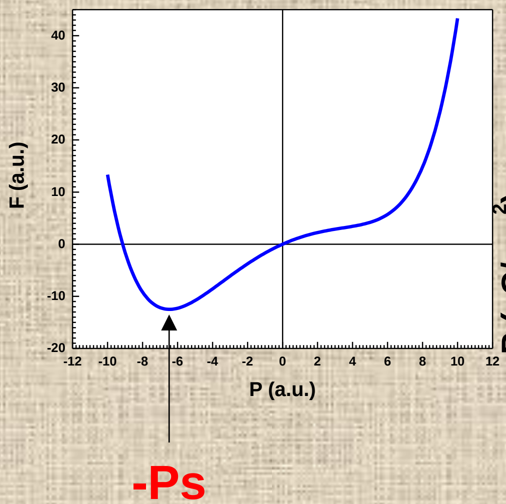
$$\chi = \frac{C}{(T - T_c)}$$

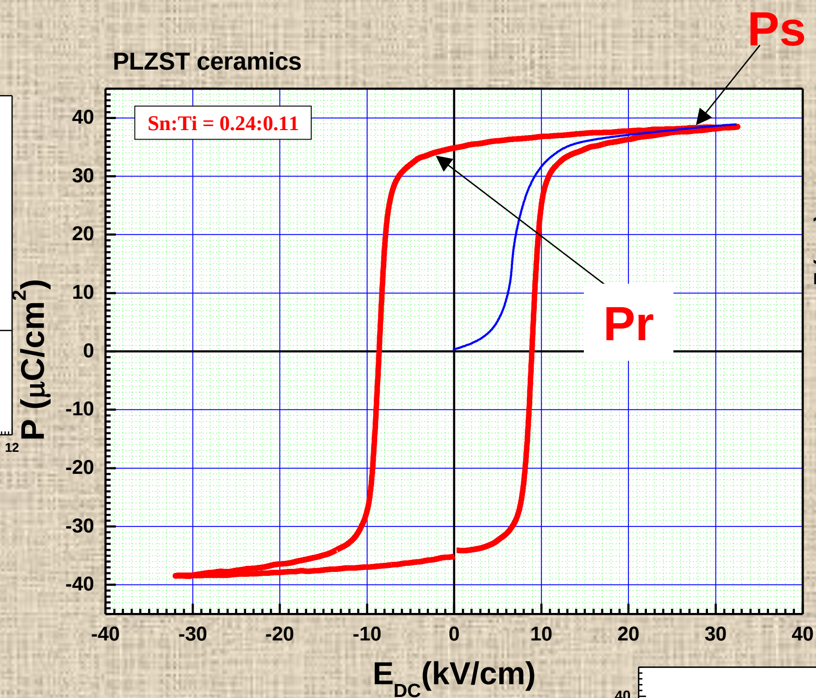
Ferroelectricity: Landau-Ginzburg phenomenological theory

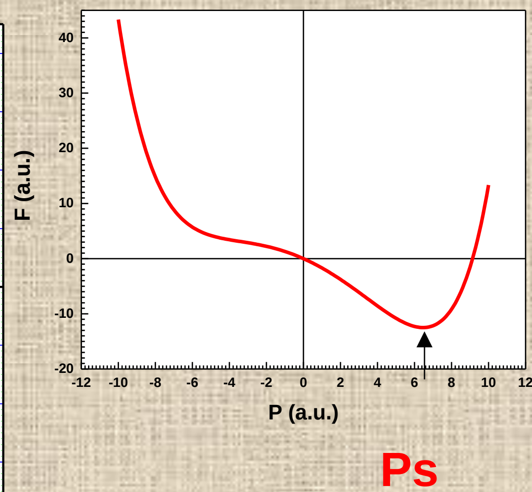
In case of b>) (C>0 also) We will have the solution for second order phase transition with two equilibrium points $-p_0$ and p_0. Both these states are equivalent



