Ferroelectrics. Disordered Ferroelectrics - Relaxors.

Eugene V. Colla
Physcs 403 Spring 2017
Outline

• Ferroelectricity
  • Main properties
    • History. Discovery. Materials
  • 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
Ferroelectricity: Two classes of ferroelectrics

**Displacement type**

**BaTiO₃**

**Order-Disorder**

- Disorder
- Order

**NaNO₂**
Ferroelectricity: Polarization reversible. (P-E hysteresis)

Plzst ceramics

Sn:Ti = 0.24:0.11

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

Single domain state

Multi domain state

$P_{\text{net}} \sim 0$

180° domain pattern


90° domains

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

BaTiO₃

 Courtesy of Benjamin Vega-Westhoff and Scott Scharfenberg, P403, Fall 2009

KH₂PO₄

 Courtesy of Allison Pohl, P403, Fall 2009

BaTiO₃

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

PMN-PT40%

191K

KD₂PO₄

PMN-PT30%
Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy

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

Order parameter (polarization)

the equilibrium solution

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

Electric field

Ignoring higher terms we can get the linear solution:

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

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

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 $b>0$ (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

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

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

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

\[ C = 1.9 \times 10^5; \]
\[ T_C = 385.2 K \]

Curie-Weiss law:

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

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, \textit{Pierre Seignette}.

Rochelle Salt originates from French city of La Rochelle where it was produced by \textit{Pierre Seignette} another name of this material is Seignette salt.

Rochelle Salt was used in medicine and food industry.
Ferroelectricity: Discovery

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

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

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.
Materials. KDP

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$_4$.

DIE NATURWISSENSCHAFTEN

23. Jahrgang
25. Oktober 1935

Eine neue seignette-elektrische Substanz.
KDP (\(\text{KH}_2\text{PO}_4\)) - potassium dihydrogen phosphate  \(T_c \sim 123\text{K}\)

\[\varepsilon'/1000\]

KDP project (2): Graph6

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

Courtesy of Alison Pohl, Physics 403, Spring 2009
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 \approx 400K
Materials. Barium Titanate.

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

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


Physics 403 Lab, August 2011

100Hz

cooling
heating

345K 395K

P (µC/cm²)
E (kV/cm)

345K
395K

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>
</tr>
<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
# 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>Lead scandium tantalate (PST)</td>
<td>PbSc$<em>{1/2}$Ta$</em>{1/2}$O$_3$</td>
<td></td>
</tr>
<tr>
<td>Lead zinc niobate (PZN)</td>
<td>PbZn$<em>{1/2}$Nb$</em>{1/2}$O$_3$</td>
<td></td>
</tr>
<tr>
<td>Lead indium niobate (PIN)</td>
<td>PbIn$<em>{1/2}$Nb$</em>{1/2}$O$_3$</td>
<td></td>
</tr>
</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>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>
<td></td>
</tr>
</tbody>
</table>

Typical complex oxides with perovskite structure:

$\text{AB}_1^{(1-x)}\text{B}_2^x\text{O}_3$  $\text{A}_1^{(1-x)}\text{A}_2^x\text{BO}_3$  $\text{A}_1^{(1-x)}\text{A}_2^x\text{B}_1^{(1-y)}\text{B}_2^y\text{O}_3$

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

L. Eric Cross\(^1\)
Smolenskii G.A.\(^2\)
1910 - 1986
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.

Perovskite Structure

$$\text{AB}_1(1-x)\text{B}_2x\text{O}_3 \quad \text{A}_1(1-x)\text{A}_2x\text{BO}_3 \quad \text{A}_1(1-x)\text{A}_2x\text{B}_1(1-y)\text{B}_2y\text{O}_3$$

A typical complex oxides with perovskite structure
Relaxors

Regular ferroelectric BaTiO$_3$

\[ T > T_c \quad \text{cubic} \]

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

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

Regular ferroelectric BaTiO$_3$

T < $T_c$  (tetragonal)

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

(cubic)

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

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

$\varepsilon'_{\text{max}}$ and $T_{\text{max}}$ depend on the measuring frequency
\( f_{\text{max}} = f_0 \exp \left[ \frac{-E_0}{T - T_{VF}} \right] \)
PMN. Frequency Dispersion.
\[ \varepsilon'(\omega, T) = \varepsilon_\infty + \Delta \varepsilon \int_{-\infty}^{\infty} \frac{g(\tau, T) \ln \tau}{1 + (\omega \tau)^2} \]
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).

PNR – polar nanodomains
COR – chemically ordered regions

Relaxors: Field Induced Ferroelectric Transition.

$E_{\text{DC}}$ is applied in (111) direction

$T_f$ – temperature of the induced relaxor – ferroelectric transition

Rhombohedral distortion

$T > T_f$

$T < T_f$
PMN. Field Induced. Ferroelectric Transition.

E-T phase diagram of PMN. Field applied in (111) direction.
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

Literature data
single crystals
ceramics

Solid solution relaxor - regular ferroelectric.

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

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

\[(\text{PMN})_{0.6}(\text{PT})_{0.4}\]
Applications of ferroelectrics

Ferroelectric materials

- DRAM capacitors, alternative gate dielectrics
- Non-volatile memories
- IR detectors
- Polarizability
- Pyroelectricity
- Microphones, accelerometers, hydrophones
- Dielectric nonlinearity
- Piezoelectricity: direct, converse
- Tunable microwave devices, varactors
- Optical nonlinearity, electro-optic activity
- Light modulators, thermal infrared switches, frequency doubling
- Sound generators, sonars, ultrasound transducers and detectors, MEMS, SAW devices

High permittivity
Applications. Nonvolatile Memory

Fast write speed (65-70ns)
High endurance (10^{14} cycles)
Low power consumption

Terahertz plasmonics in ferroelectric-gated graphene

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

^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\([Zr_xTi_{1-x}]O_3\)

Soldered control and mass wires

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>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>

Transducer stack for ultrasonic sonar application (TRS Ceramics)