Class 9: Polar materials and ferroelectrics

Fig. 1.1. Dielectric hysteresis loop for Rochelle salt (Valasek, 1921).

Fig. 1.2. Circuit for investigating hysteresis loop (Sawyer and Tower, 1930).

Valasek, 1921

From Megaw, Ferroelectricity in Crystals.
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Hydrogen-bonded ferroelectricity in Rochelle’s salt.

From Megaw, Ferroelectricity in Crystals.

Fig. 2.1. Rochelle salt: projection of structure on 001. Figures beside atom give heights above plane $z = 0$ in hundredths of cell edge; to convert into Ångstrom units multiply by $c/100$. Positions of screw axes indicated by arrows. Environments of representative atoms shown by dotted lines; where these are crossed by a short line at right angles, they involve an atom in the cell vertically above or below that whose height is marked.
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Fig. 1.5. Dielectric hysteresis loops for Rochelle salt at different temperatures (Sawyer and Tower, 1930).

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Hydrogen-bonded ferroelectricity in potassium dihydrogen phosphate (KDP).

From Megaw, Ferroelectricity in Crystals.
Fig. 1.6. Diagrammatic illustration of twinning in a pseudo-symmetric structure.

(a) Crystal above transition point (high-symmetry form)
(b), (c) Low-symmetry form: two possible orientations
(d) Twinned crystal, with low-symmetry form in both orientations.

From Megaw, Ferroelectricity in Crystals.
### Classification of substances related to perovskite

<table>
<thead>
<tr>
<th>I. Substances occurring only in ideal cubic form</th>
<th>SrTiO$_3$, SrZrO$_3$, SrHfO$_3$, SrSnO$_3$, SrFeO$_3$, BaZrO$_3$, BaHfO$_3$, BaSnO$_3$, BaCeO$_3$, EuTiO$_3$, LaMnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>II. Substances having at least one form with a distorted small-cell structure (C = cubic, T = tetragonal, O = orthorhombic, R = rhombohedral, ? = doubtful or not fully investigated)</td>
<td>BaTiO$_3$ (C, T, O, R), KNbO$_3$ (C, T, O, R), KTaO$_3$ (C, ?), RbTaO$_3$ (C, T), PbTiO$_3$ (C, T)</td>
</tr>
<tr>
<td></td>
<td>(b) cell size $\sqrt{2}a$ x $2a$ x $\sqrt{2}a$</td>
</tr>
<tr>
<td></td>
<td>(c) cell size $2a$ x $4a$ x $\sqrt{2}a$</td>
</tr>
<tr>
<td></td>
<td>(d) cell size $\sqrt{2}a$ x $2\sqrt{2}a$ x $2a$</td>
</tr>
<tr>
<td></td>
<td>(e) cell size $2a$ x $2a$ x $a$</td>
</tr>
<tr>
<td></td>
<td>(f) others</td>
</tr>
<tr>
<td>IV. Substances having structures based on close-packing</td>
<td>(a) FeTiO$_3$, CdTiO$_3$, LiNbO$_3$, (LiTaO$_3$)</td>
</tr>
<tr>
<td></td>
<td>(a) IImenite type</td>
</tr>
<tr>
<td></td>
<td>(b) LiNbO$_3$ type</td>
</tr>
</tbody>
</table>

Substances in brackets have not been investigated in detail and classification is partly by analogy.

---

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Antiferrodistortive transition in SrTiO₃ in R-point of the Brillouin zone

Splitting of the structural soft mode (Raman active below $T_a$)

![Diagram of SrTiO₃ structure]

- $A_{1g}$
- $E_g$
- $T_a$

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### Ferroelectric SM

#### Structural SM (doublet)

Mode frequencies on STO ceramics

(Petzelt et al., PRB 64, 184111 (2001))

<table>
<thead>
<tr>
<th>Species</th>
<th>Activity</th>
<th>Mode Frequency</th>
<th>Species</th>
<th>Activity</th>
<th>Mode Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3F_{1u}$</td>
<td>IR</td>
<td>93,176,548</td>
<td>$3A_{2u}$</td>
<td>IR</td>
<td>15,172,548</td>
</tr>
<tr>
<td>$1F_{2u}$</td>
<td>HR</td>
<td>266</td>
<td>$1B_{2u}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1E_{g}$</td>
<td>-</td>
<td>-</td>
<td>$1A_{1g}$</td>
<td>R</td>
<td>52</td>
</tr>
<tr>
<td>$1E_{g}$</td>
<td>-</td>
<td>-</td>
<td>$2B_{2g}$</td>
<td>R</td>
<td>144,447</td>
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<tr>
<td>$1E_{u}$</td>
<td>IR</td>
<td>436</td>
<td>$2E_{g}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$1A_{1u}$</td>
<td>-</td>
<td>-</td>
<td>$1B_{2g}$</td>
<td>R</td>
<td>229</td>
</tr>
<tr>
<td>$1A_{2g}$</td>
<td>-</td>
<td>-</td>
<td>$1A_{2g}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total (Γ point)</td>
<td>$3F_{1u} + 1F_{2u}$</td>
<td>$1A_{1g} + 1A_{1u} + 2A_{2g} + 3A_{2u} + 2B_{1g} + 2B_{2g} + 2B_{2u} + 3E_{g} + 3E_{u}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mode activity</td>
<td>3 IR</td>
<td>8 IR + 7 R</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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![Graphs showing polarization and dielectric constant vs. temperature.](image)
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Temperature (K)

- 100 kHz
- 36.2 GHz
- 270 GHz (9 cm⁻¹)
- $\varepsilon_0$ from IR fit including $X$ mode
- $\varepsilon_0$ from IR fit without $X$ mode
- Curie-Weiss
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SrTiO₃ ceramics

![Graph showing Raman spectroscopy of SrTiO₃ ceramics with peaks labeled TO₂, LO₁, TO₃, LO₃, TO₄, LO₂, E_g+B₁g, and E_g+B₂g.](image)
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\[ \text{SrTiO}_3 \]

**Experiment:**
- Crystal (Hyper-Raman)
- 2 \( \mu \text{m} \)-grained ceramics (BWO)
- 2 \( \mu \text{m} \)-grained ceramics (MW)
- 100 nm-grained ceramics (dielectric meas. 100 kHz)

**Theoretical model:**
- 2 \( \mu \text{m} \)-grained ceramics, \( \varepsilon(\text{GB})=100, \, \xi=7 \text{ nm} \)
- 100 nm grained, \( \varepsilon(\text{GB})=100, \, \xi=7 \text{ nm} \)
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Order-disorder model for \( \text{BaTiO}_3 \) phase transitions

Ordered \( \text{Ba} \)

Dynamically disordered \( \text{Ti} \)
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TO1 mode in BaTiO$_3$ single crystal

Temperature (K)

Frequency (cm$^{-1}$)

Luspin_80 (IR refl.)
Vogt_82 (HR)
Laabidi_90 (R)
Perry_65 (R)
Burns_78 (R)
Dougherty_94 (femt. ISRS)
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Unpolarized Raman spectra of BaTiO$_3$ crystals (after Perry and Hall 1965)