Ferroelectricity: Landau-Ginzburg phenomenological theory

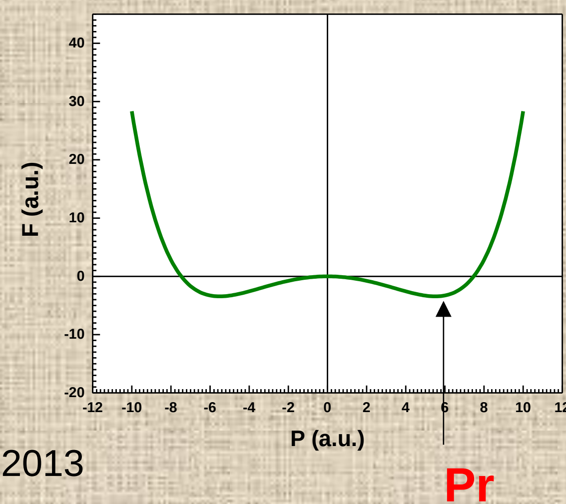






Including EP term can illustrate the P-E hysteretic behavior

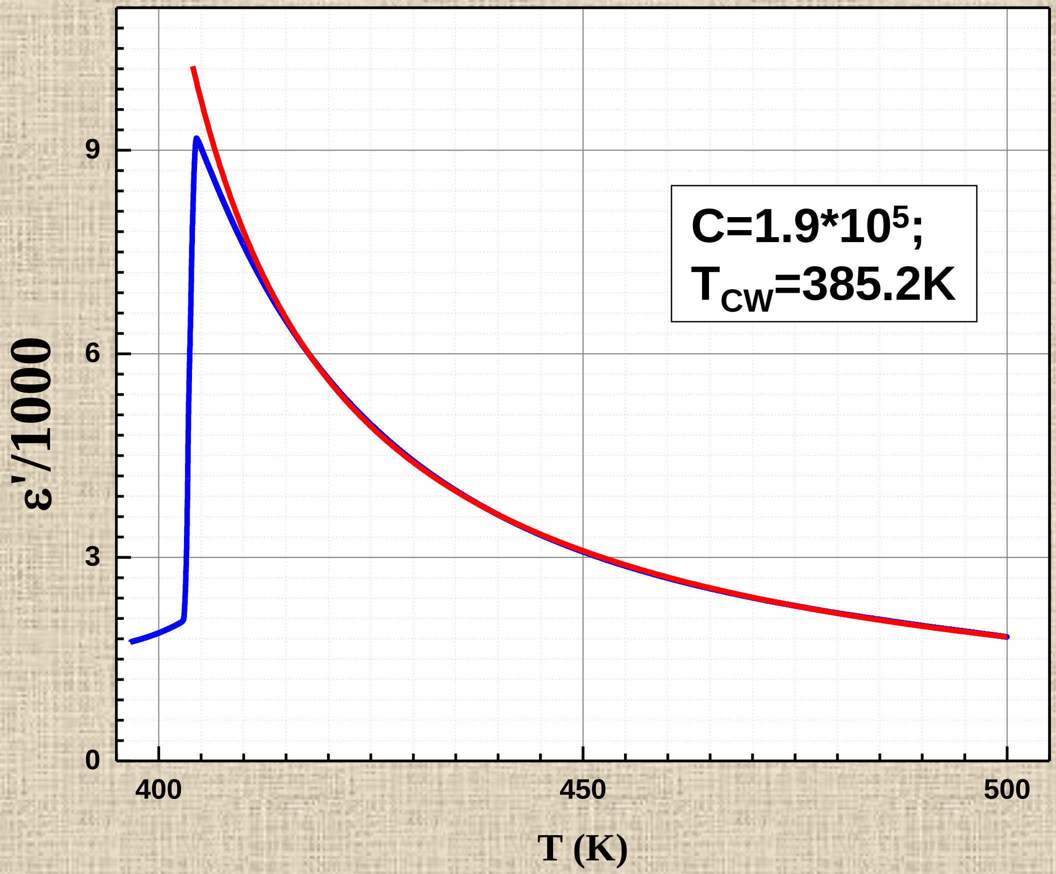
$$F_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \ldots - EP$$



