Ferroelectrics.
Disordered Ferroelectrics

Eugene V. Colla
Physics 403 Fall 2021
• 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

**Displacement type**

**Order-Disorder**

BaTiO$_3$

NaNO$_2$
Ferroelectricity: Polarization reversible. (P-E hysteresis)

PLZST ceramics

Sn:Ti = 0.24:0.11

$P \ (\mu C/cm^2)$

$E_{DC} \ (kV/cm)$

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

Single domain state

Multi domain state

90° domains

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

180° domain pattern

Ferroelectricity: Domains

BaTiO$_3$

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

KH$_2$PO$_4$

Courtesy of Allison Pohl, P403, Fall2009

PMN-PT40%

PMN-PT30%

BaTiO$_3$

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

191K

KD$_2$PO$_4$
Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy

\[ F_p = \frac{1}{2} aP^2 + \frac{1}{4} bP^4 + \frac{1}{6} cP^6 + \ldots - EP \]

Order parameter (polarization)

Electric field

the equilibrium solution

\[ \frac{\partial F}{\partial P} = 0 \]

Ignoring higher terms we can get the linear solution:

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

\[ \chi = \frac{\partial P}{\partial E} = \frac{1}{a} \]

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

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

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In case of $b > 0$ (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

\[ F_p = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \cdots - EP \]
Ferroelectricity: Susceptibility

\[
P = \varepsilon_0 \chi \vec{E} \quad \quad \quad \quad \quad \quad D = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \vec{E} + \varepsilon_0 \chi \vec{E} = \varepsilon_0 (1 + \chi) \vec{E} = \varepsilon_0 \varepsilon \vec{E}
\]

For ferroelectrics \( \varepsilon \gg 1 \) and \( \varepsilon \approx \chi \)

Curie-Weiss law:

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

\( \text{BaTiO}_3 \)

\( C = 1.9 \times 10^5; \quad T_C = 385.2\,\text{K} \)
Rochelle Salt  $\text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O}$

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$_4$H$_4$O$_6$·4H$_2$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

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

Joseph Valasek (1897-1993)
University of Minnesota

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

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

Fig. 3. Piezoelectric response as a function of temperature [2]
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.
KDP (KH$_2$PO$_4$) - potassium dihidrophosphate

1935


Georg Busch
1908-2000

Paul Scherrer
1890-1969

\[ T_c \approx 123K \]
KDP (KH$_2$PO$_4$) - potassium dihidrophosphate

$T_c \approx 121-123$ K

$T > T_c$

$T < T_c$

KDP project (2): Graph6

KDP (sample 4) c-cut

$T_c \approx 121.5$ K

$\varepsilon'/1000$

1000kHz

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 (KD$_2$PO$_4$) – deuterated potassium dihydrogen phosphate

$T < T_c$  $T = T_c$  $T > T_c$
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))

$T_c \sim 400\text{K}$


Physics 403 Lab, August 2011

Courtesy of Liu M. & Lopez P, Physics 403, Spring 2013
Ferroelectricity: Typical ferroelectric materials

<table>
<thead>
<tr>
<th></th>
<th>(T_C) (K)</th>
<th>(P_s) ((\mu)C/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>KDP type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{KH}_2\text{PO}_4)</td>
<td>123</td>
<td>4.75</td>
</tr>
<tr>
<td>(\text{KD}_2\text{PO}_4)</td>
<td>213</td>
<td>4.83</td>
</tr>
<tr>
<td>(\text{RbH}_2\text{PO}_4)</td>
<td>147</td>
<td>5.6</td>
</tr>
<tr>
<td>Perovskites</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{BaTiO}_3)</td>
<td>408</td>
<td>26</td>
</tr>
<tr>
<td>(\text{KNbO}_3)</td>
<td>708</td>
<td>30</td>
</tr>
<tr>
<td>(\text{PbTiO}_3)</td>
<td>765</td>
<td>&gt;50</td>
</tr>
<tr>
<td>(\text{LiTiO}_3)</td>
<td>938</td>
<td>50</td>
</tr>
<tr>
<td>(\text{LiNbO}_3)</td>
<td>1480</td>
<td>71</td>
</tr>
</tbody>
</table>

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

Springer Handbook of Condensed Matter and Materials Data
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.
## New Perovskite Materials - Relaxors

