Ferroelectricity. Phase transition. Material properties
Ferroelectricity.

Outline

- Ferroelectricity. Definition
- Discovery
- Main properties
- Phenomenological theory
- Some materials
- Relaxors
- Applications
2.1 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 $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$

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

Fig. 3. 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: Discovery

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

Fig. 3. Dielectric constant of an X cut Rochelle salt crystal free to move plotted as a function of the temperature.
Ferroelectricity: Two classes of ferroelectrics

Displacement type

Order-Disorder

BaTiO$_3$

NaNO$_2$
Ferroelectricity: Polarization reversible (P-E hysteresis)

PLZST ceramics

Sn:Ti = 0.24:0.11

E_{DC} (kV/cm)

P (\mu C/cm^2)
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

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

BaTiO₃

Courtesy of Allison Pohl, P403, Fall 2009

KH₂PO₄

PMN-PT 40%

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

BaTiO₃

191K

KD₂PO₄

PMN-PT 30%
Ferroelectricity: Landau-Ginzburg phenomenological theory

Free energy $F_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \ldots - EP$

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 $b > 0$ ($C > 0$ 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

\[ \vec{P} = \varepsilon_0 \chi \vec{E} \]

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

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

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

$KH_2PO_4$

Edc = 1.2 kV/cm

T_{cw} = 121 K
C = 3000

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

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>
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<tbody>
<tr>
<td>KH$_2$PO$_4$</td>
<td>123</td>
<td>4.75</td>
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<tr>
<td>KD$_2$PO$_4$</td>
<td>213</td>
<td>4.83</td>
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<tr>
<td>RbH$_2$PO$_4$</td>
<td>147</td>
<td>5.6</td>
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<td>Perovskites</td>
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<tr>
<td>BaTiO$_3$</td>
<td>408</td>
<td>26</td>
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<tr>
<td>KNbO$_3$</td>
<td>708</td>
<td>30</td>
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<tr>
<td>PbTiO$_3$</td>
<td>765</td>
<td>&gt;50</td>
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<tr>
<td>LiTiO$_3$</td>
<td>938</td>
<td>50</td>
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<tr>
<td>LiNbO$_3$</td>
<td>1480</td>
<td>71</td>
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</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

4/12/2011 Physics 403 Spring 2011
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]


Frequency dispersion of \(\varepsilon'\) at different temperatures

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Ferroelectricity: Solid solution relaxor-regular ferroelectric.

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

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

Phase diagram

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

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

Paraelectric (cubic)

“Relaxor” state (pseudocubic) 
\[(\text{PMN})_{0.9}(\text{PT})_{0.1}\]

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

\[0.035\text{mm}\]

610K

Literature data
- single crystals
- ceramics

4/12/2011

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Ferroelectricity: Relaxors - some applications

### 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>
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<tr>
<td>Rochelle salt (30C)</td>
<td>9.2</td>
<td>27</td>
<td>0.3</td>
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<tr>
<td>Barium titanate ceramic</td>
<td>1700</td>
<td>190</td>
<td>0.52</td>
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<tr>
<td>Lead zirconate titanate PZT 45/55</td>
<td>450</td>
<td>140</td>
<td>0.60</td>
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<tr>
<td>PMN-PT (sc)</td>
<td>4200</td>
<td>2200</td>
<td>0.92-0.94</td>
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<tr>
<td>PZN-PT (sc)</td>
<td>2500</td>
<td>2400</td>
<td>0.91-0.93</td>
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