Ferroelectricity: Susceptibility

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

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

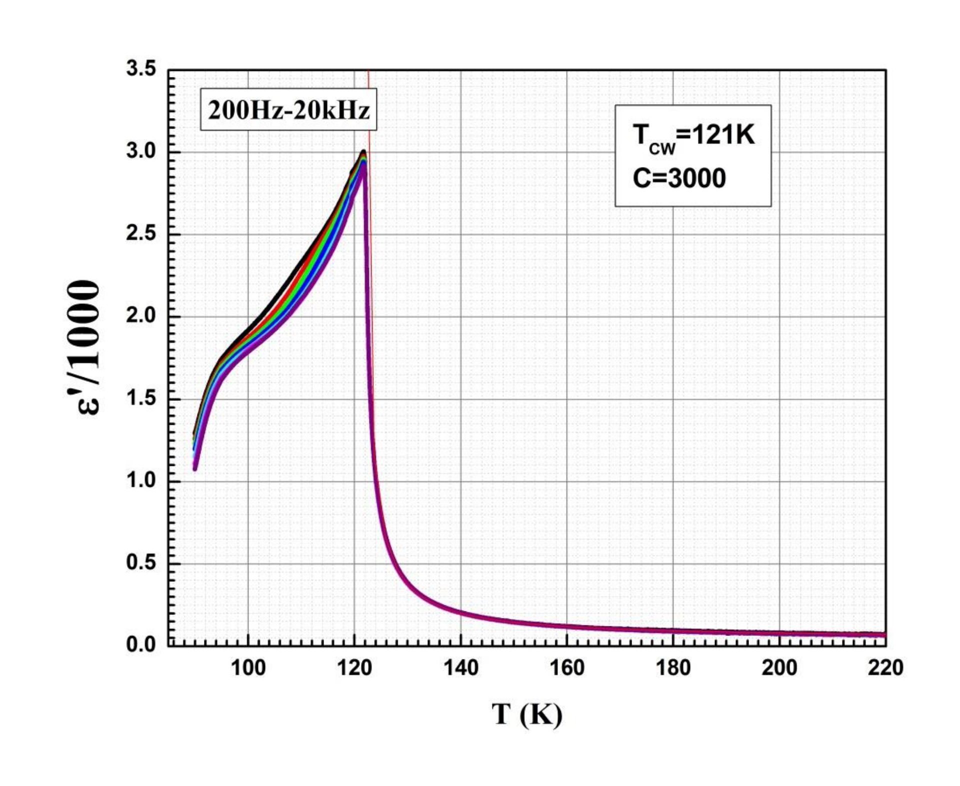


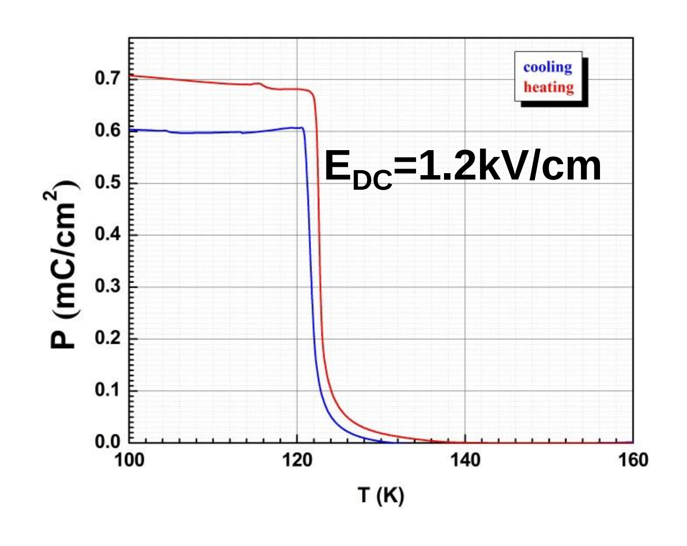
Curie-Weiss law:

