Ferroelectrics. Disordered Ferroelectrics – Relaxors.

Eugene V. Colla
Physics 403 Fall 2017
• 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

Order-Disorder

disorder

order

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: 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

BaTiO$_3$

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

KH$_2$PO$_4$

Courtesy of Allison Pohl, P403, Fall 2009

BaTiO$_3$

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

PMN-PT40%

PMN-PT30%

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Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy

Order parameter (polarization)

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

the equilibrium solution

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

Electric field

Ignoring higher terms we can get the linear solution:

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

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

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

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

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

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

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

Curie-Weiss law:

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

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)

Joseph Valasek (1897-1993)
University of Minnesota

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.
KDP (KH$_2$PO$_4$) - potassium dihydrophosphate

1935


Georg Busch 1908-2000

Paul Scherrer 1890-1969

Fig. 1. Temperaturverlauf der Dielektrizitätskonstanten $\varepsilon$ an KH$_2$PO$_4$.

DIE NATURWISSENSCHAFTEN


Eine neue seignette-elektrische Substanz.
KDP (KH$_2$PO$_4$) - potassium dihydrogen phosphate

$T_c \sim 123K$

KDP project (2): Graph6

KDP (sample 4) c-cut

$T_c \sim 121.5K$

100kHz

T > $T_c$

T < $T_c$

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)

\[ T_c \approx 400\,\text{K} \]

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

Fig. 15. Confirmation of Curie-Weiss laws in (Ba-Sr)/TiO₂ (600 kc).

Arthur R. von Hippel
1898-2003

A. Von Hippel, Rev. Mod. Phys. 22,221, 1950
Materials. Barium Titanate.

tetragonal
orthorhombic
rhombohedral

$\varepsilon'$

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

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


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><strong>KDP type</strong></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><strong>Perovskites</strong></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
# New Perovskite Materials - Relaxors

<table>
<thead>
<tr>
<th>B-site complex</th>
<th>Lead magnesium niobate (PMN)</th>
<th>( \text{PbMg}<em>{\frac{1}{3}}\text{Nb}</em>{\frac{2}{3}}\text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead scandium tantalate (PST)</td>
<td>( \text{PbSc}<em>{\frac{1}{2}}\text{Ta}</em>{\frac{1}{2}}\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>Lead zinc niobate (PZN)</td>
<td>( \text{PbZn}<em>{\frac{1}{2}}\text{Nb}</em>{\frac{1}{2}}\text{O}_3 )</td>
<td></td>
</tr>
<tr>
<td>Lead indium niobate (PIN)</td>
<td>( \text{PbIn}<em>{\frac{1}{2}}\text{Nb}</em>{\frac{1}{2}}\text{O}_3 )</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Both sites complex</th>
<th>Lead lanthanum zirconate titanate (PLZT)</th>
<th>( \text{Pb}_{1-x}\text{La}_x\text{Zr}<em>y\text{Ti}</em>{1-y}\text{O}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium lead zinc niobate</td>
<td>( \text{K}<em>{\frac{1}{3}}\text{Pb}</em>{\frac{2}{3}}\text{Zn}<em>{\frac{2}{9}}\text{Nb}</em>{\frac{7}{9}}\text{O}_3 )</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{AB}_{1-x}\text{B}_x\text{O}_3 \quad \text{A}_{1-x}\text{A}_x\text{BO}_3 \quad \text{A}_{1-x}\text{A}_x\text{B}_{1-y}\text{B}_y\text{O}_3 \]  

*typical complex oxides with perovskite structure*

---

L. Eric Cross\(^1\) (1923-2016)  
Smolenskii G.A.\(^2\) (1910 – 1986)

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

A typical complex oxides with perovskite structure:

\[
\begin{align*}
\text{AB}_1(1-x)\text{B}_x\text{O}_3 & \quad \text{A}_1(1-x)\text{A}_2_x\text{BO}_3 & \quad \text{A}_1(1-x)\text{A}_2_x\text{B}_1(1-y)\text{B}_2_y\text{O}_3
\end{align*}
\]
Regular ferroelectric BaTiO$_3$

$T > T_c$ (cubic)

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

(cubic)

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Relaxors

Regular ferroelectric $\text{BaTiO}_3$

$T < T_c$ (tetragonal)

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

$T < T_c$ (cubic)

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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.
$f_{\text{max}} = f_0 \exp \left[ \frac{-E_0}{T - T_{VF}} \right]$
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

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.

(a) \( t=7 \text{s} \)
\( E_{\text{DC}} = 3.13 \text{V/cm} \)
0.1mm electrodes

(b) \( t=23 \text{s} \)

\( E_{\text{DC}} (kV/cm) \)
\( T (K) \)

\( \varepsilon'/1000 \)
\( \varepsilon''/100 \)

\( I_p (nA) \)
\( P (\mu \text{C/cm}^2) \)

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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)

- Literature data
- Single crystals
- Ceramics

Paraelectric (cubic)  
Ferroelectric

"Relaxor"

PMN: 0.97  
PT: 0.03

0.035mm

(a)

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Applications of ferroelectrics

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

Ferroelectric materials
Applications. Nonvolatile Memory

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

Terahertz plasmonics in ferroelectric-gated graphene

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

Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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

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 $\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$

Soldered control and mass wires

Reflecting surface

Courtesy of

Active Structures Laboratory

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