Outline

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

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Ferroelectricity: Two classes of ferroelectrics

**Displacement type**

- BaTiO_3

**Order-Disorder**

- Disorder
  - NaNO_2

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

PLZST ceramics

P (μC/cm²) vs. E_Dc (kV/cm)

Sn:Ti = 0.24:0.11

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Ferroelectricity: Domains

Single domain state

Multi domain state

90° domains

180° domain pattern


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

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

BaTiO₃

Courtesy of Allison Pohl, P403, Fall2009

KH₂PO₄

PMN-PT40%

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

BaTiO₃

191K

KD₂PO₄

PMN-PT30%

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Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy

Order parameter (polarization)

Electric field

the equilibrium solution

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

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

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

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

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

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

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

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

**Curie-Weiss law:**

\( \text{BaTiO}_3 \)

\( C = 1.9 \times 10^5 \); \( T_C = 385.2 \text{K} \)
Rochelle Salt  $\text{KNaC}_4\text{H}_4\text{O}_6*4\text{H}_2\text{O}$

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

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

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

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

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

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

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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 dihydrophosphate

1935


Georg Busch
1908-2000

Paul Scherrer
1890-1969

Fig. 1. Temperaturverlauf der Dielektrizitätskonstanten $\varepsilon_{33}$ an KH$_2$PO$_4$.
KDP (KH$_2$PO$_4$) - potassium dihydrogen phosphate

$T_c \sim 121-123$ K

$T_c \sim 121.5$ K

KDP project (2): Graph6

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

Courtesy of Alison Pohl, Physics 403, Spring 2009
DKDP (KD$_2$PO$_4$) – deuterated potassium dihydrogen phosphate

$T_c \approx 230K$
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))

$T_c \approx 400K$

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

Fig. 15. Confirmation of Curie-Weiss laws in (Ba$_x$Sr$_{1-x}$)TiO$_3$ (600 kc).

Arthur R. von Hippel
1898-2003
Materials. Barium Titanate.

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

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


![Graph showing the temperature dependence of the permittivity (\(\varepsilon\)) and the polarization (P) for cooling and heating processes. The graphs are labeled with frequencies of 100Hz and 100KHz.]

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><strong>KDP type</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( KH_2PO_4 )</td>
<td>123</td>
<td>4.75</td>
</tr>
<tr>
<td>( KD_2PO_4 )</td>
<td>213</td>
<td>4.83</td>
</tr>
<tr>
<td>( RbH_2PO_4 )</td>
<td>147</td>
<td>5.6</td>
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<tr>
<td><strong>Perovskites</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( BaTiO_3 )</td>
<td>408</td>
<td>26</td>
</tr>
<tr>
<td>( KNbO_3 )</td>
<td>708</td>
<td>30</td>
</tr>
<tr>
<td>( PbTiO_3 )</td>
<td>765</td>
<td>&gt;50</td>
</tr>
<tr>
<td>( LiTiO_3 )</td>
<td>938</td>
<td>50</td>
</tr>
<tr>
<td>( 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>PbIn$<em>{1/2}$Nb$</em>{1/2}$O$_3$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>A-site complex</th>
<th>Lead lanthanum titanate (PLT)</th>
<th>Pb$_{1-x}$La$_x$TiO$_3$</th>
</tr>
</thead>
<tbody>
<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>

**Typical complex oxides with perovskite structure**

**New Perovskite Materials - Relaxors**

<table>
<thead>
<tr>
<th>L. Eric Cross</th>
<th>Smolenskii G.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pennsylvania State University, USA</td>
<td>2. A.F. Ioffe Institute, USSR</td>
</tr>
</tbody>
</table>

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

Regular ferroelectric BaTiO$_3$

$T > T_c$ (cubic)

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

(cubic)

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

Regular ferroelectric BaTiO$_3$

$T < T_c$ (tetragonal)

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

$T < T_c$ (cubic)

Mg$^{+2}$ or 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.
\[ f_{\text{max}} = f_0 \exp \left[ \frac{-E_0}{T - T_{VF}} \right] \]
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 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).
Same structure but different behavior

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

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

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

---

**Graph**

- **S'** vs. $T/T_c$
- **KDP** and **BTO**

---

**Image**

- BaTiO$_3$
- KH$_2$PO$_4$

---

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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

\[ \epsilon' \]

\[ T = 200 \text{ K} \]

\[ \text{KD}_2\text{PO}_4 \]

\[ \text{time (h)} \]

\[ \text{T (K)} \]
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.

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

$T_{\text{VF}} = 163.5 \text{ K}$
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:
- Literature data
- Single crystals
- Ceramics

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

(a) Solid solution relaxor-regular ferroelectric.

- \((\text{PMN})_{0.9}(\text{PT})_{0.1}\)
- \((\text{PMN})_{0.6}(\text{PT})_{0.4}\)
- \((\text{PMN})_{0.7}(\text{PT})_{0.3}\)

\(0.0\ 0.1\ 0.2\ 0.3\ 0.4\ 0.5\)

\(300\ 400\ 500\)

\(T_c\) (K)

Relaxor

Paraelectric (cubic)

Ferroelectric

PMN: 0.97

PT: 0.03

PT: \(\text{PbTiO}_3\), ferroelectric with Curie temperature 763K.

Solid solution relaxor-regular ferroelectric.
Applications of ferroelectrics

Ferroelectric materials

- DRAM capacitors, alternative gate dielectrics
- Non-volatile memories
- IR detectors
- High permittivity
- Polarizability
- Pyroelectricity
- Dielectric nonlinearity
- Microphones, accelerometers, hydrophones
- 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

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Applications. Actuators

(a) Piezo actuator
    Control valve
    Nozzle

(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

Soldered control and mass wires

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

Reflecting surface

Courtesy of

Active Structures Laboratory

http://scmero.ulb.ac.be
## Ferroelectricity: Relaxors - Applications

<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>0.60</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>

### Piezoelectric properties of different materials

- Actuators
- Transducers
- Adaptive optics
- Capacitors
- Line motors for SFM

Transducer stack for ultrasonic sonar application (TRS Ceramics)