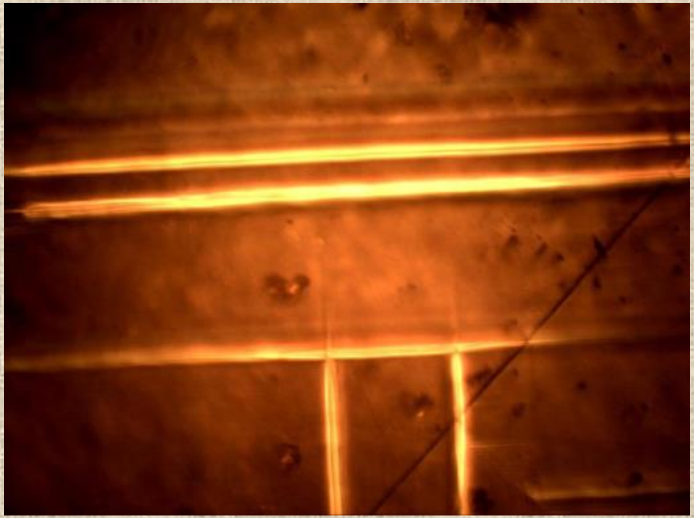
$$\varepsilon = \frac{C}{(T - T_{CW})} + \varepsilon_{00}$$