<table>
<thead>
<tr>
<th>B-site complex</th>
<th>Lead magnesium niobate (PMN)</th>
<th>PbMg$<em>{1/3}$Nb$</em>{2/3}O_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lead scandium tantalate (PST)</td>
<td>PbSc$<em>{1/2}$Ta$</em>{1/2}O_3$</td>
</tr>
<tr>
<td></td>
<td>Lead zinc niobate (PZN)</td>
<td>PbZn$<em>{1/2}$Nb$</em>{1/2}O_3$</td>
</tr>
<tr>
<td></td>
<td>Lead indium niobate (PIN)</td>
<td>PblIn$<em>{1/2}$Nb$</em>{1/2}O_3$</td>
</tr>
<tr>
<td>A-site complex</td>
<td>Lead lanthanum titanate (PLT)</td>
<td>Pb$_{1-x}$La$_x$TiO$_3$</td>
</tr>
<tr>
<td>Both sites complex</td>
<td>Lead lanthanum zirconate titanate (PLZT)</td>
<td>Pb$_{1-x}$La$_x$Zr$<em>y$Ti$</em>{1-y}$O$_3$</td>
</tr>
<tr>
<td></td>
<td>Potassium lead zinc niobate</td>
<td>K$<em>{1/3}$Pb$</em>{2/3}$Zn$<em>{2/9}$Nb$</em>{7/9}O_3$</td>
</tr>
</tbody>
</table>

A$_{1-x}$B$_x$O$_3$  A$_{1-x}$A$_x$BO$_3$  A$_{1-x}$A$_x$B$_{(1-y)}$B$_y$O$_3$  typical complex oxides with perovskite structure

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

Relaxors

Regular ferroelectric BaTiO$_3$

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

$T > T_c$ (cubic)

(cubic)

Ba   O   Ti

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

Regular ferroelectric $\text{BaTiO}_3$

$T < T_c$ (tetragonal)

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

$T < T_c$ (tetragonal)

$T > T_c$ (cubic)

$\text{Ba}$ $\text{O}$ $\text{Ti}$ $\text{Pb}$ $\text{O}$ $\text{Mg}^{2+}$ or $\text{Nb}^{5+}$
Temperature dependencies of $\varepsilon'$ measured in a broad frequency range: 3mHz - 1MHz

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

$\varepsilon'$ does not follow Curie-Weiss law
\[ f_{\text{max}} = f_0 \exp \left[ \frac{-E_0}{T - T_{\text{VF}}} \right] \]
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 ordered 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

Same structure but different behavior

PMN

BaTiO$_3$

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.

**BTO courtesy of James Graessle**
Disorder in Regular Ferroelectrics. KDP family

$\text{KH}_2\text{PO}_4$ \hspace{1cm}$\text{KDP} - T_c \sim 120 \text{ K}$

$\text{KD}_2\text{PO}_4$ \hspace{1cm}Deuterated analog $\text{DKDP} \, T_c \sim 230 \text{ K}$

$\varepsilon' / \varepsilon'_\text{max} \quad \frac{T}{T_c}$

$\varepsilon' / \varepsilon'_\text{max}$

$\text{BaTiO}_3$

$\text{KH}_2\text{PO}_4^{1x}$

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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

~ 270 hours of aging

T=200 K

KD\(_2\)PO\(_4\)

cooling

aging
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.

\[ f = f_0 \exp \left( \frac{-E_a}{T_{\text{max}} - T_{VF}} \right) \]

\[ T_{\text{VF}} = 163.5 \, \text{K} \]
Applications of Ferroelectrics

KDP single crystals are mostly used as nonlinear optical materials

KDP powder is widely used as fertilizer
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

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

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

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

\(T_c\) (K)

Paraelectric (cubic)

Ferroelectric

Relaxor

Literature data

single crystals

ceramics

Solid solution relaxor-regular ferroelectric.

PT: PbTiO\(_3\), ferroelectric with Curie temperature 763K

(Literature data)

- single crystals
- ceramics

**Relaxor**

 parach 0.97 (PT) 0.03

 parach (1-x) (PT) (x)

 phase diagram

 PT: PbTiO\(_3\), ferroelectric with Curie temperature 763K

 PT: PbTiO\(_3\), ferroelectric with Curie temperature 763K.
Applications of ferroelectrics

- DRAM capacitors, alternative gate dielectrics
- Non-volatile memories
- IR detectors
  - Pyroelectricity
  - Microphones, accelerometers, hydrophones

- Polarizability
- High permittivity
- Dielectric nonlinearity
- Piezoelectricity:
  - Direct
  - Converse
- Optical nonlinearity, electro-optic activity
- Tunable microwave devices, varactors
- Light modulators, thermal infrared switches, frequency doubling
- Sound generators, sonars, ultrasound transducers and detectors, MEMS, SAW devices
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

Terahertz plasmonics in ferroelectric-gated graphene

Dafei Jin, Anshuman Kumar, Kin Hung Fung, Jun Xu, and Nicholas X. Fang

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

Lead Zirconium Titanate piezo scanner

PI (www.pi.ws)
Applications. Sonars
Military Applications

APPLICATIONS:

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

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

Fish Finder

Courtesy
Applications. Adaptive Optics

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

Soldered control and mass wires

Reflecting surface

Courtesy of http://scmero.ulb.ac.be

http://scmero.ulb.ac.be
### Actuators

#### Transducers

- Adaptive optics
- Capacitors
- Line motors for SFM

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#### Piezoelectric properties of different materials

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

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Transducer stack for ultrasonic sonar application (TRS Ceramics)