Ferroelectricity. Phase transition. Material properties

BaTiO$_3$

PMN-PT(30%)

PMN-PT(40%)

DKDP

KDP

PZN-PT(9%)
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 \( \text{KNaC}_4\text{H}_4\text{O}_6*4\text{H}_2\text{O} \)

![Image of Rochelle Salt crystal](image)

![Chemical structure of Rochelle Salt](image)

![Graph showing dielectric constant as a function of temperature](image)

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

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

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

Joseph Valasek (1897-1993)
University of Minnesota

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

order

disorder

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)

Sn:Ti = 0.24:0.11

Ferroelectricity: Polarization reversible
(P-E hysteresis)
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, Fall 2009

BaTiO$_3$

KH$_2$PO$_4$

PMN-PT40%

BaTiO$_3$

KH$_2$PO$_4$

191K

KD$_2$PO$_4$

PMN-PT30%

Crystal from Forschungsinstitut für mineralische und metallische Werkstoffe - Edelsteine/Edelmetalle
Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy \( F_P = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + ... - EP \)

To find the equilibrium solution we need to find the minima of \( F_P \) 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 $b>0$ (or $C>0$ 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

\[ F_p = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \ldots - EP \]
Ferroelectricity: Susceptibility

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

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

Curie-Weiss law:

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

\( C = 1.9 \times 10^5 \); \( T_{CW} = 385.2 \text{K} \)
Ferroelectricity: Typical ferroelectric materials

$\text{KH}_2\text{PO}_4$

$E_{\text{DC}} = 1.2 \text{kV/cm}$

$T_{cw} = 121 \text{K}$

$C = 3000$

200Hz-20kHz

Courtesy Max Candocia, P403 Spring 2011
Ferroelectricity: Typical ferroelectric materials

$\text{BaTiO}_3$
Ferroelectricity: Typical ferroelectric materials

<table>
<thead>
<tr>
<th></th>
<th>$T_c$(K)</th>
<th>$P_s$ (µC/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”

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

\[ <P> \sim 0 \]

PNZST (film)

\[
\begin{align*}
\uparrow & \quad \downarrow \\
\downarrow & \quad \uparrow \\
\uparrow & \quad \downarrow \\
\downarrow & \quad \uparrow
\end{align*}
\]

PLZST (ceramic)

\[
\begin{align*}
\downarrow & \quad \uparrow \\
\uparrow & \quad \downarrow \\
\downarrow & \quad \uparrow \\
\uparrow & \quad \downarrow
\end{align*}
\]

Courtesy of E. Colla and City University of Hong Kong
Antiferroelectricity in $\text{BaTiO}_3$


Ferroelectricity and Antiferroelectricity in $\text{BaTiO}_3^*$

W. N. LAWLESS**

Interdisciplinary Materials Research Center, Rensselaer Polytechnic Institute, Troy, New York
and
Corning Research Laboratory, Corning, New York
(Received April 19, 1967)

Fig. 2. Antiferroelectric arrays on a simple-cubic lattice: (a), alternating planes, AP(100); (b) alternating-rows, AP(110).

Courtesy of Alan Selewa and Nathaniel Scheidler
(Physics403 class, 2014, unpublished)
Ferroelectricity: Relaxors - PMN Pb(Mg\textsubscript{1/3} Nb\textsubscript{2/3})O\textsubscript{3}

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

Ferroelectricity: Solid solution relaxor-regular ferroelectric.

PT: PbTiO$_3$, ferroelectric with Curie temperature 763K

Regular ferroelectric (tetragonal)

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

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

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

"Relaxor" state (pseudocubic)

Paraelectric (cubic)

\[(\text{PMN})_{1-x} (\text{PT})_x\]

Phase diagram

Literature data
- single crystals
- ceramics
Relaxors: Field induced Transition. \( \text{PMN Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \)
Relaxors: Field induced Transition. PMN Pb(Mg$_{1/3}$ Nb$_{2/3}$)O$_3$

![Graph of E_DC vs Tc (K)]

- **FE**
- **GL1**
- **GL2**
- **PE**

Courtesy of Joseph Strehlow and John Whitman
### 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>

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

Transducer stack for ultrasonic sonar application (TRS Ceramics)
Overview of Deformable Mirror Technologies for Adaptive Optics and Astronomy

P-Y Madec
European Southern Observatory, Karl Schwarzschild Str 2, D-85748 Garching

Maximum stroke of an actuator: \( \delta = N \times d_{33} \times V \)

- \( N \): number of piezo plates
- \( d_{33} \): piezo coefficient (\(\mu\)m/V)
- \( V \): applied voltage (V)
Ferroelectricity: Relaxors - some applications

Ferroelectric RAM

Comparison between FRAM and other Memories

<table>
<thead>
<tr>
<th>Comparison of Features</th>
<th>FRAM</th>
<th>EEPROM</th>
<th>FLASH</th>
<th>SRAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Memory Type</td>
<td>Non-volatile</td>
<td>Non-volatile</td>
<td>Non-volatile</td>
<td>Volatile</td>
</tr>
<tr>
<td>Write Method</td>
<td>Overwrite</td>
<td>Erase + Write</td>
<td>Erase + Write</td>
<td>Overwrite</td>
</tr>
<tr>
<td>Write Cycle Time</td>
<td>150ns</td>
<td>5ms</td>
<td>10μs</td>
<td>55ns</td>
</tr>
<tr>
<td>Read/Write Cycles</td>
<td>$10^{13}$</td>
<td>$10^6$</td>
<td>$10^5$</td>
<td>Unlimited</td>
</tr>
<tr>
<td>Booster Circuit</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Data Backup Battery</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Courtesy of KEITHLEY
Ferroelectricity: Relaxors - some applications

Actuators