Ferroelectricity: Typical ferroelectric materials

KH_2PO_4



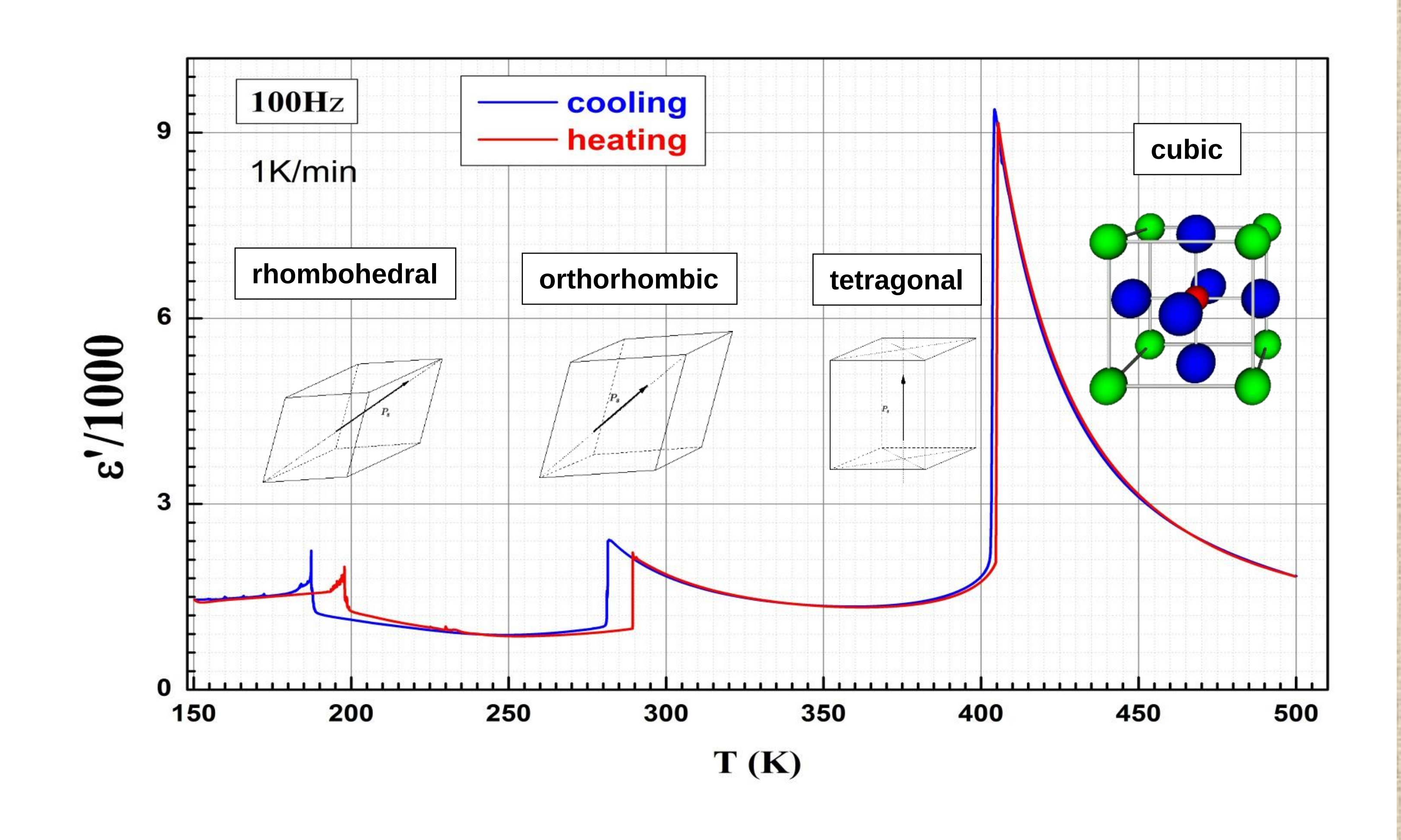




Courtesy Max Candocia, P403 Spring 2011

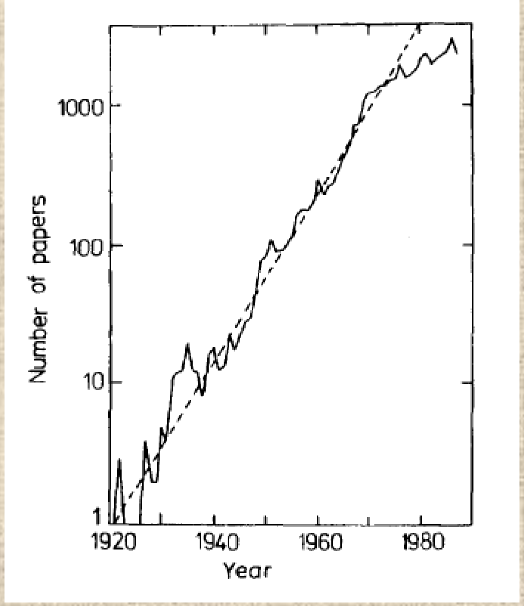
Ferroelectricity: Typical ferroelectric materials

