Ferroelectricity. Phase transition. Material properties

- BaTiO₃
- DKDP
- KDP
- PMN-PT(9%)
- PMN-PT(30%)
- PMN-PT(40%)
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  $\text{KNaC}_4\text{H}_4\text{O}_6\cdot4\text{H}_2\text{O}$

![Rochelle Salt Image](image)

![Molecular Structure](image)

![Diagram](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 $\text{KNaC}_4\text{H}_4\text{O}_6*4\text{H}_2\text{O}$

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

Joseph Valasek (1897-1993)
University of Minnesota

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

Fig. 3. Piezoelectric response as a function of temperature [2]
Ferroelectricity: Two classes of ferroelectrics

Displacement type

Order-Disorder

BaTiO$_3$

NaNO$_2$

8/2/2016  Physics 403 Summer 2016
Ferroelectricity: Polarization reversible (P-E hysteresis)

PLZST ceramics

Sn:Ti = 0.24:0.11

8/2/2016
Ferroelectricity: Domains

Single domain state

Multi domain state

$P_{net} \approx 0$

$180^\circ$ domain pattern

$90^\circ$ domains


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$_3$

Courtesy of Allison Pohl, P403, Fall 2009

KH$_2$PO$_4$

PMN-PT40%

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

PMN-PT30%

191K

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

Free energy \( F_P \)  
Order parameter (polarization) \( P \)  
Electric field \( EP \)

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

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:

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

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 $b > 0$ (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.
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

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

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

\[ C = 1.9 \times 10^5; \]
\[ T_{CW} = 385.2 K \]

Curie-Weiss law:

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

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

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

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

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>KDP type</th>
<th>( T_c (K) )</th>
<th>( P_s (\mu C/cm^2) )</th>
</tr>
</thead>
<tbody>
<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>
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<table>
<thead>
<tr>
<th>Perovskites</th>
<th>( T_c (K) )</th>
<th>( P_s (\mu C/cm^2) )</th>
</tr>
</thead>
<tbody>
<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

\[ <P> \approx 0 \]

PNZST (film)

PLZST (ceramic)

Courtesy of E. Colla and City University of Hong Kong
Antiferroelectricity in BaTiO$_3$

*Journal of the Physical Society of Japan, Vol. 23, No. 2, August, 1967*

**Ferroelectricity and Antiferroelectricity in 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)

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

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Courtesy of Alan Selewa and Nathaniel Scheidler (Physics403 class, 2014, unpublished)
Ferroelectricity: Relaxors - PMN Pb(Mg$_{1/3}$ Nb$_{2/3}$)O$_3$

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.

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

\[(PMN)_{(1-x)}(PT)_{(x)}\] phase diagram

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

Regular ferroelectric (tetragonal)

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

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

Paraelectric (cubic)

“Relaxor” state (pseudocubic)
Ferroelectricity: Relaxors - some 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>

Actuators
Transducers
Adaptive optics
Capacitors
Line motors for SFM

Piezoelectric properties of different materials

Transducer stack for ultrasonic sonar application (TRS Ceramics)