$BaTiO_3$



Ferroelectricity: Typical ferroelectric materials

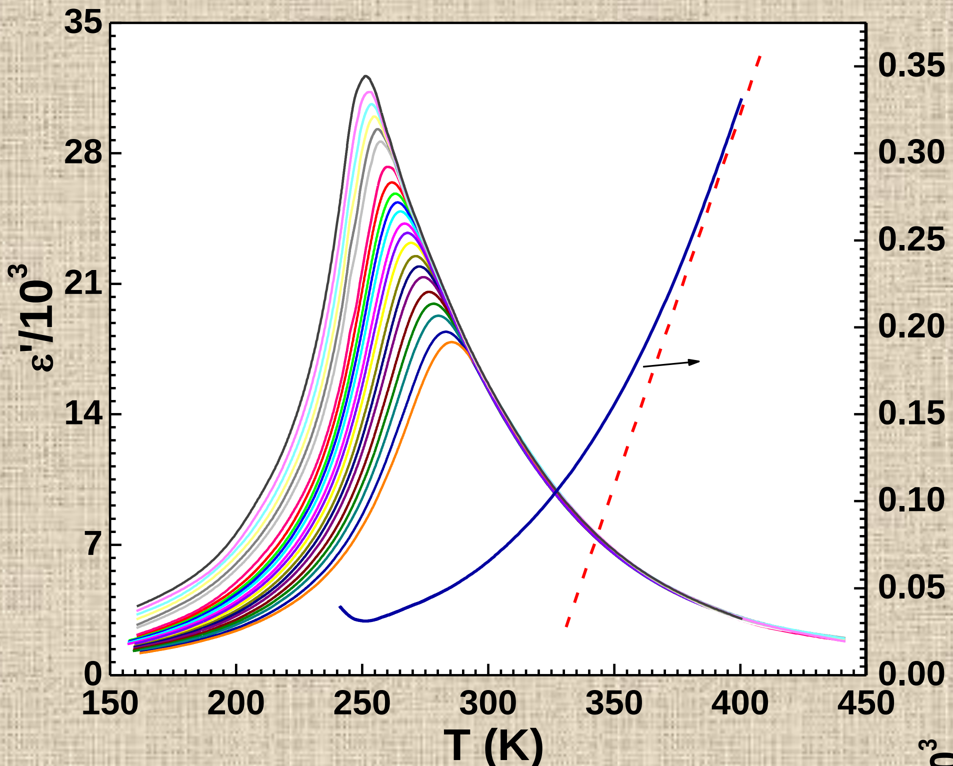
		T_C(K)	Ps (μC/cm^2)
KDP type	KH_2PO_4	123	4.75
	KD_2PO_4	213	4.83
	RbH_2PO_4	147	5.6
Perovskites	$BaTiO_3$	408	26
	KNbO3	708	30
	$PbTiO_3$	765	>50
	$LiTiO_3$	938	50
	$LiNbO_3$	1480	71



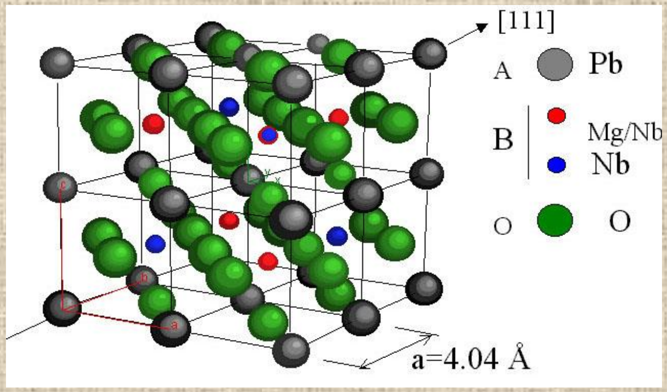
Number of publications concerning ferroelectricity.
From Jan Fousek "*Joseph Valasek and the Discovery of Ferroelectricity*"

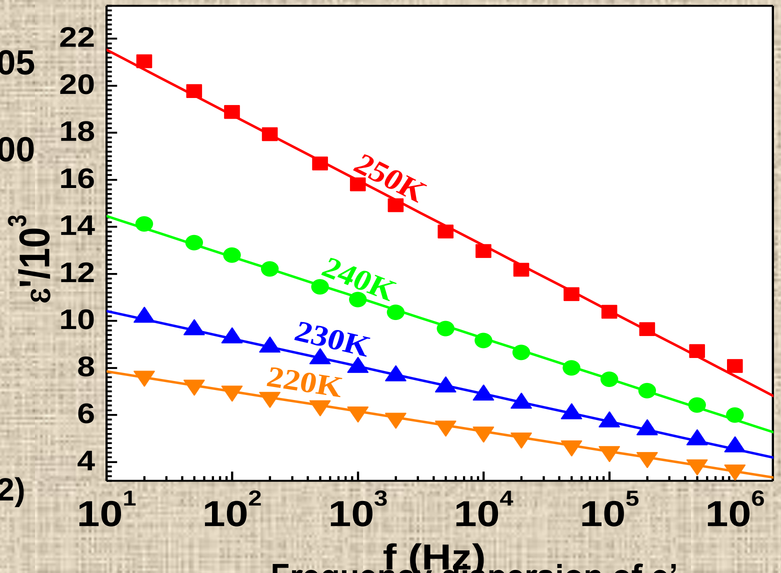
Number of ferroelectric substances discovered in each year.
Springer Handbook of Condensed Matter and Materials Data

Ferroelectricity: Relaxors - PMN $Pb(Mg_{1/3}Nb_{2/3})O_3$



Temperature dependencies of the real part of the dielectric constant measured in a broad frequency range: $3*10^{-3}$ -10^{6} Hz [1,2]





Frequency dispersion of e' at different temperatures

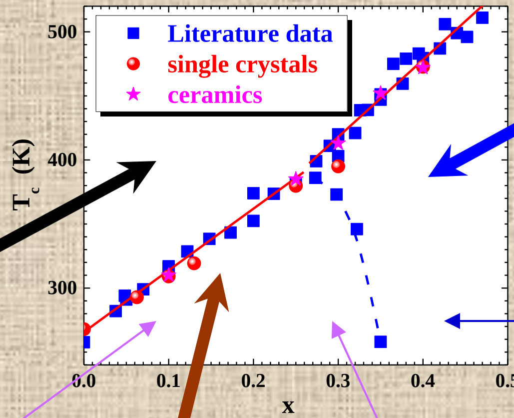
1. E.V. Colla et all., J. Phys.: Cond. Matter, 4,3671, (1992)
2. E.V. Colla et all. J. Appl. Phys., 83, 3298, (1998)

Ferroelectricity: Solid solution relaxor-regular ferroelectric.

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

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

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



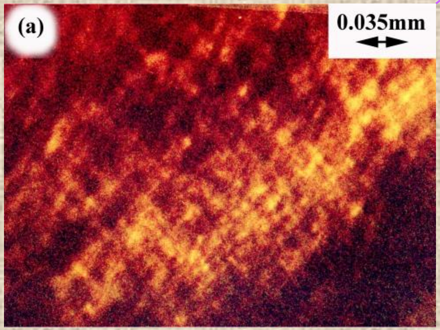
Paraelectric (cubic)

Regular ferroelectric (tetragonal)

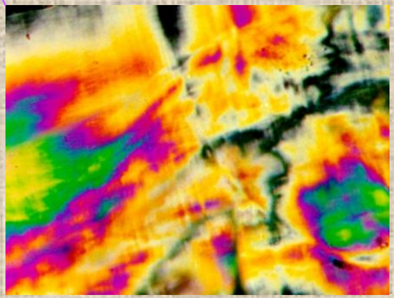
$(PMN)_{0.6}(PT)_{0.4}$

"Relaxor" state (pseudocubic)

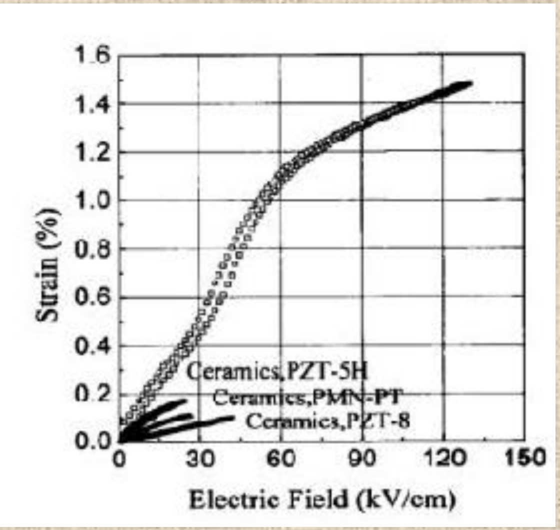
$(PMN)_{0.9}(PT)_{0.1}$



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



Ferroelectricity: Relaxors - some aplications



DARPA PIEZOCRYSTALS

Actuators
Transducers
Adaptive optics
Capacitors
Line motors for SFM

TRS Ceramics

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